Synthesis of a Novel Macroinimer Based on Thiophene and Poly(ε-caprolactone) and Its Use in Electrochromic Device Application

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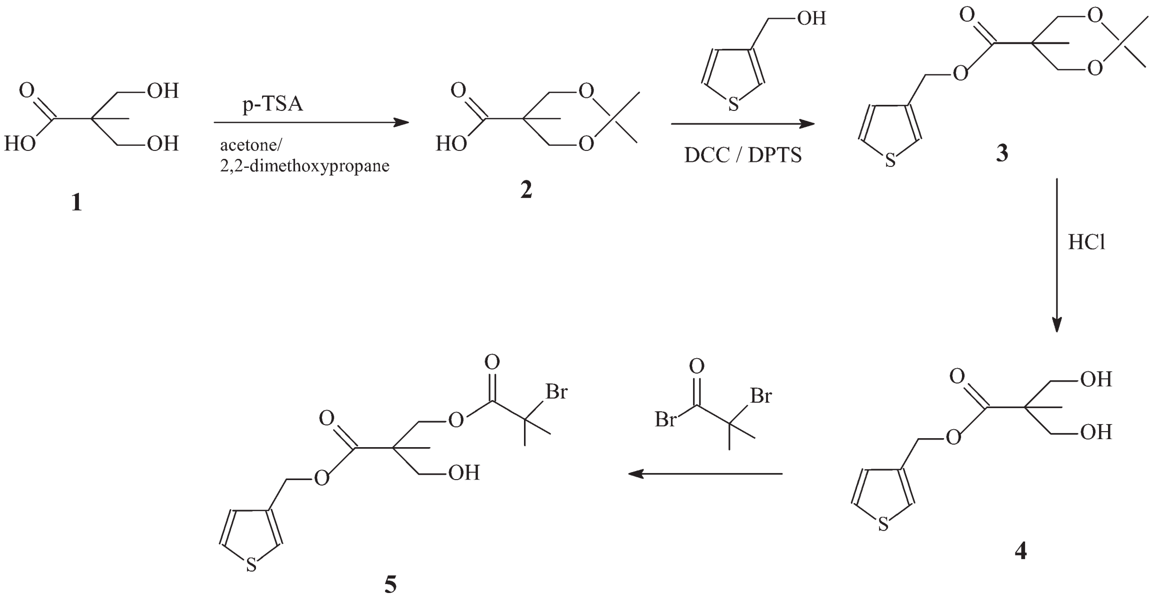
ABSTRACT: Synthesis of a novel macroinimer comprising poly(ε-caprolactone) (PCL) and thiophene (Th) and its use in electrochromic device (ECD) application have been reported. First, a novel Th monomer (**5**) with miktofuntional initiator groups (primary hydroxyl and tertiary bromide at the third position of the thiophene ring) was synthesized in a four-step reaction sequence. Density functional theory-predicted bond lengths, angles, and vibrations of **5** were in good agreement with available experimental vibrational spectra. Subsequently, ring-opening polymerization of ε-caprolactone (ε-CL) was carried out in bulk using **5** as the initiator and tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) as the catalyst at 115 °C, which led to α-thiophene end-capped PCL macroinimer (PCL-Th). Furthermore, PCL-Th macroinimer was used in electrochemical copolymerization with pyrrole (Py) and Th. PCL-Th/PTh copolymer film synthesized on indium tin oxide-coated glass slide showed electrochromic behavior. Optical analyses of the PCL-Th/PTh copolymer film indicated that the copolymer film was suitable to be used as an anodically coloring material for ECD applications. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4180–4192, 2011

KEYWORDS: conductive polymers; copolymerization; electrochromic device; macroinimer; ring-opening polymerization

INTRODUCTION Conjugated polymers synthesized via polymerization of electroactive monomers have been the subject of a great deal of research, because these polymers display novel properties and have quite a number of applications in rechargeable batteries,[1,2] electrochromic devices,[3,4] sensors,[5] and enzyme immobilization.[6] However, their limited processibility and poor mechanical properties set a barrier for their utilization in such applications. To overcome this problem, efforts have been directed toward obtaining polymeric structures comprising diverse polymer chains carrying electroactive moieties.[7] One way to access such architectures is to use polymer telechelics,[8,9] which bear one or more functionalities at chain ends. Depending on the choice of functionality, telechelics can act as macromonomers,[10] and macroinitiators[11–14] for different modes of polymerization, such as step-growth,[15] controlled radical polymerizations,[16–21] and electropolymerization.[22–24] It is even more interesting that a macromolecule is able to behave as an initiator and a monomer simultaneously, termed as a macroinimer. Use of such telechelics in further chain growth facilitates a versatile combination of chemically different monomer units, covalently linked in a single macromolecule. The resulting polymer will possibly display hybrid properties.

Polythiophenes are a class of conjugated polyheterocycles, which have been extensively investigated due to the synthetic versatility of the thiophene monomer in obtaining electron conducting copolymers with side chain functionalities.[25] Previously, α-thiophene end-capped poly(ε-caprolactone) (PCL)[26] and poly(methyl methacrylate) (PMMA)[27a] polymers were prepared by ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) techniques, respectively. 3-Thiophenemethanol for ROP and trichloro acetylcarbamate derivative of thiophene for ATRP were used as the initiators to obtain the corresponding polymers with thiophene end functionalities. Then, their electropolymerizations with Py and Th through the incorporated α-thiophene units were carried out. In another study,[27b] a thiophene derivative bearing a tertiary bromide moiety at second position of thiophene ring was reported and used as an ATRP initiator for the synthesis of α-thiophene end-capped poly(*tert*-butyl acrylate). Thiophene-terminated polyacrylate was then copolymerized with 3-hexylthiophene by oxidative polymerization ($FeCl_3$ being the oxidant) to get rod-coil and coil-rod-coil block copolymers. We believe that combining the aforementioned routes in the preparation of an electron conducting terpolymer, poly(thiophene-*co*-ε-caprolactone-*co*-methyl

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthetic route of thiophene monomer with miktofunctional initiator groups.

methacrylate), might yield distinct mechanical properties besides interesting electrochromic behavior.

In this article, as part of a broader study, we report the synthesis of a novel thiophene monomer with miktofunctional initiator sites for ROP and ATRP at the third position of the thiophene ring in a four-step reaction sequence (Scheme 1). Detailed calculations based on density functional theory (DFT) were also carried out to shed more light on the accurate prediction of geometry and IR spectroscopic characteristic for the thiophene monomer in the gas phase. The primary hydroxyl initiating site of the thiophene monomer was first used in the ROP of ε-caprolactone (ε-CL), which led to PCL macroinimer with α-thiophene and tertiary bromide end groups (PCL-Th). Furthermore, the copolymer of PCL-Th with Th was electrochemically synthesized by using the former as a macromonomer and electrochromic and spectroelectrochemical behaviors of the copolymer film (PCL-Th/PTh) were studied. Finally, we constructed a dual-type electrochromic device (ECD) based on PCL-Th/PTh copolymer film and poly(3,4-ethylenedioxythiophene) (PEDOT). The device was assembled in a sandwich configuration of electrochromic materials (PCL-Th/PTh and PEDOT) deposited on indium tin oxide (ITO) glass electrodes. In the construction of the device, PEDOT was used as the cathodically coloring material, whereas PCL-Th/PTh served as the anodically coloring agent. Further potential of PCL-Th macroinimer bearing Br initiating site for ATRP of methyl methacrylate (MMA) in the block copolymer formation, consecutive electropolymerization with Th yielding poly(thiophene-*co*-ε-caprolactone-*co*-methyl methacrylate), and ECD characteristics of the terpolymer will be reported elsewhere.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, 99%; Riedel) was dried by refluxing over Na and then distilled in a dry argon atmosphere. Triethylamine (TEA, 99.5%) was obtained from Fluka, dried over CaH_2, and stored over 3-Å molecular sieves. Acetonitrile (ACN) and other solvents were purified by conventional procedures. ε-CL (97%; Aldrich) was distilled over CaH_2 and stored over dry 4-Å molecular sieves *in vacuo*. Thiophene (Th, 98%; Aldrich) and pyrrole (Py, 99%; Aldrich) were distilled before use. 2,2-Bis(hydroxymethyl)propionic acid (98%; Aldrich), 2,2-dimethoxypropane (98%; Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%; aldrich), stannous octanoate [$Sn(Oct)_2$, 95%; Aldrich], 3,4-ethylenedioxythiophene (EDOT, 97%; Aldrich), 3-thiophenemethanol (98%; Aldrich), propylene carbonate (PC, 99.7%; Aldrich), tetrabutylammonium tetrafluoroborate (TBAFB, 99%; Aldrich), and PMMA (Mw: 120,000; Aldrich) were used without further purification. All other reagents were purchased from Aldrich and used as received. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was obtained through the reaction of anhydrous *p*-toluenesulfonic acid (*p*-TSA; Aldrich) with 4-dimethylamino pyridine. ITO-coated glass slide (Aldrich) has resistance of 8–12 Ω.

