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I. Kerman[a]; L. Toppare[a]; F. Yilmaz[b]; Y. Yagci[b]
[a] Department of Chemistry, Middle East Technical University, Ankara, Turkey [b] Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey

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Thiophene Ended ε-Caprolactone Conducting Copolymers and their Electrochromic Properties

I. KERMAN,[1] L. TOPPARE,[1] F. YILMAZ,[2] AND Y. YAGCI[2]

[1]Department of Chemistry, Middle East Technical University, Ankara, Turkey
[2]Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey

ε-Caprolactone was polymerized by ring-opening polymerization (ROP), using thiophene methanol as the initiator and stannous octoate as the catalyst to yield poly(ε-caprolactone) with a thiophene end group. Homopolymerization of thiophene functionalized poly (ε-caprolactone) (PCL) was achieved by a constant current electrolysis method. Copolymerizations of PCL with thiophene and pyrrole were achieved in acetonitrile (ACN)-tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couple via constant potential electrolysis. Characterization of the samples were performed by nuclear magnetic resonance spectroscopy (NMR), cyclic voltammetry (CV), fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Electrical conductivities were measured by the four-probe technique. Spectroelectrochemical behavior of PCL/PTh film, which was deposited on ITO-glass, was investigated by UV-Vis Spectrophotometer. Furthermore, it is found to be an anodically coloring copolymer that electrochemically switches between gray-blue oxidized state and pale red reduced state, exhibiting electrochromic behavior.

Keywords polypyrrole, polythiophene, poly-ε-caprolactone, electrochromism, conducting polymers

Introduction

The area of conducting polymers has become the subject of research since polyacetylene was found to exhibit high electronic conductivity in 1977 (1). Their advantageous properties such as environmental stability, homogeneity, and reversibility enhanced the practical use of conducting polymers in various applications (2). Those applications ranging from rechargeable batteries to electrochromic displays increased the interest in conducting polymers (3). Electrically conducting polymers could be synthesized by either chemical or electrochemical polymerization methods. The most preferred one is polymerization via electrochemical means since it is simple, reproducible, reactions can be carried out in room temperature, polymer films are directly deposited onto electrode surface and can be peeled off easily (4). However, having poor mechanical and physical properties,

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Address correspondence to L. Toppare, Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey. E-mail: toppare@metu.edu.tr; Yusuf Yagci, Department of Chemistry, Istanbul Technical University, Ankara 06531, Turkey. E-mail: yusuf@itu.edu.tr

conducting polymers lack the ease of processibility. Several attempts have been described to overcome this problem such as, syntheses of conducting polymer composites, graft and block copolymers (5–7). Introducing pyrrole and thiophene functionalized alkyl groups into the main chain is another method to impart new chemical and physical properties to conducting polymers (8, 9).

Being potentially electrochromic materials, electroactive and conducting polymers are also employed in spectroelectrochemical analysis. Electrochromism is a persistent color change with a change in applied potential (10). The color change is due to the energy difference between the π-bonding orbital (conduction band) and the π^*-antibonding orbital (valence band), which lies within the visible region. Upon oxidation, the intensity of the π to π^* transition decreases, and the two low-energy transitions emerge to produce a second color (11). Attachment of different functional groups to polymers results in the change of band gap values. Since coloration of the polymer is closely related to the band-gap, it is possible to control their colors by structural modification (12). In this work, thiophene functionalized poly-ε-caprolactone was synthesized by ring opening polymerization. Copolymers with pyrrole and thiophene were electrochemically synthesized in acetonitrile/TBAFB, solvent/electrolyte system, and characterizations were performed via NMR, FT-IR, CV and SEM. In order to understand the optical properties of the copolymer films, their electrochromic and spectroelectrochemical behavior have also been studied.

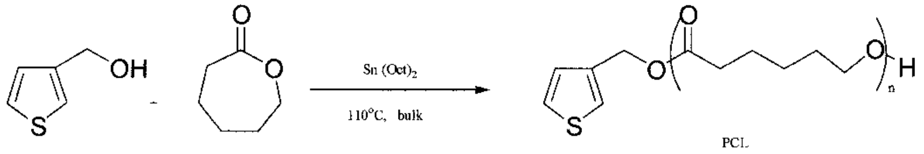
Experimental

Materials

Pyrrole (Py) and thiophene (Th) (Aldrich) were distilled before use. Acetonitrile (ACN) (Merck), Dichloromethane (DCM) and Borontrifluoride-ethylether (BFEE) (Sigma) were used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) was used as received. ε-Caprolactone and thiophene methanol were purchased from Aldrich.

