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Compositional control of electrochromic properties in copolymers of *N*-vinylcarbazole and *N*-phenyl-2-(5′-vinyl-2′-thienyl)-5-(2″-thienyl)-pyrrole

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Abstract

Three compositionally different copolymers derived from *N*-vinylcarbazole and *N*-phenyl-2-(5′-vinyl-2′-thienyl)-5-(2″-thienyl)-pyrrole were synthesised chemically and characterised. The composition of the copolymers was estimated using FT-IR spectroscopy and in situ spectroelectrochemistry and spectrocolorimetric measurements were performed on the solid state electrochromic devices fabricated using these copolymers as working electrodes. The colour contrasts of these devices in both the neutral and the doped states were measured by spectrocolorimetry conforming to the Commission International de l'Eclairage (CIE) methods. The CIE colour coordinate values in the p-doped state of the devices could be correlated to the comonomer ratios in these copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochromic; Copolymers; Tailorability

1. Introduction

Organic polymers are under extensive investigation as electrochromic materials because of the advantages they offer in tailorability of colour and processability. Among these, linear conjugated polymers based on polythiophene containing various substituents like linear and branched alkyl chains, oxyalkyl chains, and aryl groups have received considerable attention [1–3]. Without such groups the processability of such materials is limited. A further complication for linear conjugated polymers is that the colour in the doped state is not easily controlled, as it stems from delocalized chromophores that lack well-defined structure. This is to be contrasted with the behaviour of non-conjugated polymers containing pendant π groups for which the chromophore is well defined and exhibits distinct colour contrast [4–8].

Although the neutral state colour of thiophene-based polymers can be significantly affected by substitution, the doped state colour is far less sensitive. It is unusual for a single conducting polymer to exhibit an electrochromic change covering the entire visible region. Nevertheless, materials that exhibit multicolour electrochromism are of interest in areas such as active camouflage. A facile method of achieving multi-spectral response can result from incorporating two electrochromic moieties, each covering a different colour change region, into a single polymer [9].

Polymer blends have been suggested as a simple way of achieving wide range colour changes for electrochromic materials. There have been numerous reports on the electrochromic properties of blends combining thermoplastics or elastomers with polypyrrole, polythiophene and polyaniline [10]. Most of these reports focus on obtaining new materials with good mechanical properties and processability. In contrast, there have been very few studies directed at deliberate modification of electrochromic properties using blends. Earlier, we have shown that variation of the composition in the polymer blends of poly(*N*-vinylcarbazole) (PVK) and poly(*N*-phenyl-2-(5′-vinyl-2′-thienyl)-5-(2″-thienyl)-pyrrole) (PSNPhS), affects the colour in a predictable way [11]. Copolymers offer another powerful method to tailor colour. A recent literature review suggests that heteroaromatic copolymers can be used to modify these and other

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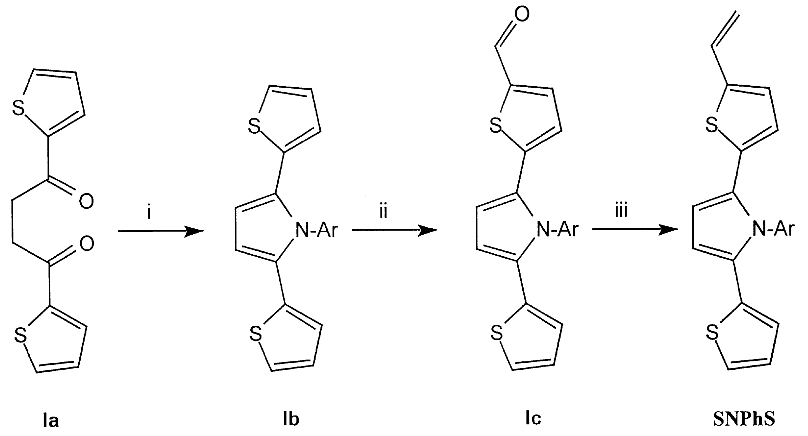


Ar = C_6H_5

i: Aniline, propionic acid ; ii: $POCl_3$, DMF; iii: CH_3PPh_3Br, *n* - BuLi

Scheme 1.