Measurements

All the calculations were done using GAUSSIAN 03W program on Windows. The geometry of **5** was optimized first using semiempirical AM1 and then B3LYP (Becke, three-parameter, Lee-Yang-Parr).[28,29] Frequency/intensity calculations were carried out using B3LYP. In all cases, the 6-31G (d,p) basis set was used. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature using Varian UNITY INOVA 500-MHz NMR (125.7 MHz for ^{13}C). The chemical shifts were relative to tetramethylsilane at $\delta = 0$ ppm for protons. $CDCl_3$ was used as the deuterated solvent for polymers. ATR-FTIR spectra were recorded on Perkin–Elmer Paragon 1000 spectrometer. Molecular weights and molecular weight distributions of the polymers were measured on an Agilent Instrument (Model 1100) consisting of a pump, a refractive index and a UV detector, and four Water Styragel columns (HR 5E, HR 4E, HR 3, and

HR 2), THF being used as eluent at a flow rate of 0.3 mL/min at 30 °C and toluene being used as an internal standard. Molecular weights were calculated on the basis of a calibration curve, drawn using monodisperse polystyrene standards.

The electrochemical polymerizations and characterizations were performed with CHI 760C potentiostat, and the thicknesses of the coated polymer films onto ITO-coated glasses were measured by using PHE101 optical ellipsometer. Spectroelectrochemical studies were carried out on Perkin–Elmer Lambda 30 UV–vis spectrometer. Scanning electron microscopy (SEM) images were taken with Philips XL30 SFEG.

Synthesis of 2,2-Bis[(2,2-propyl)dioxymethyl]propionic Acid (2)

2,2-Bis[(2,2-propyl)dioxymethyl]propionic acid (**2**) was synthesized through the reaction of 2,2-bis(hydroxymethyl)propionic acid (**1**), 2,2-dimethoxypropane, and *p*-TSA in acetone, according to a published procedure.[30]

Synthesis of 2,2,5-Trimethyl-(1,3)dioxane-5-carboxylic Acid Thiophene-3-yl Methyl Ester (3)

3-Thiophenemethanol (1.2 g, 10.52 mmol), **2** (2.17 g, 12.50 mmol), and DPTS (0.67 g, 2.13 mmol) were dissolved in CH_2Cl_2 (50 mL). DCC (2.58 g, 12.50 mmol), dissolved in CH_2Cl_2 (10 mL), was then immediately added, and the mixture was stirred at room temperature for 24 h. The insoluble urea (byproduct) was filtered out, and the filtrate was evaporated to dryness. The remaining product was purified by column chromatography, in which silica gel was used as the stationary phase and *n*-hexane as the eluent. Compound **3** was obtained as a white solid.

Yield = 1.95 g, 68%. ^{1}H NMR (500 MHz; δ, ppm from TMS in $CDC1_3$ at ambient temperature) 1.22 (3H, s —CH_3), 1.38 (3H, s, —CH_3), 1.42 (3H, s, —CH_3), 3.65, (2H, d, —CH_2), 4.15, (2H, d, —CH_2—), 5.18 (2H, s, —CH_2—) and 7–7.4 (3H, m, 2, 4, and 5 positions in the thiophene ring).

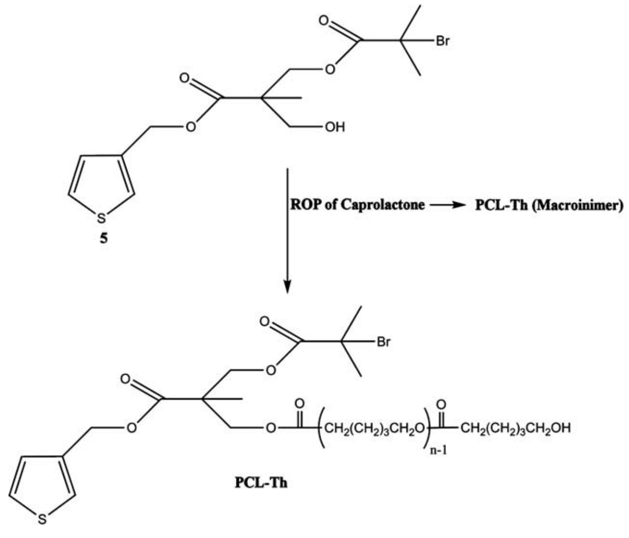
Synthesis of 3-Hydroxy-2-hydroxymethyl-2-methyl-propionic Acid Thiophene-3-yl Ester (4)

Compound **3** (1.9 g, 7.03 mmol) was dissolved in a mixture of 30 mL of THF and 15 mL of 1 M HCl (aqueous). The reaction mixture was stirred for 4 h at room temperature. After filtration of the insoluble salts, the reaction mixture was concentrated and extracted with 160 mL of CH_2Cl_2 and 40 mL of water. The combined organic phases were dried over Na_2SO_4, and filtered. The filtrate was evaporated to dryness, and the product was obtained as a white solid.

Yield = 1.55 g, 96%. ^{1}H NMR (500 MHz; δ, ppm from TMS in $CDC1_3$ at ambient temperature) 1.15 (3H, s —CH_3), 2.75 (2H, broad, OH), 3.85, (4H, m, —CH_2), 5.16 (2H, s, —CH_2—) and 7–7.4 (3H, m, 2, 4, and 5 positions in the thiophene ring).

Synthesis of 2-(2-Bromo-2-methyl-propioyloxymethyl)-3-hydroxy-2-methyl-propionic Acid Thiophene-3-yl Ester (5)

Compound **4** (1.50 g, 6.52 mmol) was dissolved in dry TEA (1.38 mL, 10 mmol) and CH_2Cl_2 (20 mL) and cooled to 0 °C. α-Bromoisobutyryl bromide (0.81 mL, 6.52 mmol) in 5 mL of CH_2Cl_2 was added dropwise to the reaction mixture within 30 min. The reaction mixture was stirred for 4 h at room temperature. After dilution with 200 mL of CH_2Cl_2, the mixture was extracted three times with saturated aqueous solution of sodium bicarbonate (150 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography over silica gel eluting by 1:10 ethyl acetate/hexane and **5** was obtained as yellowish oil.



SCHEME 2 Synthesis of PCL-Th.

Yield = 1.6 g, 65%. Anal. calcd. for $C_{13}H_{17}BrO_5S$: C, 42.75%; H, 4.69%; S, 8.78%. Found: C, 42.95%; H, 4.80%; S, 8.55%. ^{1}H NMR (500 MHz; δ, ppm from TMS in $CDC1_3$ at ambient temperature): 1.24 (3H, s, —CH_3), 1.92 (6H, s, —CH_3), 2.22, (1H, broad, —OH), 3.85, (2H, m, —CH_2—), 4.25–4.45, (2H, dd, —CH_2—), 5.20 (2H, s, —CH_2—) and 7–7.4 (3H, m, 2, 4, and 5 positions in the thiophene ring). ^{13}C NMR (125.7 MHz; δ, ppm from TMS in $CDC1_3$ at ambient temperature): 18.5, 30, 49.5, 55, 62, 65, 68, 120–140, 172, 174.

