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Conducting Copolymers of Random and Block Copolymers of Electroactive and Liquid Crystalline Monomers with Pyrrole and Thiophene

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Block and random copolymers having 3-methyl thienylmethacrylate and 6-(4-cyanobiphenyl-4′-oxy)hexyl acrylate moieties were utilized as precursor polymers in this study. Electrochemical copolymerizations were performed in the presence of thiophene or pyrrole in acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB) at constant potential. The characterizations were performed by cyclic voltammetry (CV), fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermal gravimetry analysis (TGA), scanning electron microscopy (SEM), conductivity measurements. Electrochromic properties of the resultant conducting copolymers were investigated by spectroelectrochemistry and colorimetry studies. It was observed that, variation in the copolymer type or composition of the precursor polymer resulted in stern effects on surface morphology, spectroelectrochemistry, color and conductivity of the resultant graft copolymer.

Keywords: electrochemical polymerization; conducting copolymers; graft copolymers; electrochromism

1 Introduction

Electrically conducting polymers have been a center of scientific interest and active multidisciplinary research for the last decade. These materials have attracted academic and industrial research groups not only because of their theoretically interesting properties but also because of their technologically promising future. Polythiophene have become the most widely studied of all conjugated polyheterocycles due to its high synthetic flexibility, this allowed the use of several polymerization methods and incorporation of various side chain functionalities (1).

Synthesis of conducting polymer composites, graft and block copolymers were shown to be effective ways to compensate the certain deficiencies of conducting polymers like poor mechanical and physical properties. The most widely used method is coating the electrode with the insulating macromonomer and performing electropolymerization in the presence of a comonomer (2–5).

Previously, we synthesized thiophene-functionalized methacrylate monomer (3-methylthienyl methacrylate) (MTM) via the esterification of 3-thiophene methanol with methacryloyl chloride and this monomer was polymerized by conventional radical polymerization (6). Also, random and block copolymers of MTM with methyl methacrylate having different compositions, were prepared (7, 8). Their electropolymerization with pyrrole and thiophene through the incorporated thiophene units was achieved.

As a part of a broader study, we used the block (BC) and random (RC) copolymers possessing liquid crystalline and thiophene functionalities with various compositions where liquid crystalline properties were previously investigated (9). Random copolymers of electroactive and liquid crystalline monomers, namely 3-thienylmethyl methacrylate (MTM) and 6-(4-cyanobiphenyl-4′-oxy)hexyl acrylate (COA), were prepared by conventional free radical polymerization, whereas 1,1-diphenylethene (DPE) (10) was employed to synthesize block copolymers. In this study, conducting copolymers of BC and RC with thiophene and pyrrole

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were obtained by graft copolymerization performed by constant potential electrolysis. The grafting process was elucidated with cyclic voltammetry (CV), fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermal gravimetry analysis (TGA), scanning electron microscopy (SEM), conductivity measurements, spectroelectrochemistry and colorimetry studies.

2 Experimental

2.1 *Materials*

Thiophene (Th, Sigma), pyrrole (Py, Aldrich), acetonitrile (AN, Merck) and dichloromethane (DCM, Merck) were purified by conventional distillation procedures prior to use. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBAFB, Aldrich) was used as purchased.

2.2 *Equipment*

The cyclic voltammograms were recorded in AN/TBAFB solvent-electrolyte couple using a system consisting of a potentiostat (Wenking POS 73), a X-Y recorder and a CV cell containing Pt foil working and counter electrodes, and a Ag/Ag^+ reference electrode. Measurements were carried out at room temperature under nitrogen atmosphere. Thermal behavior of the samples was investigated via a Du Pont 2000 thermal gravimetry analyzer and differential scanning calorimetry by a heating rate of 10°C/min under N_2 atmosphere. Scanning electron microscopy (SEM) studies were performed by a JEOL JSM-6400. The IR spectrum was recorded on a Nicolet 510 FTIR spectrometer. Samples were prepared in disk form and dispersed in KBr. Conductivities were measured by a standard four-probe method at room temperature by using osmium contacts. Spectroelectrochemical studies were carried out on a HP8453A UV-Vis Spectrophotometer. Colorimetry measurements were obtained by a Coloreye XTH Spectrophotometer (GretagMacbeth).