Synthesis of Thiophene Functionalized Poly-ε-caprolactone

The synthesis of PCL involved the reaction of thiophene methanol (0.41 M) with ε-caprolactone (8.5 M), in the presence of stannous 2-ethyl-hexanoate (stannous octoate) as the catalyst (Scheme 1). Ingredients were added into a previously flamed and nitrogen purged Schlank tube, equipped with a magnetic stirrer. Polymerization of ε-caprolactone was carried out in bulk, at 110°C. After a given time, mixture is diluted with CH_2Cl_2 and poured into a ten-fold excess of cold methanol and precipitated. The precipitate was allowed to dry at room temperature in vacuum for three days.



Scheme 1.

Cyclic Voltammetry (CV)

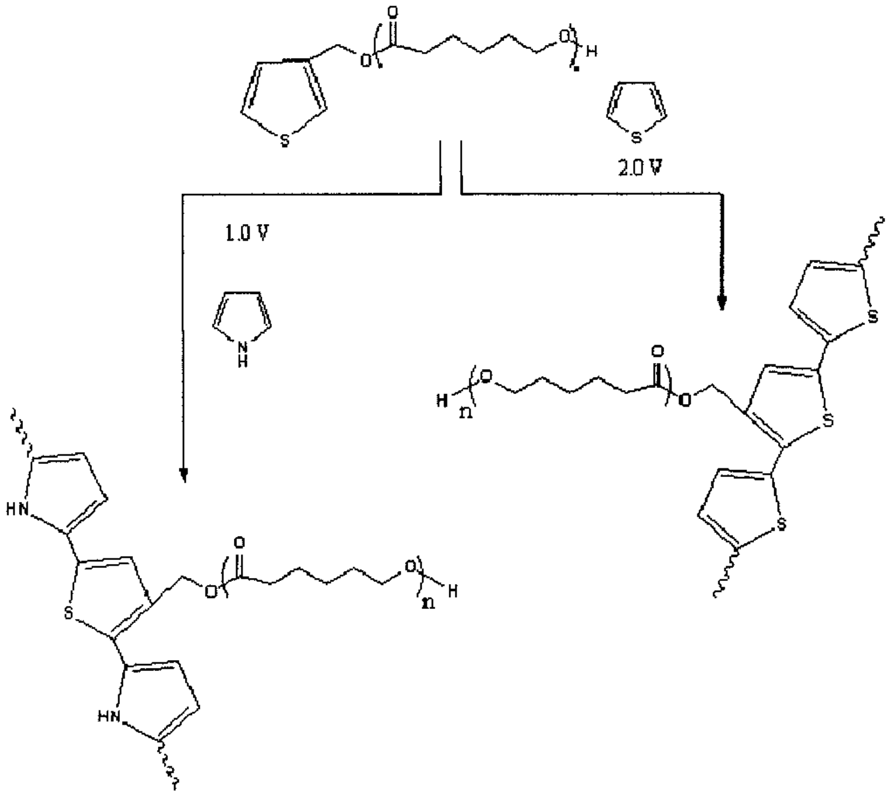
The oxidation/reduction behavior of PCL and PCL, in the presence of thiophene and pyrrole, were investigated by CV. The system consists of a Wenking POS 2 potentiostat/galvanostat and X-Y recorder. The measurements were performed in a CV cell which is equipped with Pt-foil working and counter electrodes and an Ag/Ag^+ reference electrode. ACN/TBAFB, solvent/electrolyte, couple was used in the process. Polymer was dissolved in the reaction medium.

Syntheses of Conducting Copolymers of PCL with Pyrrole and Thiophene

Copolymer films of PCL were synthesized by constant potential electrolysis, using a Wenking POS 73 potentiostat. Electrolyses were performed in a one compartment cell, under nitrogen atmosphere, using platinum (Pt) foils as the working and counter electrodes while Ag/Ag^+ was utilized as the reference.

The synthesis of PCL/Py was performed in ACN/TBAFB solvent/electrolyte system, using 0.02 M Py, 0.05 M supporting electrolyte and 0.44 M PCL. Electrolysis was performed at +1.0 V (Scheme 2).