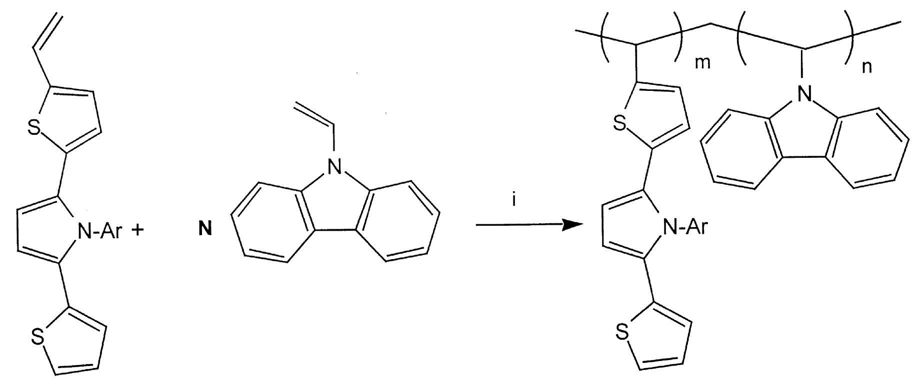
properties in a desired manner by synergistically combining the properties of the comonomers [12]. Copolymers have also been employed to obtain thermoplastic electrochromic materials [10].

Polymers based on *N*-vinylcarbazole (NVC) and its derivatives are known to exhibit electrochromic properties [13–15]. PVK changes from colourless in the neutral state to green in the doped state. Another polymer that possesses electrochromic properties is PSNPhS whose colour changes from yellow to greyish brown when oxidised. Utilising the above strategy, we have synthesised copolymers of NVC and *N*-phenyl-2-(5′-vinyl-2′-thienyl)-5-(2″-thienyl)-pyrrole (SNPhS) with varying compositions. The electrochemical and electrochromic properties, along with their potential for generating the colours of vegetation and soils observed in nature, will be discussed in this paper.

2. Experimental

2.1. General

NVC was purchased from Aldrich Chemicals, Inc. and was used without further purification. The synthesis of the SNPhS is depicted in Scheme 1. Details of the synthesis are described elsewhere [11]. The diketone was ring closed using aniline; the aldehyde group was introduced using Vilsmeyer formylation and was subsequently converted to the vinyl group by the Wittig reaction. All the compounds



i: BF_3 -Et_2O; CH_2Cl_2; 0 °C

CO-1: M:N = 1:4; **CO-2: M:N** = 3:2; **CO-3: M:N** = 4:1

Scheme 2.

synthesised gave satisfactory spectral (UV, IR, ^{1}H NMR) and elemental analyses. The copolymers were synthesised cationically starting from different feedstock ratios of the comonomers, as outlined in Scheme 2.

2.2. Solid state electrochromic device fabrication

Copolymer films were cast using a casting rod (Acculab Jr™ No. 30) from a chloroform solution (4% w/v, 2 ml) onto 15 cm by 6 cm ITO/Mylar™ (Altair O™, Southwall Technologies, Inc.) strips. These films were dried in the open air. A polymer electrolyte was prepared by mixing poly(methylmethacrylate) ($M_w = 120\,000$) (500 mg), propylene carbonate (1 ml), ethylene carbonate (2 g), and tetrabutylammonium tetrafluoroborate (300 mg) in acetonitrile (3 ml) and was spun cast onto the blank ITO. The entire device was assembled in a sandwich composite. The electrochromic material, cast onto ITO/Mylar, serves as the anode in the electrochromic device and the blank ITO/Mylar acts as the cathode.

2.3. Electrochemical and in situ spectroelectrochemical studies

Cyclic voltammetry was performed on the copolymer films cast on to ITO/Mylar using an EG&G PAR 263 potentiostat. The voltammograms were collected using the Research Electrochemistry Software (version 4.0, EG&G Instruments Inc.) on an IBM compatible 486 personal computer. The cyclic voltammograms are not compensated for the *IR* drop occurring across the face of the ITO electrode. In situ spectroelectrochemical measurements of the copolymers were recorded in 0.2 M solution of tetramethylammonium trifluoromethanesulfonate (TMATFMS) in acetonitrile in a specially modified quartz cuvette described previously [16]. A silver wire was used as a pseudo reference electrode. A cuvette containing a blank Altair O™ strip in the electrolyte solution was placed in the reference beam of the spectrophotometer. Spectra were recorded on a Perkin Elmer Lambda 9 between 325 and 1600 nm with an incremental change to the applied potential.