2.3 *Cyclic Voltammetry*

A thin layer of the copolymers (BC or RC) were deposited on a platinum working electrode by casting from 1% (w/v) dichloromethane solution. Ag wire was used as the reference and Pt wire as the counter electrode. The voltammograms were recorded in acetonitrile (AN)–tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couple using a system consisting of a potentiostat (Wenking POS 73) and a X-Y recorder at room temperature under nitrogen atmosphere.

2.4 *Synthesis of Monomers and Copolymers*

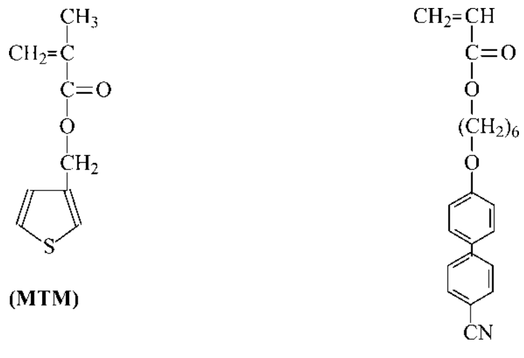
Synthesis of monomers, 6-(4-cyanobiphenyl-4′-oxy)hexyl acrylate (COA) (11) and 3-methylthienyl methacrylate (MTM) (6) of the structure presented in Scheme 1, and their random and block copolymers (9) with the compositions, given in Table 1, were achieved according to the procedures described elsewhere. Random copolymers were synthesized via radical polymerization of appropriate COA/MTM feed mixtures of two different chemical compositions in the presence of AIBN as an initiator. DPE method was used synthesize block copolymers of the liquid crystalline monomer (COA) and the electroactive monomer MTM.

2.5 *Synthesis of Conductive Copolymers of BC and RC with Th and Py by Electrochemical Polymerization*

Electrochemical polymerization was carried out in the presence of thiophene or pyrrole (0.02 M), after depositing either BC, RC1, and RC2 (1%, w/v solution in CH_2Cl_2) onto Pt, this electrode was used as the working electrode. The overall process is described for RC in Scheme 2. Polymerizations were performed on this working electrode with 0.05 M supporting electrolyte, TBAFB by applying a constant potential of +2.0 V and 1.1 V for thiophene and pyrrole copolymerizations, respectively. After electrolysis, the working electrode was washed several times with AN to remove supporting electrolyte adhered on the surface of the polymer film. After drying the electrode at room temperature, the polymer films were peeled off from the electrode and were allowed to stand in CH_2Cl_2 for several hours in order to dissolve and get rid of the ungrafted polymers.

2.6 *Spectroelectrochemistry*

Spectroelectrochemical analyses of the copolymers were carried out to investigate the band structure of the new product. For spectroelectrochemical studies, the copolymer films were deposited from a solution of 40 mg of RC-1or BC in the presence of 15 μL thiophene in 0.05 M TBAFB in 15 mL DCM, on indium tin oxide-coated glass slide (ITO) at constant potential of 2.0 V vs Ag/Ag^+. Spectroelectrochemistry was monitored while the polymer was



(MTM)

(COA)

Sch. 1. Structures of monomers.

Table 1. Composition of the copolymers of MTM and COA

	Copolymer composition (mol%[a])			
Code	MTM	COA	*Mn*[b]	*Mw*/*Mn*
BC	73	17	11500	2.29
RC1	21	79	8400	2.16
RC2	14	86	26200	1.67

[a] Determined by ^{1}H-NMR.
[b] Determined by GPC according to polystyrene standards.
MTM: 3-methylthienyl methacrylate.
COA: 6-(4-Cyanobiphenyl-4′-oxy)hexyl acrylate.