Electrolyses in the presence of 0.02 M thiophene were conducted at +2.0 V in a medium consisting of 0.44 M PCL, 0.05 M TBAFB in 30 ml ACN. After polymerizations, films were washed intensively with convenient solvents, in order to remove unreacted PCL, and excess supporting electrolyte



Scheme 2.

Galvanostatic Polymerization of PCL

1.5 M PCL and 0.2 M TBAFB were dissolved in 15 ml of DCM. Constant current electrolysis was carried out in a one-compartment cell equipped with Pt working and counter electrodes, allowing the passage of 0.02 mA current at 0°C. A brown, greasy, insoluble polymer grew on the electrode surface. It was washed with DCM and dried at room temperature.

Spectroelectrochemistry

For spectroelectrochemistry, indium doped-tin oxide (ITO) coated glass slides were used as the working electrode while using Pt wire as counter, and Ag/Ag^+ as reference electrodes.

2 mM PCL and 2 μl Th were dissolved in BFEE. Films were coated onto ITO-electrodes in this medium, using a UV cuvette as an electrolysis cell, at +1.6 V constant potential. Spectroelectrochemical studies were carried out by recording UV-Vis spectra of the copolymer film at various potentials, in ACN/TBAFB system. Agilent 8453 UV-Vis spectrometer was used for that purpose.

Colorimetry Analysis

Colorimetry analysis was run in order to describe the color quantitatively. The most commonly used system for this purpose was established by the Comission Internationale de l'Eclairage (International Comission of Illumination), which is known as CIE system of colorimetry. Of the three most commonly used CIE color spaces, 1967 $L*$ $a*$ $b*$ system was chosen because of its general use in industry (12). Color of the fully oxidized and fully reduced states of the copolymer were read by GretagMacbeth Color-eye XTH.

Results and Discussion

Synthesis of PCL

The pseudo-anionic ROP is often referred to as coordination-insertion ROP, since the propagation is thought to proceed by coordination of the monomer to the active species, followed by insertion of the monomer into the metal-oxygen bond by rearrangement of the electrons (13, 14).

The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxy end group. Many reactions catalyzed by metal complexes are highly specific and, by careful selection of metal and ligands, reactions can be generated to form a desired polymer structure. The covalent metal alkoxides with free *p* or *d* orbitals react as coordination initiators and not as anionic or cationic initiators. Stannous octoate and aluminum isopropoxide are the most frequently used initiators catalysts in ROP of lactones (cyclic ester).

In view of the reported role of hydroxyl group as an initiator in ring-opening polymerization, the polymerization of ε-caprolactone in the presence of thiophene methanol as the initiator and $Sn(Oc)_2$ as the catalyst was expected to produce PCL containing a thiophene end group. As seen from Table 1, the measured and calculated M_n values are in good agreement indicating that each thiophene molecule generates one growing end.

Table 1
Synthesis of thiophene functionalized poly(ε-caprolactone)[a]

$[I]x10^{-2}$ (mol/L)	Time (hour)	Conversion (%)	Mn_{theo}	Mn_{GPC}	Mw/Mn	$Mn_{H\text{-}NMR}$
41	140	100	2300	2100	1.37	2350

[a]Temp. 110C°, [ε-CL]o = 8.5 mol/L (in bulk), [I]/[ε-CL]: 1/20 and $[Sn(Oct)_2]/[I]$: 1/400.

¹H-NMR Spectroscopy

^{1}H-NMR spectrum was taken on Bruker-Instrument-NMR Spectrometer (DPX-400), using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. ^{1}H-NMR spectrum of PCL in $CDCl_3$ is shown in Figure 1. In the ^{1}H-NMR spectrum of the polymer not only the specific signals of poly(ε-caprolactone) (PCL) can be found, but also absorptions belonging to the rest of thiophene methanol. Figure 1 shows the ^{1}H-NMR spectrum of polymeric macromonomer in $CDCl_3$. The peak at **g** (5.1 ppm) implies the presence of protons of β methylene groups of thiophene. The peaks at **h, i, j** (7.0–7.3 ppm) observed correspond to three protons on thiophene rings. ^{1}H-NMR results clearly indicate the presence of the pre-assumed structure.