Synthesis of PCL-Macroinimer (PCL-Th) by ROP of ε-CL

The PCL macroinimer (PCL-Th) was prepared by ROP of ε-CL in bulk with $Sn(Oct)_2$ as the catalyst (Scheme 2). Polymerization was carried out at 115 °C in an inert atmosphere for a given time. A typical polymerization procedure was as follows: To a previously flamed schlenk tube equipped with a magnetic stirring bar, a certain amount of initiator (**5**), catalyst, and monomer were added in that order. The mixture was deoxygenated by flushing with O_2-free argon for 10 min, after which the tube was tightly sealed and immersed in a thermostatic oil bath at 115 ± 1 °C. After a certain polymerization time, the mixture was diluted with CH_2Cl_2 and precipitated into 10-fold cold methanol under vigorous stirring. The precipitate was then isolated by filtration and dried at room temperature *in vacuo*. The polymer yield was determined gravimetrically. Details of the experimental conditions of the polymerization are given in Table 1.

Preparation of Electrochromic Layers (PCL-Th/PTh and PEDOT) on ITO Surface

A three-electrode cell containing ITO-coated glass slide as the working electrode, a platinum foil as the counter

TABLE 1 Synthesis of PCL-Th via ROP Technique

Entry	M	$[M]_o$ (mol L^{--1})	$[M]_o/[I]_o$	I	Time (h)	Con. (%)	$M_{n,Theo}$	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n [a]
PCL-Th [b]	ε-CL	9.02	40	**5**	46	87	4,337	4,132	4,800	1.11

M, monomer; I, initiator (inimer).

[a] Calculated from GPC calibrated with linear polystyrene standards.

[b] Polymerization was carried out at 110 °C ([Initiator]/[Sn(Oct)$_2$] = 300).

electrode, and a silver wire as the reference electrode were used for electrodeposition of PCL-Th/PTh and PEDOT by potentiostatic methods. A 10 mM solution of EDOT in 0.1 M TBAFB/ACN was used to deposit PEDOT film onto ITO-coated glass electrode at 1.5 V versus Ag/Ag$^+$ for 10 s. In the electrochemical polymerization of PCL-Th/PTh, BFEE was used as both solvent and supporting electrolyte. First, PCL-Th was dissolved in dichloromethane (1%, w/v) and then coated on one side of ITO by spin-casting. PCL-Th coated ITO was used as the working electrode. After introducing 10 mM Th to the reaction medium, the copolymerization was performed at 1.9 V versus Ag/Ag$^+$ for 7 s. The electrochemistry experiments were carried out at room temperature under inert argon atmosphere. The electrochemical polymerizations and characterizations were performed with a CHI 760C potentiostat, and the thicknesses of the coated polymer films onto ITO-coated glasses was measured around 100 nm by Optical Elipsometry “Phe101.”

Preparation of Gel Electrolyte

For the construction of dual type electrochromic device, gel electrolyte was prepared in the following form containing ACN + PC + PMMA + TBAFB. The ratio of the composition of ACN:PC:PMMA:TBAFB was 70:20:7:3 by weight. A high vapor pressure solvent, ACN, was used to dissolve the PMMA and to allow an easy mixing of the gel components. TBAFB as the key supporting elements of the proposed gel and PC as the plasticizer were added to the gel mixture. The procedure was as follows: After dissolving TBAFB in ACN, PMMA was added into the solution. The complete dissolution of PMMA was achieved by vigorous stirring and heating. When PMMA was completely dissolved, PC was introduced to the solution. The mixture was stirred and heated until a highly conducting transparent gel was formed.

Construction of Electrochromic Device

ECD was assembled with a configuration of ITO/PCL-Th/PTh||gel electrolyte||PEDOT/ITO as shown in Figure 1. Cathodically coloring layer PEDOT and anodically coloring layer PCL-Th/PTh were synthesized on ITO according to the mentioned procedures. The device was dried under atmospheric conditions.

Electrochemical Synthesis of the Homopolymers and the Copolymers

Electrochemical synthesis of homopolymers of Th and Py and their copolymers with the PCL-Th were conducted by constant potential electrolysis, using a CHI842AB galvanistat/potentiostat, under argon atmosphere at room temperature. Electrolyses were performed in a one compartment cell consisting of a Ag/Ag$^+$ reference electrode, an auxiliary Pt wire electrode, and a Pt foil ($A = 1$ cm^2) working electrode.

Homopolymerization of Th (40 μL) was performed in 10 mL ACN solution at 2.0 V using TBAFB (0.03 M) as the supporting electrolyte. PCL-Th (2 mg, 4.8 × 10^{-4} mmol according to $M_{n,NMR}$ calculation) and Th (40 μL) were electrocopolymerized separately in ACN (10 mL) in the presence of TBAFB (0.03 M) at 2.0 V (Scheme 3).

Py (40 μL) was homopolymerized electrochemically in ACN (10 mL) by using TBAFB (0.03 M) as the supporting electrolyte at a constant potential (1.0 V). The copolymer of PCL-Th (2 mg, 4.8 × 10^{-4} mmol according to $M_{n,NMR}$ calculation) with Py (40 μL) was prepared electrochemically in ACN (10 mL) in the presence of TBAFB (0.03 M) at 1.0 V (Scheme 3).

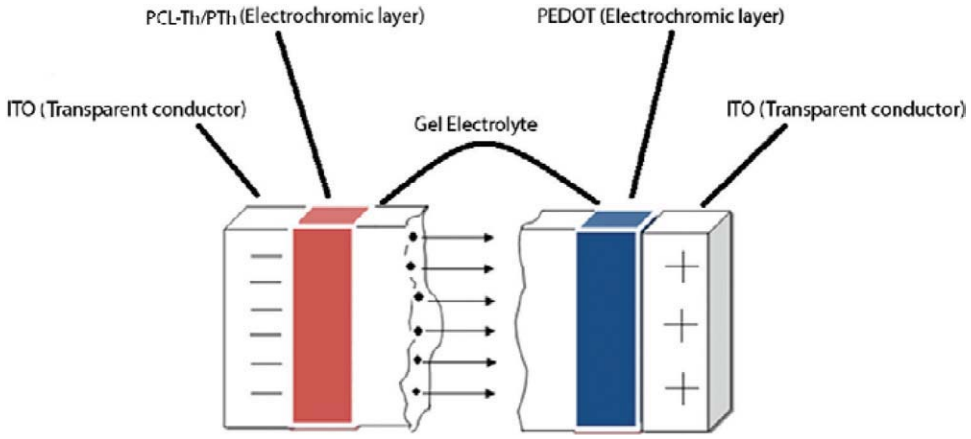
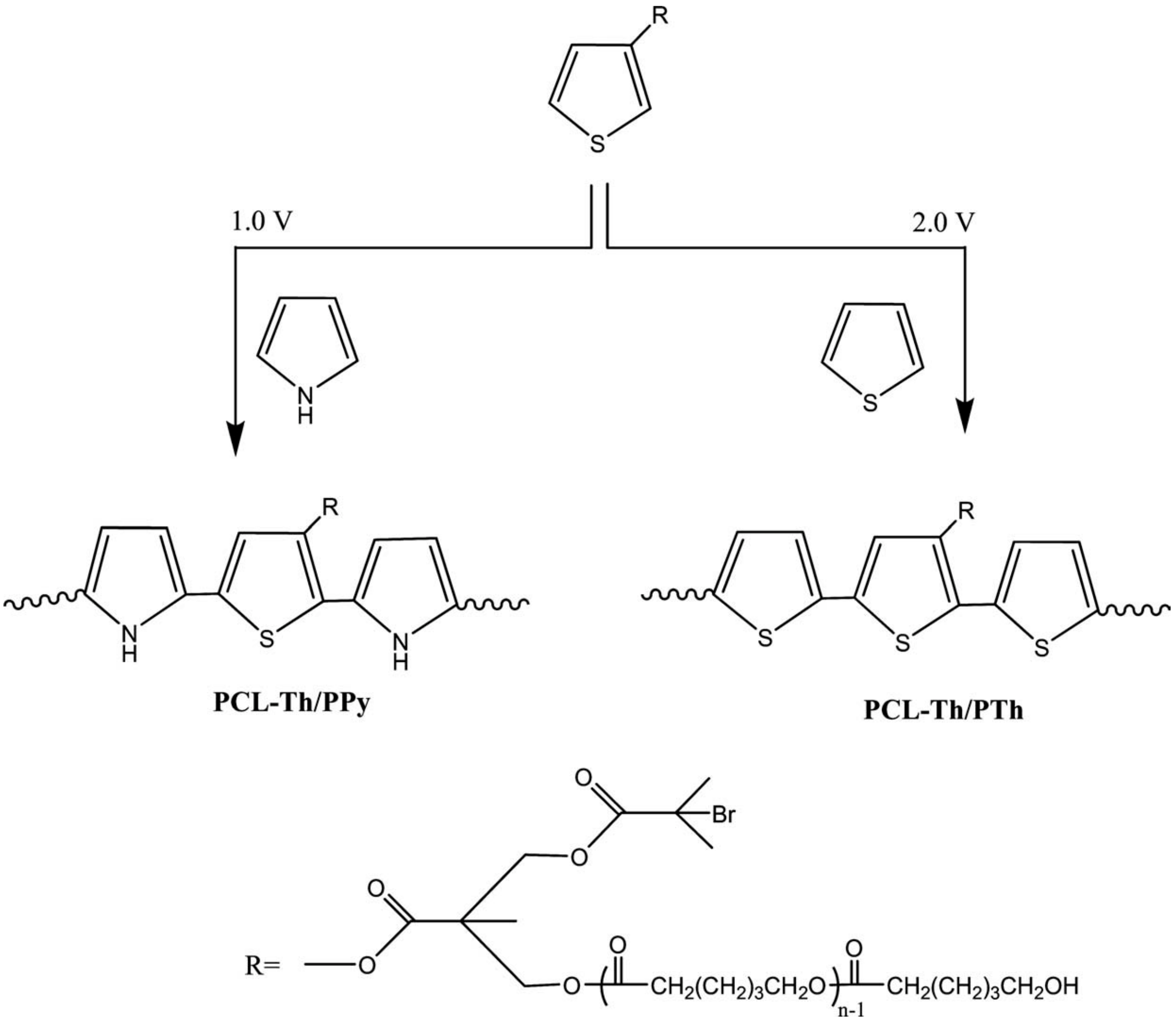