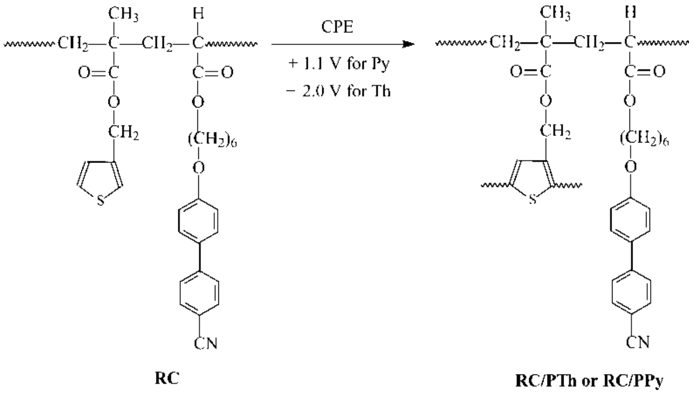
sequentially stepped between its fully reduced and oxidized forms, in the same electrolytic system in the absence of monomer.

3 Results and Discussion

3.1 FTIR

Due to the insoluble nature of the reaction products obtained after electropolymerization, characterization of the copolymers was not possible by NMR technique. Therefore, FTIR spectroscopy was used as a tool to characterize and compare the structures at various stages of the process.

The initial macromonomers (RC or BC) were characterized by 3103 cm^{-1} (aromatic C-H stretching), 2940 cm^{-1} (aliphatic C-H stretching), 1726 cm^{-1} (C=O stretching), 2224 cm^{-1} (C≡N stretching), 1604cm^{-1} (phenyl group), 1260–1000 cm^{-1} (C-O-C symmetric and asymmetric stretching), 788 cm^{-1} (thienylene out of plane C-H$_{\alpha}$ stretching), 1068, 1050 cm^{-1} (in plane C-H deformations), 1415, 1347 cm^{-1} (aromatic C=C, C-C ring stretching). FTIR spectra of the synthesized conducting copolymers (RC/PTh and BC/PTh) revealed unperturbed presence of peaks originating from the initial thiophene containing structures (especially 1726 cm^{-1}) in addition to evolution of new bands, at 1626 cm^{-1} due to polyconjugation, at 1081 cm^{-1} due to dopant anion, at 840 cm^{-1} (2,3,5-trisubstituted thiophene), all of which accompanied by the reduction in the peak intensity at 788 cm^{-1} (thienylene out of plane C-H$_{\alpha}$ stretching). Thus, all these results were considered as the proof for the electrografting process which was further supported by other means of characterization techniques.



Sch. 2. Electrochemical route for the synthesis of conductive copolymers (RC/PTh or RC/PPy) of random copolymer (RC) with pyrrole (Py) or thiophene (Th).

3.2 Cyclic Voltammetry

The oxidation/reduction behavior of the RC and BC and their copolymers in the presence of thiophene or pyrrole was investigated via cyclic voltammetry. CV experiments were carried out in 0.05 M TBAFB/AN solvent-electrolyte couple under nitrogen atmosphere. Among the precursor polymers, only BC revealed an oxidation peak at 1.75 V, which could be related to the increased content of thiophene functionalized group MTM (Figure 1-a). In order to investigate the CV behavior of the copolymers, we performed CV studies