Thermal Behavior

Thermal behavior of the precursor polymer was investigated by using a Du Pont 2000 Thermal Gravimetry Analyzer and Differential Scanning Calorimetry. DSC thermogram was obtained under nitrogen atmosphere, in the range of 25°C to 450°C at a heating rate of 10°C/min. DSC thermogram of PCL shows a sharp melting point at 55.08°C and it is stable up to 312°C (Figure 2a). A second endotherm is observed at

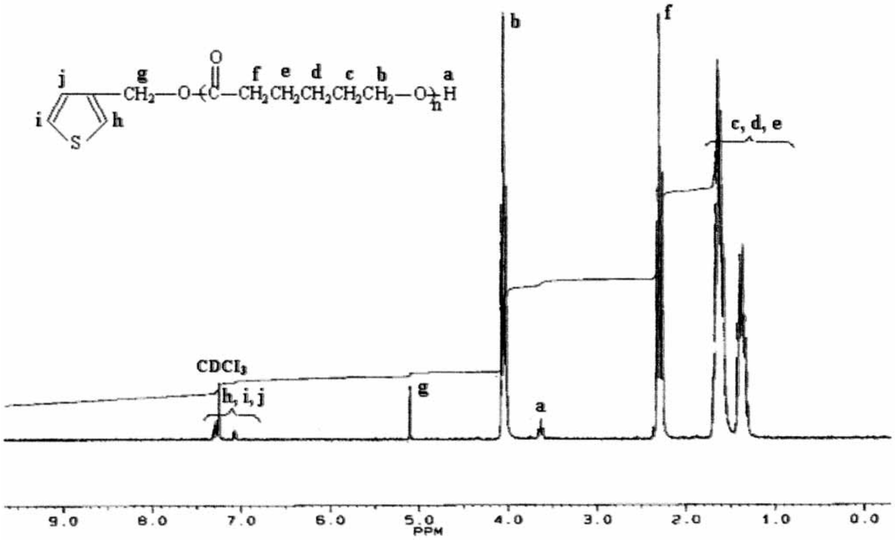


Figure 1. ^{1}H-NMR spectrum of PCL.