FIGURE 1 Schematic illustration of a dual ECD based on PCL-Th/PTh and PEDOT electrochromic polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 Electrochemical copolymerization of PCL-Th with Th and Py.

The obtained copolymer films were rinsed thoroughly with ACN to remove TBAFB, unreacted monomer, and precursor polymer.

RESULTS AND DISCUSSION

Theoretical Results

Geometry Optimization

The molecular structure of **5** is shown in Figure 2, and the optimized geometric parameters obtained by B3LYP/ 6-31G (d,p) level in vacuum are presented in Table S1 (See Supporting Information). It should be emphasized that we were able to compare the calculated and experimental geometric data of the thiophene part of **5** only, due to unavailability of the experimental data of the whole molecule. The DFT-predicted C═C bonds in the thiophene ring, C(18)—C(19) and C(20)—C(21), were close to experimental values, and they were about 0.01 Å shorter than the corresponding experimental ones. From the comparison of calculated and experimental geometric data, it was concluded that the distortions originating from the other part of **5** were small, especially with regard to the bond lengths, with a maximal deviation of 0.024 Å in the calculated data.

In addition, small distortions with a maximal deviation of 0.9° in calculated bond angles in the thiophene ring were obtained. All the geometric data for the thiophene ring, calculated at either 6-31g(d) or 6-311g(d, pd) basis set level were very close to the experimental results.[31]

Vibrational Frequencies

The calculated IR absorption spectrum (4000–200 cm^{-1}) of **5** in the gas-phase at the B3LYP/6-31G (d,p) level is shown in the Figure S1 (Supporting Information). The calculated values show a good correlation with the experimental data obtained from the literature,[28,29,32–34] most of the bands having been correctly predicted (see Supporting Information Table S2). To compare the calculated vibrations with the experimental observations, scaling of the vibrational frequencies was implemented. For the frequencies calculated with B3LYP, a scaling factor of 0.963 is commonly accepted.[35]

The most pronounced vibrational features of **5** were the intense peaks at 1744 and 1730 cm^{-1} corresponding to

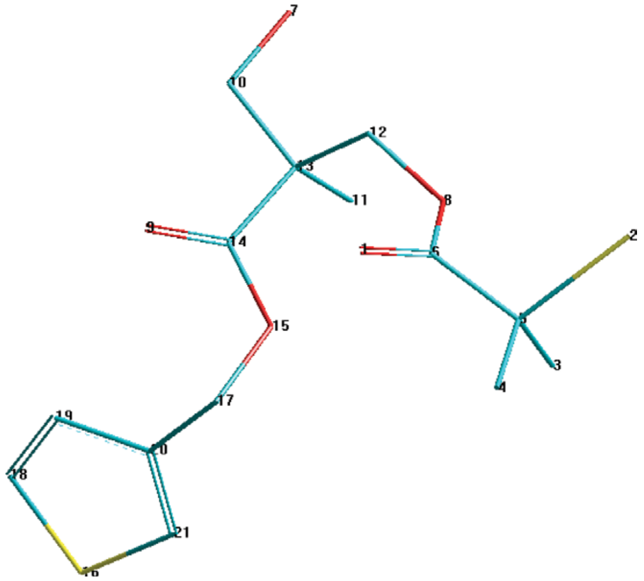


FIGURE 2 Geometry optimized structure and atom numbering of **5** at the B3LYP/6-31G (d,p) level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

C=O stretching in the ester group. The second most intense peak was observed at 1268 cm^{-1} for CH_2 wagging of the whole molecule. Typical hydroxyl stretching was predicted at 3628 cm^{-1}. In-plane stretching of C—H at 3152–3126 cm^{-1} in thiophene ring was very well established. One of the other well predicted strong mode was C=C in-plane stretching of thiophene, located at 1424 cm^{-1}. Thiophene ring of the molecule showed the C—S ring deformation stretching at 618 and 609 cm^{-1} for calculated and experimental values, respectively. C—Br stretching was precisely predicted to emerge at 626 cm^{-1}.

Experimental Results

The novel thiophene monomer with two miktofuntional initiator groups **(5)** was prepared according to Scheme 1. First, a diacetal of bis(hydroxymethyl)propionic acid (**2**) as a core compound was obtained from **1**. The reaction of **2** with 3-thiophenemethanol resulted in a thiophene functional compound (**3**) with DCC and DPTS in high yields after purification with column chromatography. The deprotection of the acetonide group of **3** was easily achieved quantitatively in the presence of 1 M HCl and afforded compound **4**. The ATRP initiator functionality was introduced into the core through an esterification reaction of one hydroxyl group of **4** with 1 equiv of α-bromoisobutyryl bromide. The disubstituted product did not form, probably due to steric hindrance. The expected structure was confirmed by FTIR, ^1H and ^{13}C NMR spectroscopies.

FTIR spectra of **5** together with PCL-Th are shown in Figure S2 (see Supporting information). There were significant changes in the FTIR spectral properties of **5** and the polymeric product. Compound **5** exhibited an intense broad absorption corresponding to the O—H stretching at 3500 cm^{-1}. The intensity of hydroxyl peak in the spectrum of PCL-Th considerably decreased after ROP as the molecular weight of the polymer increased. It was also observed that ROP caused an increase in the intensity of carbonyl group, futher indicating the incorporation of ε-CL monomer in ROP.

Figure 3(a,b) displays ^1H and ^{13}C NMR spectra of **5**, respectively. ^1H NMR spectrum of **5** clearly showed the signals that arose from ATRP initiator ($—CBr(CH_3)_2$, **i**, $\delta = 1.85$), and monofunctional hydroxyl group ($—CH_2OH$, **f**, $\delta = 2.24$). The signals at around 7.01–7.38 ppm were assigned to the aromatic protons (**a**, **b**, and **c**) of thiophene ring. The proton-decoupled ^{13}C NMR of **5** provided further support of the desired structure due to the presence of two different carbonyl peaks as expected. The resonance signals at 175 and 172 ppm were due to the presence of two different ester carbonyl carbons (C_f and C_m) in **5**. The signals of the carbon atoms of the thiophene ring in 5 were also observed at 125 ppm (C_a), 127 ppm (C_b), ppm, and 128 ppm (C_3). The observation of these peaks in ^1H and ^{13}C NMR spectra proved that **5** was successfully synthesized.