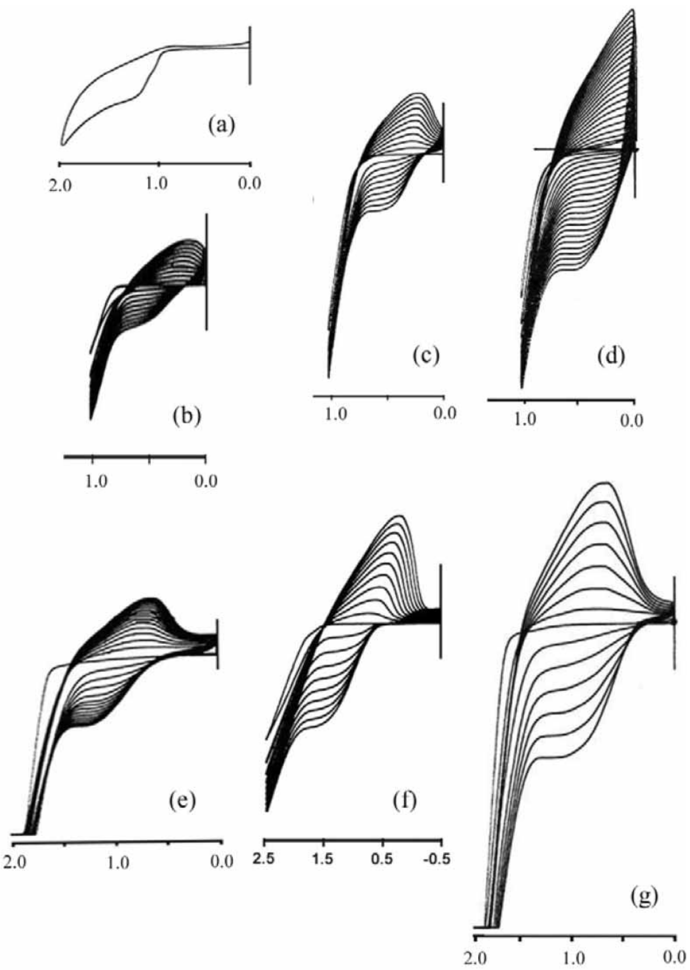


Fig. 1. Cyclic voltammograms of (a) pure BC, (b) BC/PPy, (c) RC1/PPy, (d) pure PPy, (e) BC/PTh (f) RC1/PTh (g) pure PTh.

under same experimental conditions in the presence of thiophene or pyrrole. For BC/PPy and BC/PTh copolymers E_{ox} values were 1.1 V and 1.3 V respectively, which were both different than that of the pure PPy (0.63 V) and PTh (1.0 V) (Figures 1-b, e). Similar differences in the redox behavior were observed in case of copolymers of RC1 and RC2 (Figures 1-c, f). In all cases, except for the pure BC, the current response for the monomer oxidation also increased with repeated scanning, indicating that the polymer formed on the electrode was porous, conductive and the current increase was due to increase of electrode surface area. There was an abrupt change in the voltammogram of all systems, both in terms of the increase in the increments between consecutive cycles and the oxidation-reduction potentials of the material were different than those of from both pure thiophene and pyrrole. This observation could be interpreted as the formation of copolymer.

3.3 *Thermal Properties*

As seen in Figure 2(a), RC1 was stable up to 292°C and a further increase in the temperature resulted in decomposition, reaching a maximum at 339°C. The thermogravimetry scan of the RC1 showed a single weight loss starting from 300°C and reaching the maximum at 378°C where the remaining residue was less than 10.29% at temperatures higher than 830°C (Figure 3(a)). Both DSC and TGA thermograms of the conducting copolymers showed that the desorption of solvent was around 100°C, as a result of imperfect drying of the samples. TGA of RC1/PTh reflected the two-step decomposition behavior (Figure 3(c)). The former step was initiated at 242°C and reached a maximum at 284°C, possibly originating from dopant removal. The second step could be interpreted as the matrix decomposition, which started at 432°C and continued up to 830°C, a leaving char residue of 38.67%. This observation was also supported by the appearance of an endotherm (Figure 2(c)) at 327.5°C, with an onset at 256.9°C. In the case of RC1/PPy, both the evolution of dopants and polymer degradation were detected over a broad temperature range, leaving 22.67% char beyond 830°C. A similar type of behavior was also observed for DSC thermograms, revealing a broad endotherm starting at 283.4°C continuing till 535°C (Figure 2(b)). Conducting copolymers of RC2 and BC also revealed a similar type of thermal behavior. It was observed that both DSC and TGA results concur well with each other, especially in terms of their onset points, since decomposition of conduting polymers occur within a temperature range.

3.4 *Conductivities of the Films*

Electrical conductivity measurements were carried out by using the standard four-probe technique at room temperature. For all the graft copolymers, conductivities of both the electrode and solution sides were in the same order of magnitude, revealing the homogeneity of the films. Conductivities of the graft copolymers formed with pyrrole generally revealed lower conductivity than their thiophene counterparts (Table 2). Among the precursor polymers, BC revealed superior performance in conductivity. This might be due to high MTM content in its composition, leading to higher thiophene functionality. Generally, there was a slight increase in the conductivities of the copolymers in comparison to the previous study (7), which could be attributed to the liquid crystalline functionality of the precursor polymer used in the current study. These results also confirmed that we were successful in converting an insulating polymer into a conductive form.