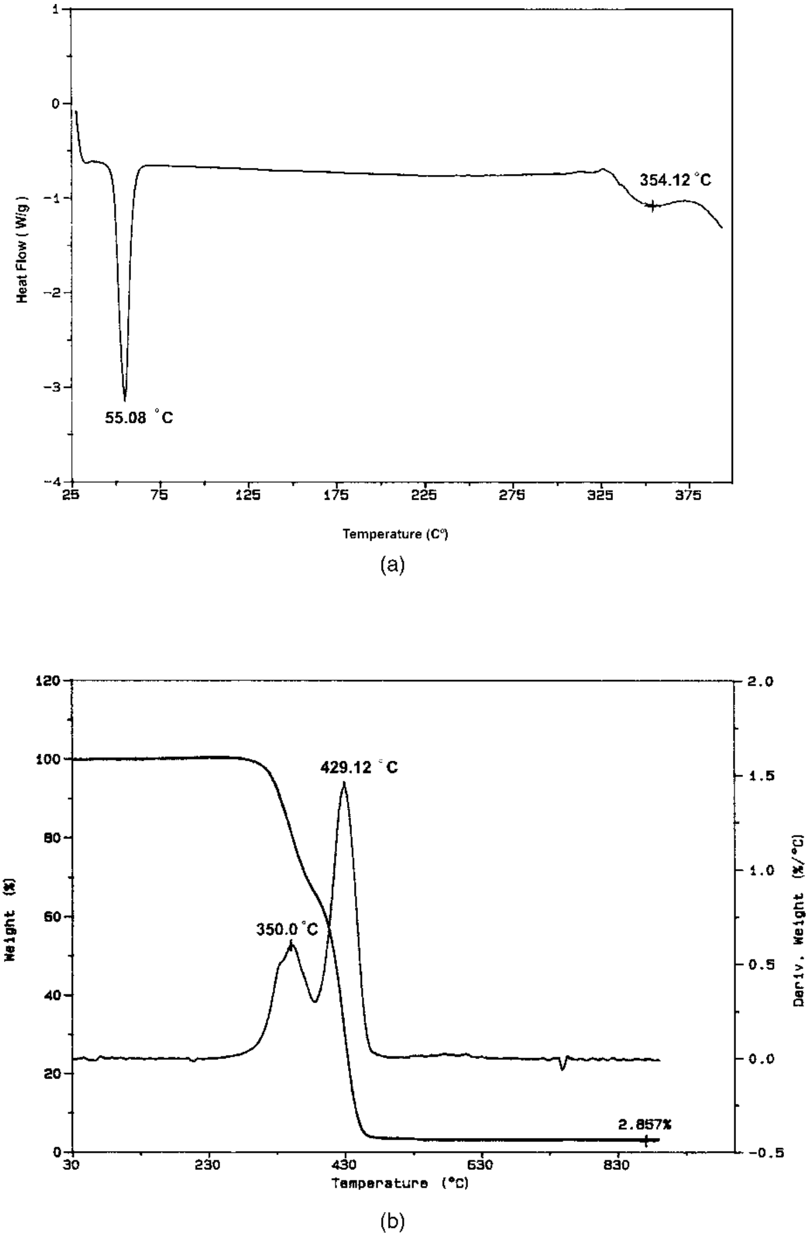


Figure 2. (a) DSC thermogram of PCL; (b) TGA thermogram of PCL.

354°C. TGA thermogram of PCL showed two weight losses at 350°C and 429.12°C (Figure 2b). The weight loss at 350°C was seen to start at around 330°C, which is also supported by the DSC thermogram. This is due to the thermal degradation of PCL, which degrades by specific chain end scission in bulk, at 280–330°C (15). The other weight loss at 429°C corresponds to decomposition of PCL. After the process, only 2.85% of the polymer is left.

Cyclic Voltammetry

Redox behavior of PCL was investigated via cyclic voltammetry. CV's of PCL in an ACN-TBAFB system implied that our precursor polymer is not electroactive since it lacks the existence of any redox peaks. Upon addition of Py into the reaction medium, an increasing redox peak with increasing scan number was observed (Figure 3b). The number of cycles observed up to a certain current value was different than that of pure polypyrrole (PPy) (Figure 3a). Moreover, the well-defined oxidation peak at +0.65 V for PPy ceased to exist, and a sharpening of the reduction peak was observed.

When the CV's of PCL was investigated in the presence of Th, a well-defined, oxidation peak at +1.1 V and a reduction peak at +0.6 V were observed. As seen in Figure (3c), it is sharper than the peak for PTh. Also, the number of cycles within the same interval of current values is different than of PTh (Figure 3d). Moreover, the rate of the current increase with continuous cycles decreased, implying that polymerization through the thiophene moieties stop after some extent.

Characterization

Homopolymerization of PCL was only achieved by galvanostatical polymerization. Electropolymerization of PCL with thiophene and pyrrole were achieved in ACN/TBAFB medium.

FT-IR

Nicolet 510 FTIR Spectrophotometer was used for FTIR studies. FTIR studies for PCL showed a characteristic, intense peak at 1727 cm^{-1}, which belongs to C=O stretching vibrations. Two peaks at 2948 cm^{-1} and 2867 cm^{-1} belong to aliphatic methylene stretchings. Peaks between 1296 cm^{-1} to 1046 cm^{-1} can be attributed to C–O–C ester group vibrations. The peak at 732 cm^{-1} is the result of aromatic C–H$_\alpha$ stretching of thiophene units.

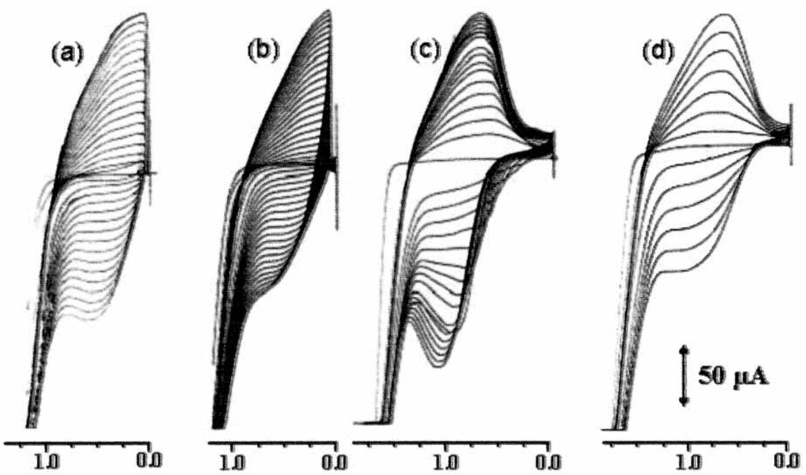


Figure 3. Cyclic voltammograms corresponding to (a) Polypyrrole, (b)PCL/Ppy, (c) PCL/PTh, (d) Polythiophene.