Compound **5** can be used as a core to prepare block copolymer (PCL-*b*-PMMA-Th) possessing thiophene moiety at the junction point. Synthetic strategy is based on a two-step reaction procedure[36] consisting of the synthesis of well-defined linear α-tertiary bromide and thiophene PCL using a miktofuntional initiator (**5**) in ROP of ε-CL, followed by the ATRP of MMA using the obtained α-tertiary bromide functional PCL as the macroinitiator. In this study, we report the α-thiophene-capped PCL. In the ROP, the use of **5** as the initiator in the presence of $Sn(Oct)_2$ as the catalyst resulted in PCL macroinimer, PCL-Th. Scheme 2 illustrates the synthesis of PCL-Th. The synthesis of block copolymer possessing thiophene functionality at the junction point of homopolymer segments, and its ECD application will be reported in a further study.

The structure of PCL-Th was confirmed by ^1H NMR spectroscopic method and GPC analysis. ^1H NMR spectrum of PCL-Th is shown in Figure 4. The signals of the methylene groups of the repeating units (**g** and **h**) and the primary hydroxyl end units (**i**) were clearly seen in the spectrum. The peak assigned to the terminal methylene protons (CH_2OH, **i,** $\delta = 3.65$ ppm, multiplet) indicated that linear PCL chains were terminated by hydroxyl end groups. The measured and theoretical integral ratio of the terminal methylene protons (H**i**) to that of methylene protons next to the thiophene ring (H**d**) is nearly the same ($H\mathbf{i}/H\mathbf{d}_{measured} = 1.01$, the theoretical value is 1.00). This observation confirms that ε-CL monomers have been inserted into the "$—CH_2CH_2O—H$" group of **5** via selective acyl-oxygen cleavage of ε-CL and that α-thiophene-ended PCL was successfully and quantitavely prepared. The theoretical number-average molecular weight ($M_{n,theo}$) of the PCL-Th macroinitiator was calculated according to $M_{n,theo} = ([M]_0/[I]_0) \times \text{conversion} \times MW_{\varepsilon\text{-CL}} + MW_{initiator}$, where $MW_{initiator}$ is the molecular weight of **5** and $[M]_0$ and $[I]_0$ are the initial concentrations of ε-CL and **5**, respectively. In addition, the NMR number-average molecular weight ($M_{n,\ NMR}$), which was determined from the ratio of the integral peak areas of

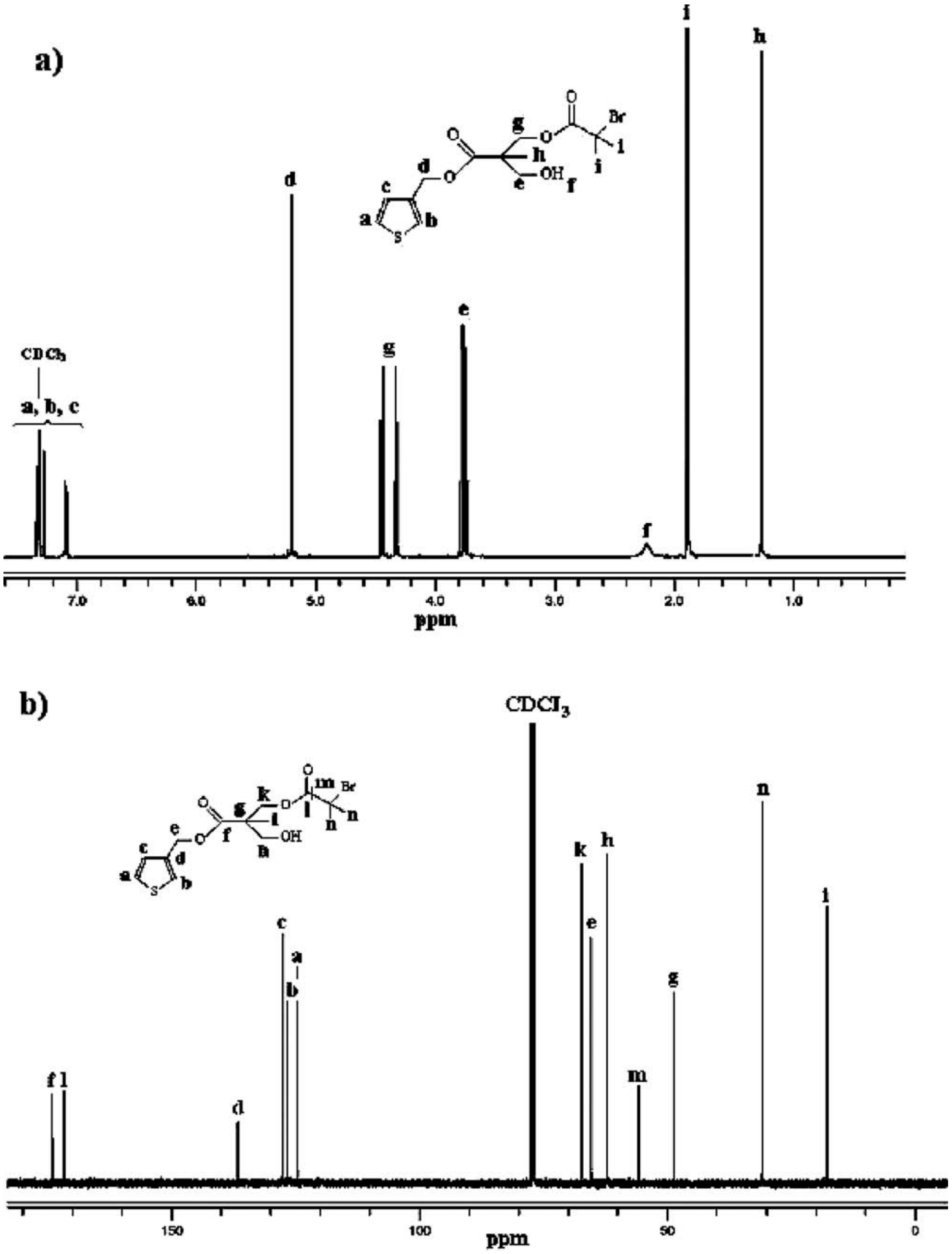


FIGURE 3 ^{1}H (a) and ^{13}C NMR (b) spectra of **5** in $CDCl_3$ at ambient temperature.

the peak, H**d**, to that of H**h**, was consistent with the theoretical M_n value. The GPC trace of PCL-Th showed a symmetrical and unimodal elution peak with a low polydispersity index.

Cyclic Voltammetry

As PCL-Th has polymerizable α-thiophene group, it can be called macromonomer and can be used in electrochemical polymerization via its thiophene unit. Therefore, electrochemical copolymerization of PCL-Th with Th and Py, *in situ* spectroelectrochemistry of PCL-Th/PTh thin film, and its ECD application were also studied.

The oxidation/reduction behaviors of PCL-Th in the presence of Th and Py were investigated by cyclic voltammetry (CV). The measurements were performed in a CV cell that was equipped with Pt-foil ($A = 1$ cm^2) working and counter electrodes and a Ag/Ag$^+$ reference electrode. Cyclic voltammograms of Th and Py and their copolymers with PCL-Th were studied in 10 mL ACN solutions containing 0.03 M TBAFB as a supporting electrolyte by applying sequential linear potential scan rate of 400 mV/s between -1.2 and 1.2 V (for Py) and between -0.8 and 2.2 V (for Th).

The CV of PCL-Th in an ACN-TBAFB system implied that the precursor polymer is not electroactive. On addition of Py into the reaction medium, there was an increase in the increments between the consecutive cycles, and the oxidation–reduction potentials of the material were different from those