2.4. Reflectance and colour measurements

A HunterLab MiniScan XE spectrocolorimeter with the large view area option to record diffuse reflectance using a D65 Daylight illuminant was used to record the reflectance spectra and colour measurements. The MiniScan system is controlled through a computer interface using HunterLab Universal software. The colour data is displayed in the CIE 1976 $L^*a^*b^*$ opponent colour scale coordinate system using the CIE 1964 10° standard observer model. L^* indicates the intensity of the reflected light, the a^* coordinate indicates a change from red (positive direction) to green (negative direction) and the b^* coordinate indicates a colour change from yellow (positive direction) to blue (negative direction) (Fig. 1). The MiniScan XE records the spectral reflectance over the range of 400 to 700 nm, with a resolution of 10 nm and a wavelength accuracy of 1 nm. The CIE coordinates are then extracted from the components of the reflected light.

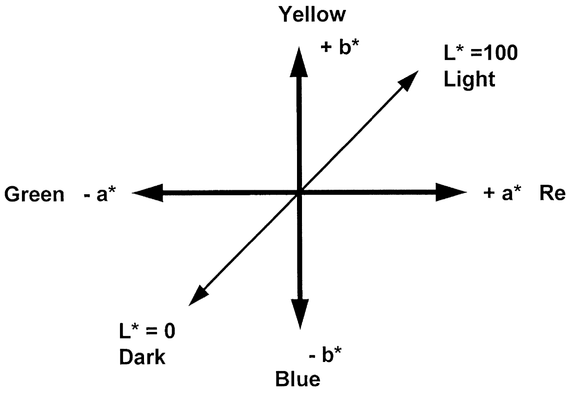


Fig. 1. The CIE $L^*a^*b^*$ opponent colour scale.

Variation in the polymer film thickness between devices causes some variation in the CIE $L^*a^*b^*$ coordinates. To minimise the error, three devices of each copolymer were constructed and a series of doping–dedoping experiments was performed. Typically, ten measurements were acquired and averaged for the doped and neutral states of each device, producing a standard deviation of ±1% for each colour coordinate measurement.

3. Results and discussion

The synthetic route adopted for SNPhS is shown in Scheme 1. The ring closure reaction proceeded with typical

Table 1
Composition based on FT-IR spectra, absorption maxima in solution, oxidation potentials, and molecular weights of the copolymers

Polymer	Feedstock ratio of SNPhS:NVC	Estimated composition SNPhS:NVC	$CHCl_3$ λ_{max} (nm)	E_{ox} (V) vs. Ag/Ag$^+$	Molecular weight, M_w
PVK[a]	—	—	289, 340	0.7	$\sim 10^6$
CO-1	20:80	30:70	289, 334, 340	0.65	243 000
CO-2	60:40	61:39	289, 334, 340	0.6	47 000
CO-3	80:20	72:28	290, 334, 340	0.33	59 000
PSNPhS	—	—	340	0.26	3412

[a] PVK was purchased from Aldrich Chemicals Inc.

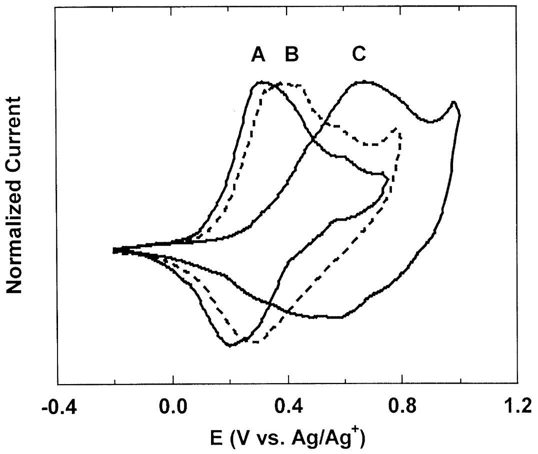


Fig. 2. Cyclic voltammograms of (A) PSNPhS, (B) CO-3 and (C) CO-2.