When IR spectrum of galvanostatically polymerized PCL was investigated, the presence of carbonyl stretching at $1724\,cm^{-1}$, C–O–C ester group vibrations between $1295\,cm^{-1}$ to $1192\,cm^{-1}$ can be seen. Additionally, dopant peaks emerged around $1047\,cm^{-1}$ indicating the conductivity of the polymer. Appearance of $C{-}H_\beta$ stretching peak at $884\,cm^{-1}$ is the result of polymerization through 2–5 positions of thiophene ring. Another peak appeared at $1620\,cm^{-1}$ is the proof of conjugation.

The IR spectrum of PCL/PTh reveals the presence of carbonyl stretching at $1727\,cm^{-1}$, and the peak at $1083\,cm^{-1}$ can be attributed to dopant anion. C–H stretching seen at $732\,cm^{-1}$ in the polymer itself, was seen to be decreased in intensity. A new peak emerged at $847\,cm^{-1}$, indicating that the polymerization proceeds through 2–5 positions of the thiophene rings. The peak at $1659\,cm^{-1}$ can be attributed to the presence of conjugation.

IR spectrum of PCL/PPy film revealed a carbonyl peak at $1731\,cm^{-1}$. This proves the presence of PCL in the resultant polymer since the carbonyl is specific to the precursor polymer.The peaks at 1293 to $1030\,cm^{-1}$ are related to C–O–C stretchings, and dopant anion. $902\,cm^{-1}$ belongs to N–H wagging, proving the presence of Py in the structure. The peak belonging to $C{-}H_\alpha$ stretching at $732\,cm^{-1}$ was decreased in intensity, and a new peak emerged at $848\,cm^{-1}$, proving the polymerization through 2–5 positions on Th ring.

Conductivities of the Films

A standard four-probe technique was used to estimate the conductivities of PCL/PPy and PCL/PTh copolymers, which were both doped with BF_4^-. Conductivity of PCL/Py was found to be 10.5 S/cm, and that of PCL/Th was found to be 1.4×10^{-2} S/cm. For both copolymers, conductivities of the solution sides and electrode sides were in the same order of magnitude, revealing the homogeneity of the films in terms of conductivity.

Morphologies of the Films

JEOL JSM-6400 scanning electron microscope was used for surface analysis. It can be seen from the SEM micrograph that, the electrode surface of the PCL/PPy film is far different than that of Py, which is smooth on the electrode side (Figure 4b). When the solution side of the PCL/PPy film was concerned, it is completely different than the well-known cauliflower structure of PPy (Figure 4a). Cauliflowers were replaced by droplet-like structures, indicating the formation of a new material.

When PCL/PTh films were investigated, the difference from pure PTh can be seen. The electrode side had star-shaped wrinkles, while the solution side bears a flowery pattern (Figures 4c and d), both of which are completely different than of PTh.

Spectroelectrochemistry

In-situ electrochemical copolymerization of PCL and PTh was investigated under +1.4 V, in BFEE, at every 10 second time intervals.The intensities of peaks 473 nm and 750 nm gradually increased, revealing the formation of the charge carriers of a typical p-type conducting polymer (Figure 5a).

The spectroelectrochemical spectrum of PCL/PTh can be seen in Figure 5b. The absorption band at 473 nm corresponds to the $\pi \rightarrow \pi^*$ transition and the color of the copolymer at neutral state is pale red. The band gap of PCL/PTh estimated at the edge of the $\pi \rightarrow \pi^*$ transition is found to be 1.83 eV. When the applied voltage