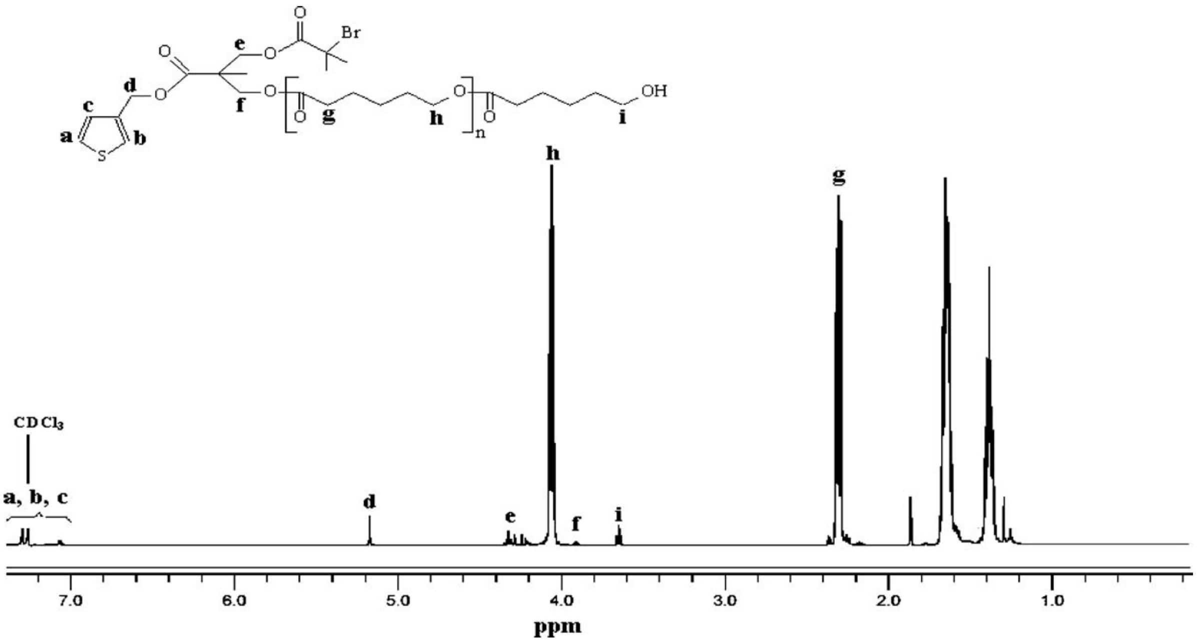


FIGURE 4 ^{1}H NMR spectrum of PCL-Th.

of pure Py. Oxidation and reduction peaks of PCL-Th/Py were observed at 0.42 and −0.55 V, respectively [Fig. 5(b)], whereas for pristine Py in Figure 5(a), the redox peaks were not at the same positions (pure PPy—$E_{p,a}$: 0.39 V and $E_{p,c}$: −0.42 V), and the peak height with the same scan number was different. These shifts are known to be indications for the reaction between Py and Th end groups of the PCL-Th.

The possibility of the reaction between Th unit at the α-chain end of PCL-Th and Th is also clearly shown in Figure 5(c). When the CV of PCL-Th was performed in the presence of Th, an oxidation peak at +1.21 V and a reduction peak at +0.48 V were observed, which were quite different from those of pristine thiophene observed at +1.12 and +0.41 V, respectively. These results imply that the reaction of the

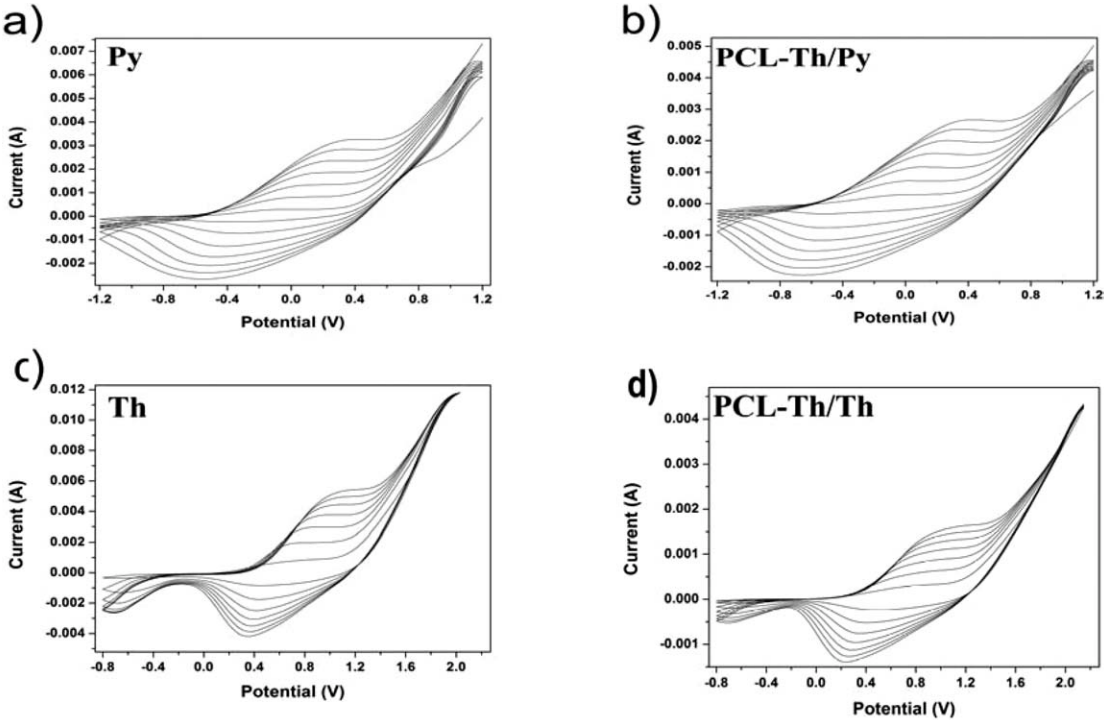


FIGURE 5 Cyclic voltammograms of pure Py (a), PCL-Th in the presence of Py (b), pure Th (c), and PCL-Th in the presence of Th in 0.03 M TBAFB/ACN on a bare Pt electrode (d). Scan rate is 0.400 V s^{-1}, versus Ag/Ag$^+$.

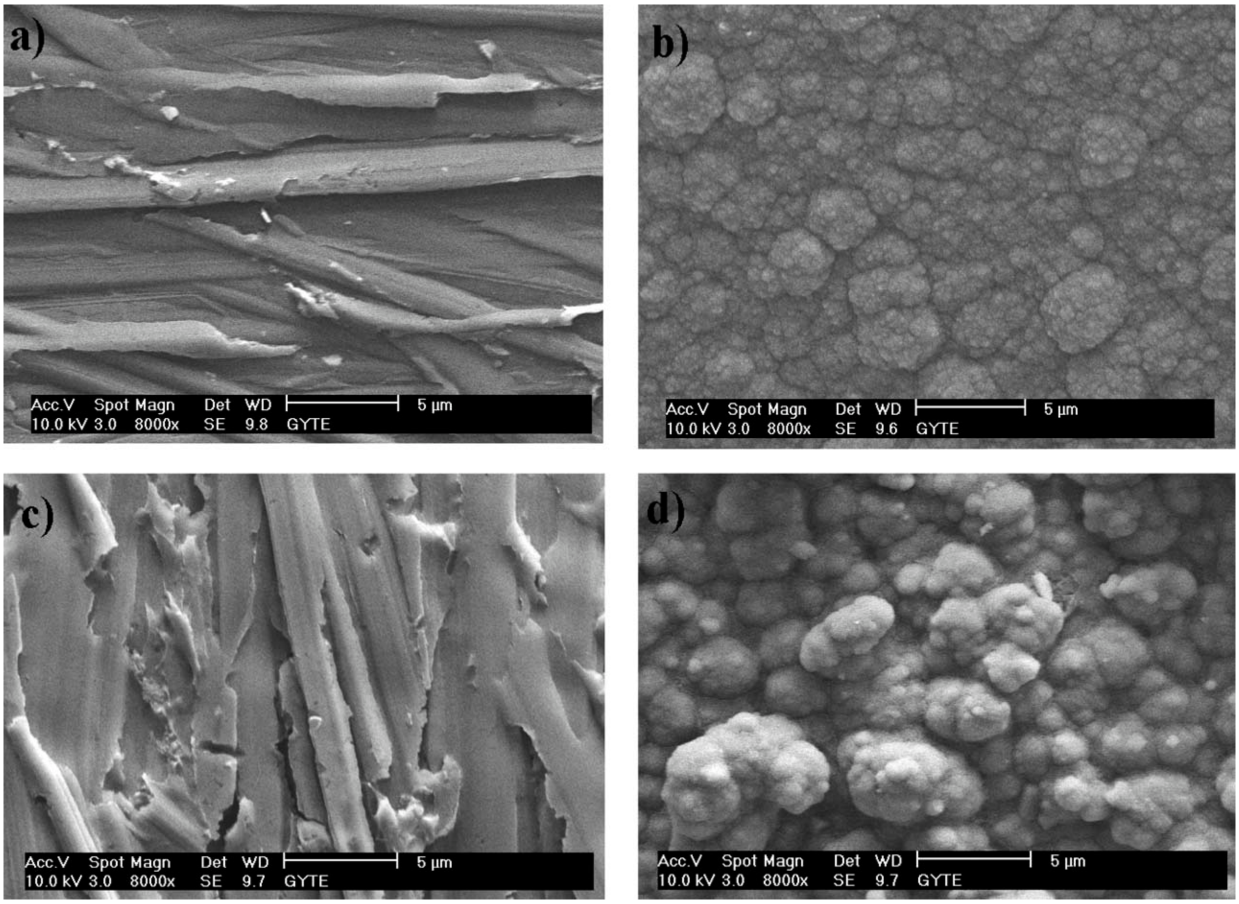


FIGURE 6 SEM images of PCL-Th/PPy (electrode side) (a), PCL-Th/PPy (solution side) (b), PCL-Th/PTh (electrode side) (c), and PCL-Th/PTh (solution side) (d).