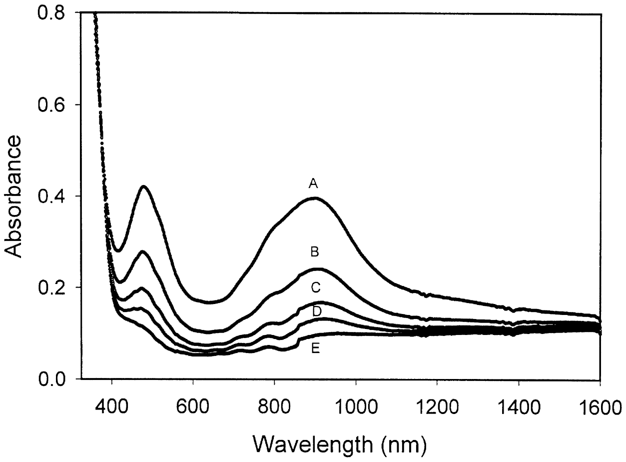


Fig. 3. In situ spectroelectrochemistry of a typical copolymer. (A) 1 V; (B) 0.9 V; (C) 0.8 V; (D) 0 V.

yields up to 60%. Both the Vilsmeyer formylation and the Wittig reaction to transform the aldehyde into a vinyl group proceed in 60–70% yields. Copolymers were synthesised according to Scheme 2. All the copolymers obtained were purified by re-precipitation from THF–hexane and were soluble in chloroform. ^1H NMR of the copolymers shows the absence of vinylic proton in the region δ 5.5–5 ppm and the appearance of broad peaks at δ 1.7–1.4 ppm indicating alkyl protons. The polymerisation is further supported by FT-IR spectra of the copolymers which showed the absence of peaks at 1620 and 980 cm^{-1} corresponding to the monomer's olefinic C–H stretch and bending vibrations respectively. The molecular weights and the absorption maxima are listed in Table 1. The UV–Vis spectra of copolymers also show absorptions corresponding to the carbazole ring and the SNPhS moiety.

The compositions of the copolymers were estimated from the FT-IR spectra. The IR absorption peak at 1323 cm^{-1} (C–H stretch) is characteristic of PVK alone, whereas the peak at 748 cm^{-1} is common to both PVK and PSNPhS. The normalised ratios of these two peaks give estimates of the compositions of the copolymers, which are in fair agreement with the feed stock ratio (Table 1).

Fig. 2 displays the cyclic voltammograms of homopolymer PSNPhS and copolymers CO-2 and CO-3. CO-3, which is rich in SNPhS, displays a reversible redox couple centred around 0.33 V versus Ag/Ag$^+$. This is only slightly shifted from that of the homopolymer, PSNPhS, which also exhibits reversible electrochemistry centred about 0.26 V versus Ag/Ag$^+$. PVK exhibits a quasi-reversible redox couple centred about 0.7 V versus Ag/Ag$^+$. The cyclic voltammogram for CO-2, which also appears quasi-reversible, has an estimated $E_{1/2}$ of 0.6 V versus Ag/Ag$^+$ and is thus strongly influenced by carbazole content.

Fig. 3 shows typical spectral changes observed upon p-doping these copolymers. Doping leads to new peaks at 500 and 900 nm in the absorption spectrum with a distinct colour change to the naked eye. All of the copolymers turn varying shades of brown in the doped state from their neutral pale yellow colour. These peaks diminish upon dedoping, and the copolymers regain the neutral colour.

To the observer the neutral state of the PVK homopolymer is colourless, whereas PSNPhS is yellow. In the doped state the appearance of PVK is green and PSNPhS is greyish brown. As the amount of SNPhS in the copolymers increases, the observed colour in the doped state qualitatively shifts towards orange (yellow and red mixture). This change can be quantified using the CIE $L^*a^*b^*$ formalism.

CIE $L^*a^*b^*$ colour coordinates measured for the copolymers in the doped and neutral states are given in Table 2. The observed changes in the $L^*a^*b^*$ values can be correlated to the copolymer composition. The a^* value, which is a measure of the red component, increases with increasing

Table 2
CIE 1976 $L^*a^*b^*$ colour coordinates for homopolymers and copolymers in the neutral and doped states

Polymer	Neutral			Doped		
	L^*	a^*	b^*	L^*	a^*	b^*
PVK	82.97	−2.31	16.55	73.74	−5.78	24.16
CO-1	71.88	3.91	25.25	67.08	4.86	17.58
CO-2	71.95	3.14	37.19	61.17	5.98	19.12
CO-3	62.44	8.83	45.67	46.69	7.52	20.00
PSNPhS	78.79	4.73	27.47	57.69	16.12	33.33