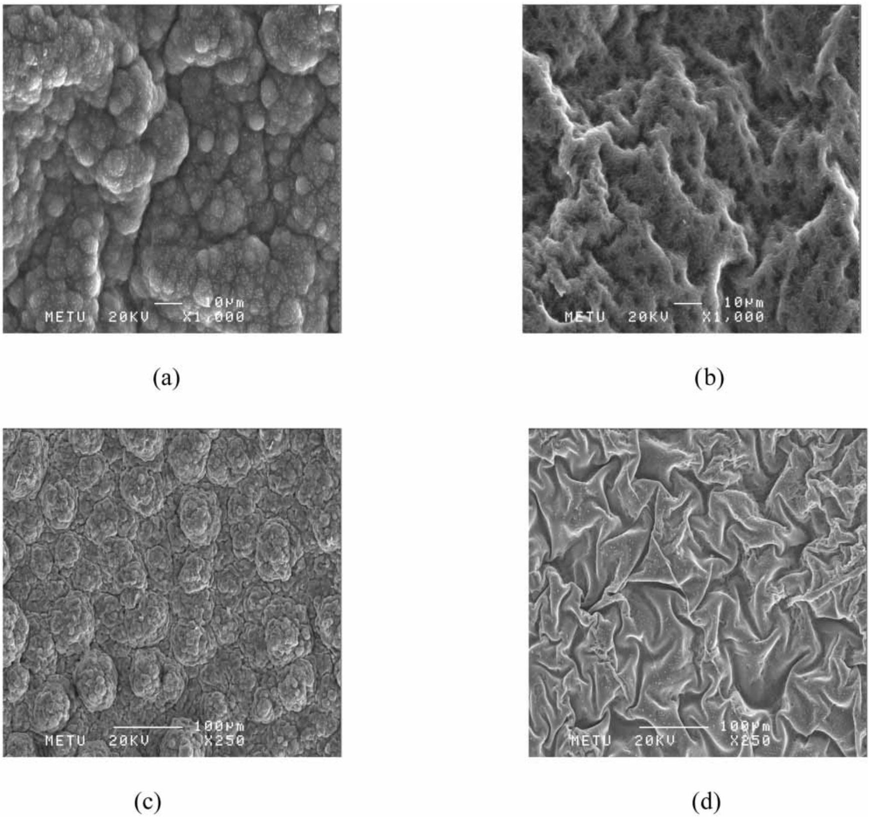


Figure 4. SEM micrographs of (a) PCL/PPy-solution side, (b) PCL/PPy-electrode side (c) PCL/PTh-solution side, (d) PCL/PTh-electrode side.

gradually increased, upon doping, lower energy transitions emerged while $\pi \rightarrow \pi^*$ transitions were stopped. These low energy transitions lead to the evolution of a new absorption band; the polaron charge carrier bands at 720 nm, which can be clearly observed in the figure. This strong shift of the maximum absorption upon applied voltage is related to the electrochromic property of the polymer.

These lower transitions lead to the production of a second color, grayish-blue. When the film was further oxidized, this 720 nm band has also decreased, and in the near-IR region, bipolaron charge carrier bands were seen to emerge. The experiment was repeated, applied potential gradually decreased this time, and no change in band gap or λ_{max} values were observed. The spectroelectrochemistry results showed that, PCL/PTh reversibly changes color between pale red and blue upon doping-dedoping processes, and the results obtained are different from those of PTh, indicating the formation of PCL/PTh copolymer (16).

Colorimetry Analyses

L*a*b values of the film were measured at the fully reduced and fully oxidized states and the data is given in Table 2. PCL/PTh copolymer was grayish-blue at its fully oxidized state, somewhat paler than PTh, but when the color of reduced states are concerned,