PCL-Th with Th occurred through the thiophene moieties at the chain end. The product (PCL-Th/PTh) did not behave like pure polythiophene.

Surface Morphology Studies

Electrocopolymerization of PCL-Th was achieved in the presence of Py and Th by constant potential electrolysis. PCL-Th/PTh copolymer film doped with TBAFB was washed in CH_2Cl_2. The reaction product was black. The surface morphologies of the electrode and solution sides of the copolymer film were investigated by SEM (Fig. 6). The surface appearance of PCL-Th/PPy copolymer film revealed that the electrode [Fig. 6(a)] and solution [Fig. 6(b)] sides of PCL-Th/PPy film were different. Although the electrode side was rough, the solution side of the film showed homogeneous compact structure in globular form. PCL-Th/PPy also exhibited different morphologies than that of pristine PPy, which had a smooth appearance on the electrode side and standard cauliflower structure on the solution side. A similiar type of behavior was also observed in the case of PCL-Th/PTh copolymer film [Fig. 6(c,d)]. The structure of the electrode side of PCL-Th/PTh was not as smooth as that of pure PTh, whereas the morphology of the solution side of PCL-Th/PTh had cauliflower-like morphology with small globules. This may be attributed to the presence of a covalent interaction between PCL-Th and Py or Th, which presents them a new identity with a new topological appearance.

In situ Spectroelectrochemistry of PCL-Th/PTh Thin Film

The electronic structure and optical behavior of PCL-Th/PTh can be explained by spectroelectrochemical measurements. *In situ* spectroelectrochemistry studies were performed in the monomer free three-electrode cell with ACN/TBAFB solution by switching between 0.2 and $+1.5$ V vs Ag-Ag$^+$ electrode. At different potentials, a series of UV–vis spectra were run as seen in Figure 7. The $\lambda_{\max}$ value at 480 nm corresponds to the π–π^* transition and the color of the PCL-Th/PTh film in the neutral state is red. During the scan from 0.2 to 1.5 V, the maximum absorbance peak decreased and the electronic band gap estimated at the edge of π–π^* transition was found to be 1.88 eV (660 nm).

As the applied potential was increased gradually, on doping, the new maximum peak emerged at 713 nm, shifted to near-IR region, and disappeared at higher potential values. The appearance of the maximum and the shift to longer wavelength indicate the occurrence of polarons (radical cation) and bipolarons on PCL-Th/PTh film on the polymer backbone.[26] These lower transitions lead to the production of a second color, blue. This strong shift of the maximum absorption on applied voltage is related to the electrochromic

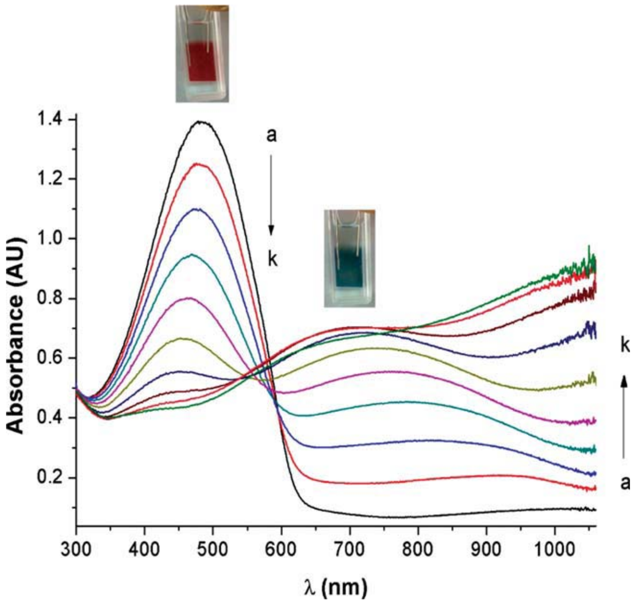


FIGURE 7 *In situ* spectroelectrochemical graphs of PCL-Th/PTh at 0.2 V (a), 0.4 V (b), 0.6 V (c), 0.8 V (d), 0.9 V (e), 1.0 V (f), 1.1 V (g), 1.2 V (h), 1.3 V (i), and 1.5 V (k).

property of the polymer. When the experiment was repeated by decreasing the applied potential gradually, no change in the band gap or λ_{max} values was observed. The spectroelectrochemistry results clearly showed that PCL-Th/PTh reversibly changes color between red and blue on doping–dedoping processes, and the results obtained are different from those of PTh, indicating the formation of PCL-Th/PTh copolymer.[38]

Colorimetry Studies

The colors of the electrochromic materials are defined clearly by colorimetry measurements. They were performed by using Konica Minolta CS-200 chronometer with viewing geometry as recommended by Commision Internatonale I'Eclariage (CIE). This system is used as a quantitative scale to define and compare colors. According to the CIE system, color is made up of three attributes; luminance (L), hue (a), and saturation (b). L, a, and b values of the PCL-Th/PTh film were measured at the fully oxidized and reduced states on the ITO/glass surface. The color of the copolymer film switched from blue in the oxidized state to red in the reduced (neutral) state. For comparison, the values for the PTh and related studies from literature are also included in Table 2. In these studies, Th end-capped polymers were synthesized using different medhods such as anionic and cationic living polymerizations and "click chemistry." They were all macromonomers due to the presence of polymerizable Th units. The films obtained from the copolymerizations of these macromonomers with Th were found to exhibit electrochromic behavior.

Switching and Stability Properties of PCL-Th/PTh Thin Film

The ability of electrochromic polymers to fast switching and rapidly color chance is important for electrochromic aplication as display and monitoring. The experiments carried out by spectroelectrochemistry showed the ability of PCL-Th/PTh film to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. The electrochromic parameters of PCL-Th/PTh were extracted by analysis of transmittance change decrement or increment of the absorption band at 500, 750, and 900 nm with respect to time, whereas the potential was stepwise switched between −0.5 and +1.5 V for a residence time of 5 s. During

TABLE 2 Electrochemical, Electronic, and Electrochromic Properties of PCL-Th/PTh and Related Studies[a]

Material	E_{pa}[b] (V)	E_{pc}[b] (V)	λ_{max} (nm)	L	a	b	E_g (eV)	Reference
PTh	0.63	0.58	495	57 (ox)	−-7 (ox)	−-2 (ox)	1.92	37
				51 (red)	52 (red)	46 (red)		
PCL/PTh	1.10	0.60	473	53 (ox)	−-5 (ox)	7 (ox)	1.83	26
				63 (red)	47 (red)	25 (red)		
(N_3P_3-(PCL-Th)$_6$)/PTh	1.30	0.45	477				1.85	7
PTHF/PTh	1.40	0.60	495	54 (ox)	−-10 (ox)	−-7 (ox)	1.88	38
				57 (red)	36 (red)	19 (red)		
PTh/PTHF/PTh	1.30	0.50	470	63 (ox)	−-1 (ox)	19 (ox)	1.91	23
				70 (red)	40 (red)	29 (red)		
PEO/PTh			515	52 (ox)	−-10 (ox)	−-4 (ox)	1.95	39
				60 (red)	61 (red)	27 (red)		
PCL-Th/PTh	0.91	0.39	480	65 (ox)	−-3 (ox)	−-4 (ox)	1.88	This study
				79 (red)	34 (red)	27 (red)		

[a] PCL: α-Thiophene end-capped poly(ε-caprolactone) (N_3P_3-(PCL-Th)$_6$): Hexa-armed and thiophene end-capped poly(ε-caprolactone) star polymer containing cyclotriphosphazene core. PTHF: Polytetrahydrofuran was terminated thiophene group at one or both end(s). PEO: α-Thiophene capped poly(ethylene oxide)

[b] Volts versus Ag/Ag$^+$.(ox), oxidized state; (red), reduced state; E_{pa}, anodic potential; E_{pc}, cathodic potential; E_g, band gap.