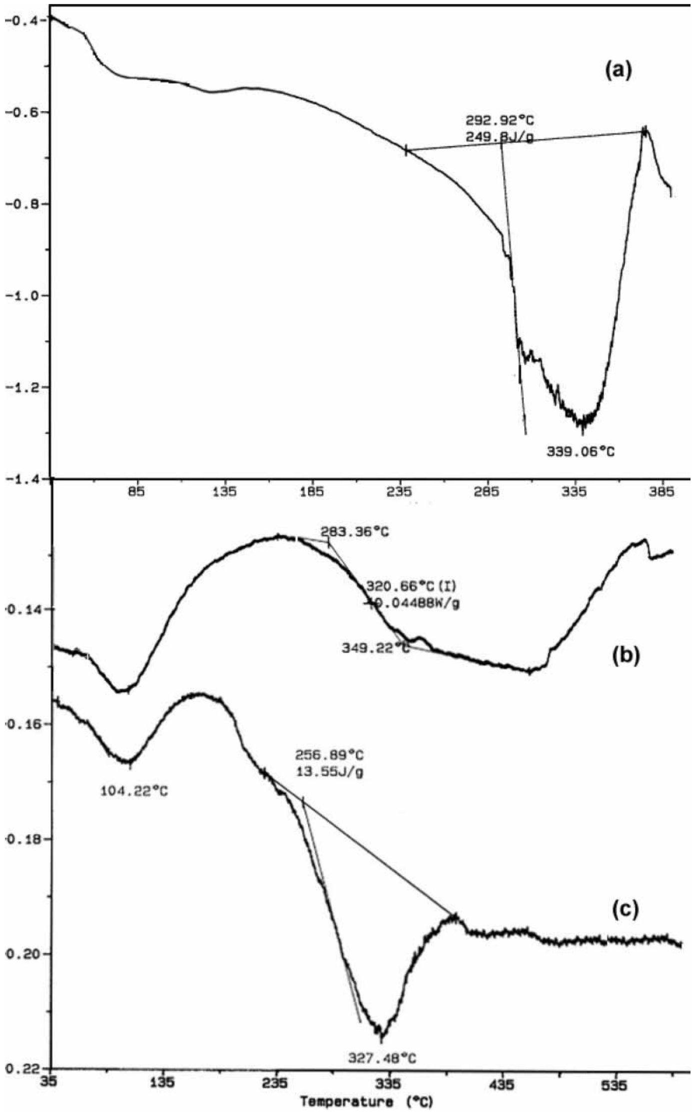


Fig. 2. DSC thermograms of (a) pure RC1, (b) RC1/PPy, (c) RC1/PTh.

3.5 *Morphologies of the Films*

SEM micrographs of all the graft copolymers synthesized in the presence of pyrrole exhibited homogeneous and

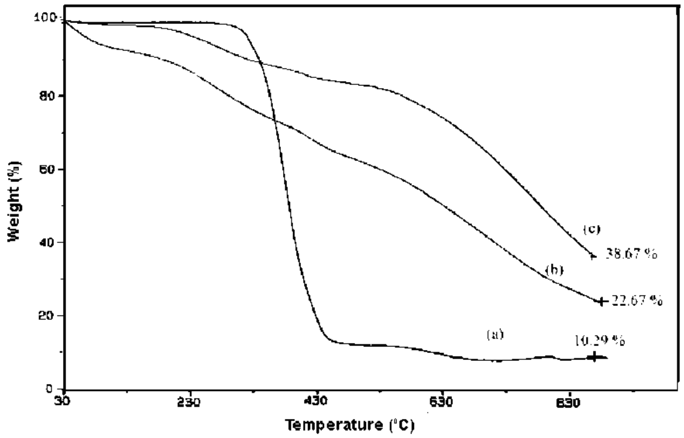


Figure 3. TGA thermograms of (a) RC1, (b) RC1/PPy, (c) RC1/PTh.