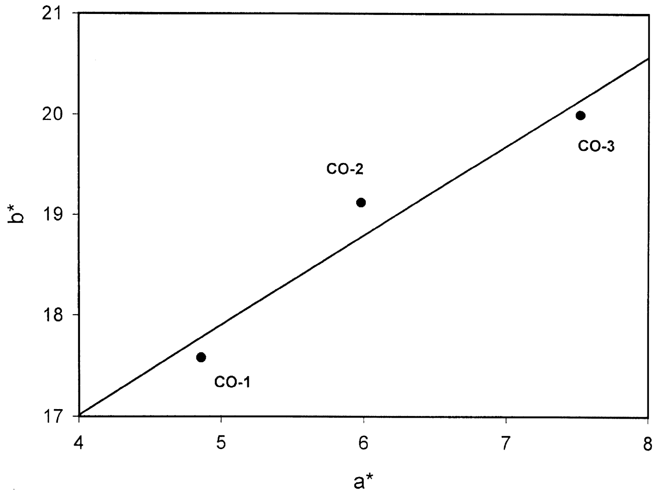


Fig. 4. Plot depicting the changes in *a** and *b** CIE colour coordinates for different copolymers in the doped state.

amount of SNPhS. This trend is readily seen in Fig. 4, which shows the change in *a** value with respect to *b** for the three copolymers.

The reflectance spectra also show this trend. The difference in reflectance spectra of the dedoped state referenced to the doped state of the copolymers and homopolymers are shown in Fig. 5. This figure illustrates the decreased reflectance in the range of 500 to 700 nm with increasing amount of SNPhS in the copolymer. The doped state of the device is usually darker and, therefore, less reflective than the dedoped state. This is especially true for PVK, as it is colourless in the neutral dedoped state but appears green when doped. This leads to a large offset from the origin in the difference spectra for PVK. The copolymer spectra show a combination of PVK and PSNPhS characteristics in accordance with their respective comonomer ratios. An earlier report on the copolymers of dithienopyrrole and dithienothiophene showed that the comonomer ratio did not greatly affect the electrochromic properties [17]. This is not surprising given the similar electrochromic properties of the respective homopolymers, poly(dithienopyrrole) and poly(dithienothiophene). In contrast, when the electrochromic behaviour is distinctly different for the homopolymers, as is the case here for PVK and PSNPhS, then copolymers based on these electrochromes can be used to control the colour change compositionally. This is almost certainly due to the discrete nature of the electrochromic moieties that constitute the copolymers.

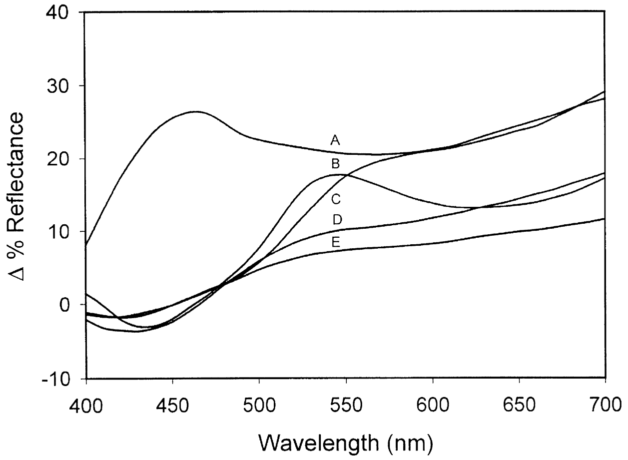


Fig. 5. Plot showing the difference in reflectance spectra for the copolymers referenced to the doped state: (A) PVK; (B): PSNPhS; (C) CO-3; (D) CO-2; (E) CO-1.

4. Conclusions

Three copolymers of NVC and SNPhS were chemically synthesised with varying comonomer ratios. Their electrochromic properties were studied using CIE *L***a***b** coordinates. Analysis of the reflectance spectra and the *L***a***b** values shows the correlation between the composition of the copolymers and their electrochromic properties. The natural tan and brown colours attained by using this novel combination of copolymers are difficult to produce by other means using poly(thiophene)-based electrochromic materials. We believe this approach offers a simple and effective alternative to fine tune electrochromic properties.

Acknowledgements

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