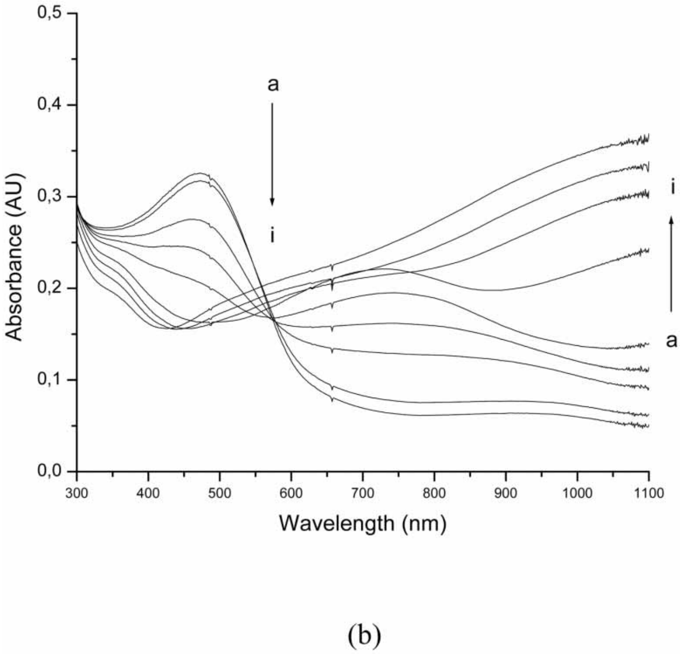


Figure 5. (a) *In-situ* copolymerization of PCL and PTh, (b) Spectroelectrochemistry of PCL/PTh, (a) + 0.2 V, (b) + 0.4 V, (c) + 0.6 V, (d) + 0.7 V, (e) + 0.8 V, (f) + 1.0 V, (g) + 1.2 V, (h) + 1.4 V, (i) + 1.5 V.

this difference is more distinctive. This variation in color as well as band gap values, may point to the formation of a new copolymer.

Electrochromic Switching

Spectroelectrochemistry results showed the ability of PCL/PTh copolymer to switch between its neutral and doped states with a change in transmittance in a fixed wavelength. Electrochromic switching behavior of the film was investigated by recording absorption

Table 2
Electrochemical, electronic, and electrochromic properties of PTh and PCL/PTh

	Epa[b]	Epc[b]	λ_{max} (nm)	L	a	b	Color (red)	Color (ox)	Eg (eV)
PTh[a]	0.63	0.58	495	(ox) 57 (red) 51	(ox)-7 (red) 52	(ox)-2 (red) 46	Bright red	Pale blue	1.92
PCL/PTh	1.1	0.6	473	(ox) 53 (red) 63	(ox)-5 (red) 47	(ox) 7 (red) 25	Pale red	Gray-blue	1.83

[a] Alkan, Selmiye, Cutler, Charlotte A., and Reynolds, John R. (2003) High Quality Electrochromic Polythiophenes via $BF_3 \cdot Et_2O$ Electropolymerization, *Adv. Funct. Mater.*, 13(4): 331–336

[b] Volts vs. Ag/Ag^+; (ox) oxidized state, (red) reduced state.

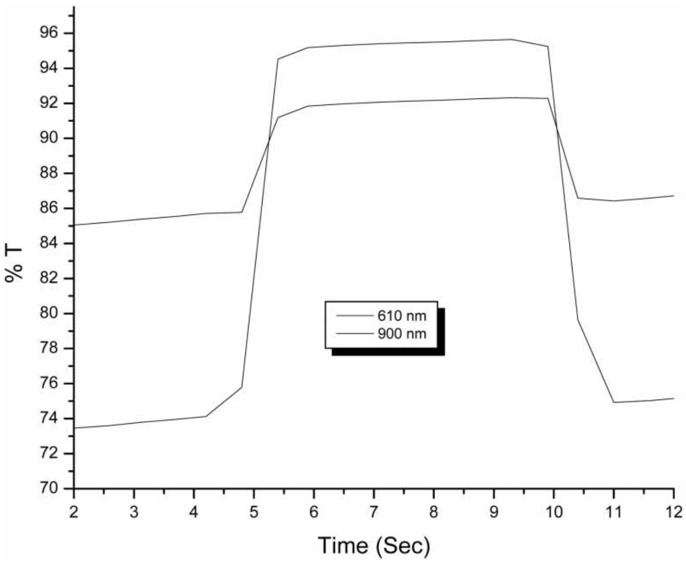


Figure 6. Electrochemical switching of PCL/PTh in BFEE.

spectra while stepping the potential between −0.5 V and +1.7 V, for a switching time of 5 sec. The contrast of PCL was measured as 6.5% and 21% at 610 nm and 900 nm, respectively. Switching time was 0.6 s (Figure 6).

Conclusions

In this work, conducting graft copolymers of thiophene-ended PCL, in the presence of either pyrrole or thiophene, were accomplished electrochemically in ACN/TBAFB solvent-electrolyte couple. Also, the homopolymerization of PCL was achieved via constant current electrolysis. The films were seen to possess conductivity. Characterizations lead us to the conclusion that, PPy and PTh grow through the thiophene moiety of the insulating polymer. Spectroelectrochemical analysis of PCL/PTh film supports the idea that an electrochromic graft copolymer is obtained. Reversible and distinctive color changes of PCL/PTh film revealed that it can be used in construction of electrochromic devices.

Acknowledgments

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