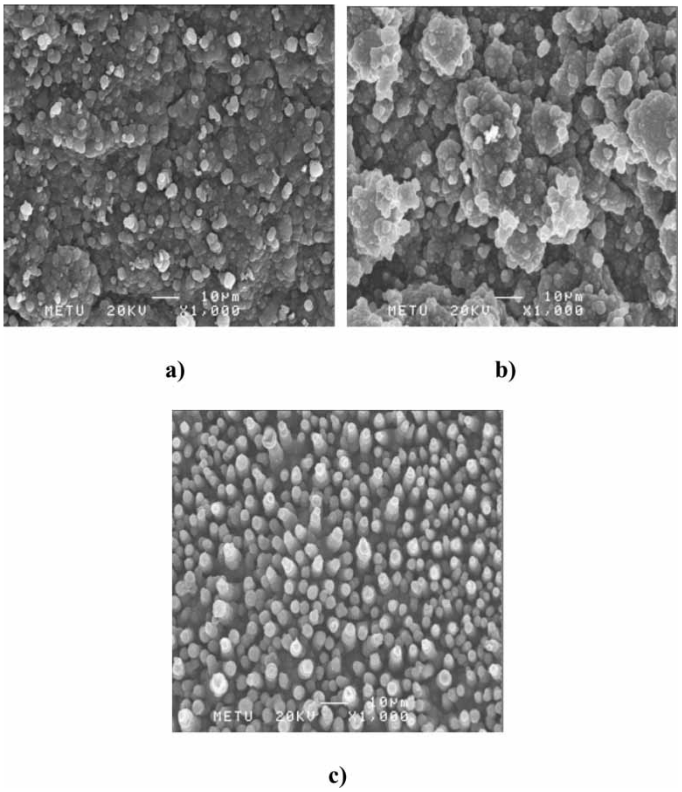
compact structures (Figures 4 a–c). RC2/PPy revealed ordered, rod-like morphology. This could be attributed to the increased COA content of RC2 in comparison to RC1 and BC. COA moieties are known to exhibit liquid crystalline behavior (12), revealing ordered morphology. The copolymer BC/PPy reflected globular morphology, which was disordered in comparison to random copolymer analogues. Morphologies of the resulting conducting copolymers with pyrrole was quite different than the pure polypyrrole cauliflower structure, hence, this could be considered as further proof of formation of conducting copolymers rather than a simple blend. A similar type of behavior was also observed in the case of copolymers with Th.

3.6 *Spectroelectrochemistry*

Electrochromism denotes the characteristic color change of a material associated with the material's reduction-oxidation states. Electrochemical switching of electrochromic materials results in different optical absorption spectra. Spectroelectrochemistry experiments reveal basic properties of conjugated polymers such as band gap (E_g) and evolution of charge carrier bands. The electrochromic films were deposited on ITO electrode via potentiostatic electrochemical copolymerization of RC2 and BC in the presence of thiophene and TBAFB in dichloromethane at 2.0 V at 0°C. Copolymer coated ITO was investigated by UV-Vis spectroscopy in the same but monomer free electrolytic system by switching the applied potential with incremental increase. UV-Vis spectrum of BC/PTh (Figure 5(a)) revealed the electronic band gap which is defined as the onset energy for the π-π^* transition, to be 2.47 eV and λ_{max} was 487 nm at 0.5 V (neutral state of the conducting polymer). As positive potentials applied, evolution of new electronic transitions related with the formation of charge carriers at 750 nm and 1000 nm was observed. Similar but less pronounced type of behavior was observed for RC2/PTh, which could be attributed to the lower conductivity of the material.

Table 2. Conductivities of graft copolymers

Sample	Conductivity (S/cm)
BC/PTh	9
BC/PPy	8×10^{-2}
RC1/PTh	7×10^{-1}
RC1/PPy	5×10^{-2}
RC2/PTh	3×10^{-1}
RC2/PPy	6×10^{-3}



a) b)

c)

Fig. 4. Scanning electron micrographs of the solution side of (a) BC/PPy, (b) RC1/PPy, (c) RC2/PPy.

Spectroelectrochemistry of pure polythiophene reflects λ_{max} at 474 nm and charge carrier bands are at 800 nm and 1100 nm. There was a remarkable difference between the pure polythiophene and synthesized copolymers, in terms spectroelectrochemical behavior, yet to be considered as further proof of copolymerization.

3.7 *Colorimetry*

Colorimetry studies perform an objective and quantitative measurement of color. Color is made up of three attributes; hue (a), saturation (b), and luminance (L). A color system such as the often-used CIE system was utilized as a quantitative scale to define and compare colors. Colorimetry measurements were performed in the same electrolyte system by using

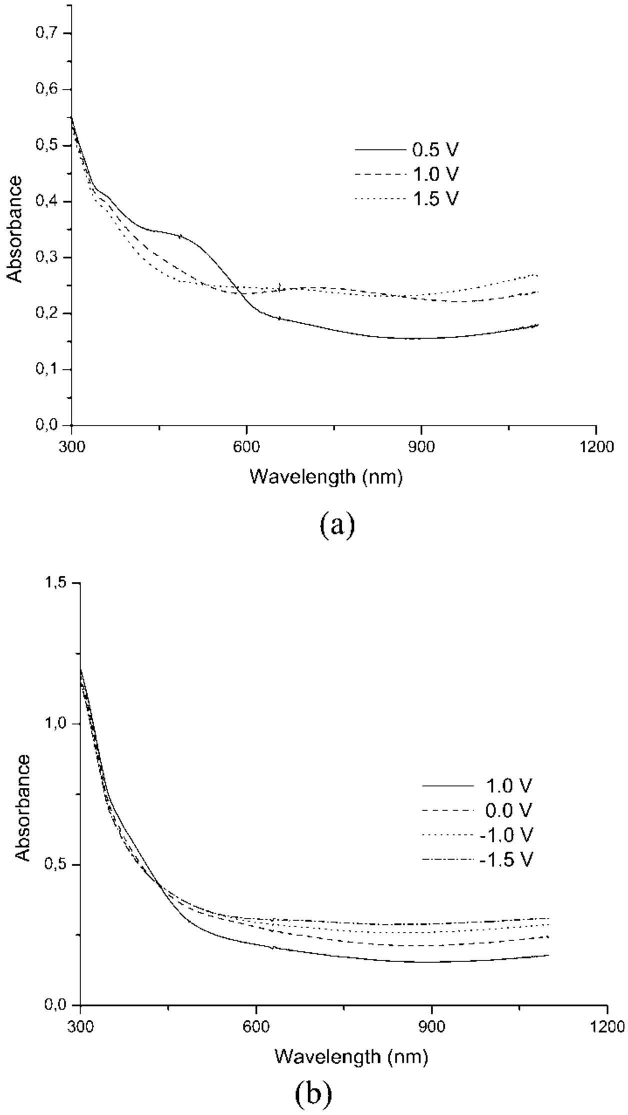


Fig. 5. Spectroelectrochemistry of (a) BC/PTh, (b) RC2/PTh.

the Coloreye XTH Spectrophotometer. The relative luminance (L) and the a, b values were measured at the fully oxidized and reduced states of the conducting polymers (Table 3). The color of the BC/PTh films switches from a light brown in the oxidized form to light yellow in the reduced state. It was observed that the type and composition of the initial copolymers play an important role in variation of color.

Table 3. Electrochromic properties of graft copolymers

Material	Color (ox)	Color (red)	L	a	b
BC/PTh	Light	Light	46[a]	1	3
	Brown	Yellow	52[b]	−5	27
RC1/PTh	Light	Light	48[a]	−1	10
	Greenish Blue	Brown	60[b]	−5	5
RC2/PTh	Gray	Light	30[a]	3	5
		Brown	49[b]	−2	0

[a](Ox) oxidized state.
[b](Red) reduced state.

4 Conclusions

Random and block copolymers of electroactive and liquid crystalline macromonomers were subjected to constant potential electrolysis in the presence of thiophene or pyrrole comonomers, in a ACN-TBAFB solvent–supporting electrolyte system at 2.0 V or 1.1 V respectively at room temperature. Characterization of graft copolymers were performed by FTIR, CV, SEM, spectroelectrochemistry, colorimetry and conductivity measurements, all of which revealed remarkable differences between the synthesized copolymers and pure PPy or PTh. It was observed that a change in the composition or copolymer type of the precursor polymer resulted in stern effects on morphology, spectroelectrochemistry, color and conductivity of the resultant graft copolymers.

5 Acknowledgments

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