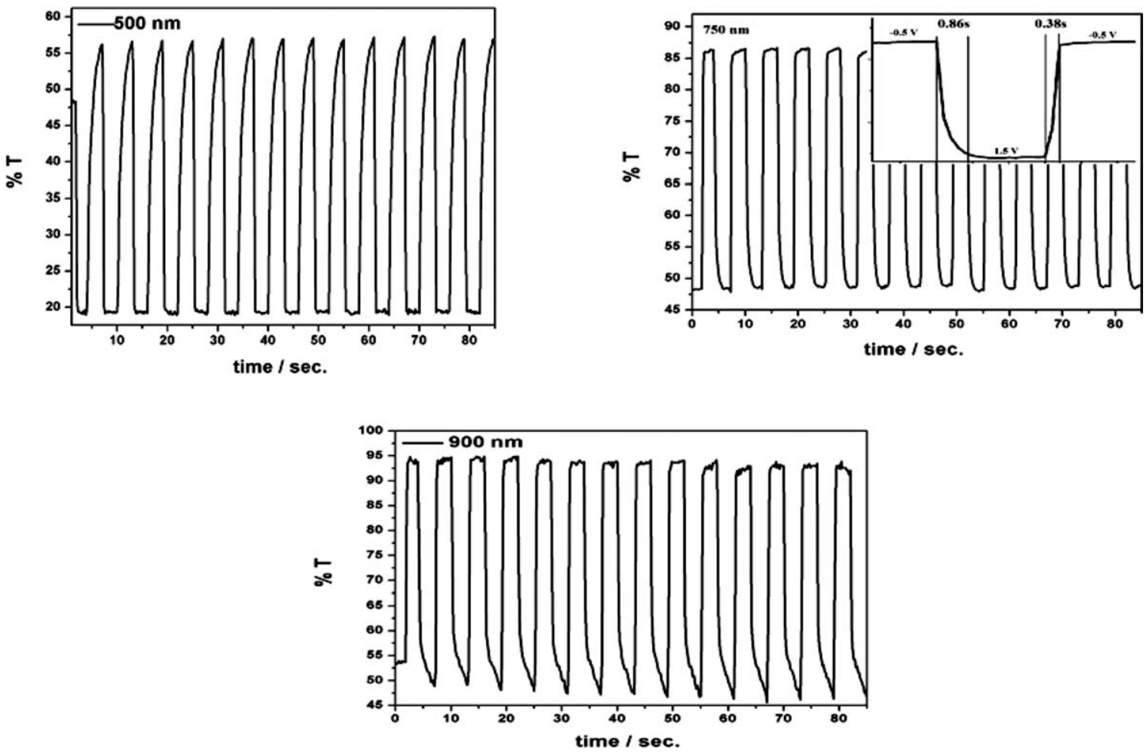


FIGURE 8 Electrochromic switching, optical absorbance change monitored at 500, 750, and 900 nm for PCL-Th/PTh film between −0.5 and 1.5 V.

this measurement, % transmittance at the wavelength of maximum contrast was determined by using a UV–vis spectrophotometer. The optical contrast measured as the difference between %T in the reduced and oxidized states were found to be 37, 39, and 47% T for 500, 750, and 900 nm, respectively. The oxidation and reduction response times were calculated as 0.25 s with a switch from −0.5 to 1.5 V and 0.88 s with a switch from 1.5 to −0.5 V at 750 nm, respectively (Fig. 8).

Redox stability is an important requirement for production of reliable electrochromic devices with long lifetimes. The stability of the PCL-Th/PTh film was investigated via CV. It was accomplished by nonstop cycling of the applied potential between −0.5 and +1.5 V versus Ag/ Ag^+ electrode with 400 mV/s scan rate. Even after 3000th run, the PCL-Th/PTh film indicated only a slight decrease in electroactivity accompanied by unperturbed color change under atmospheric conditions (Fig. 9).

PCL-Th/PTh film can be useful for electrochromic application due of the reversible redox behavior, stability, reasonable switching time, ease of fabrication, and low cost. For this purpose, PCL-Th/PTh film was used as an anodically coloring electrochromic layer in a dual-type ECD construction.

Spectroelectrochemistry of PCL-Th/PTh‖PEDOT Electrochoromic Device

ECD is a two-electrode electrolytic cell, which changes light transmission properties in response to externally applied voltage across the two electrodes and thus allow to control the amount of light passing through. A typical ECD is a sandwich-like structure with two glass plates and an electrolyte. Each glass plate is coated on the inside with an optically transparent and electrically conducting layer of indium-tin oxide (ITO), which operates as an electrode. Optically transparent ITO electrodes are coated with complementary electrochromic materials, which may be organic or inorganic substances. The operation of electrochromic devices relies on their electrochromic materials that are able to interconvert between two or more color states upon oxidation or reduction, that is, on electrolytic loss or gain of electrons.

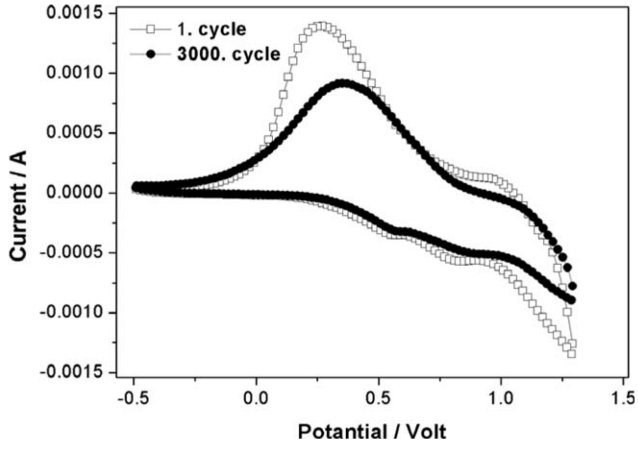


FIGURE 9 Cyclic Voltammogram of PCL-Th/PTh film as a function of repeated scans 400 mV/s.

ECD was assembled with a configuration of ITO|PCL-Th/PTh||Gel electrolyte||PEDOT|ITO as shown in Figure 1. The dual-type ECD was prepared as follows: first, anodically coloring polymer (PCL-Th/PTh) and cathodically coloring polymer (PEDOT) were coated on ITO/glass surfaces potentiodynamically. Then, the gel electrolyte (see Experimental part) was spread over the faces of PCL-Th/PTh and PEDOT layers on ITO. Finally, PCL-Th/PTh and PEDOT layers with gel electrolyte were stacked face-to-face.

Optoelectrochemical spectra of the dual-type PCL-Th/PTh and PEDOT ECD as a function of applied voltage from +0.2 to +1.7 V are shown in Figure 10. At 0.2 V, the device revealed a maximum absorption at 480 nm and its color was red. At this stage, the copolymer was in its neutral state revealing red and PEDOT was in its oxidized form (highly transparent blue) revealing on significant absorption at the visible region and hence the color of the ECD was red. On incremental increase in the applied potential, simultaneous reduction of the PEDOT and oxidation of PCL-Th/PTh layers, which were signified with the decrease in the intensity of the peak at 450 nm and increase in the intensity of the peak at 622 nm, were observed. At 1.7 V as the spectral signatures of both layers become dominant, the color of the device turned into blue, indicating that the PEDOT and copolymer were in their fully neutral and oxidized states, respectively.

Switching Properties of ECD

Color-switching times of ECDs are of primary importance in display applications. It should have low response time (in order of a few seconds) and resistance to applied potential between its reduced and oxidized states. The graph demonstrating the switching time for the device is given in Figure 11. The change in optical contrast of the device was recorded as 630 nm, as the potential was switched between −0.2 and +1.7 V with a residence time of 5 s. The optical contrast of the device at 630 nm was found to be 22%. The oxidation (switching from −0.2 to 1.7 V; red to blue) and reduction (switching from 1.7 to −0.2 V; blue to red) response time of the device were 0.39 and 0.95 s, respectively. The device also retained its performance by 75% even after 3000th cycle.

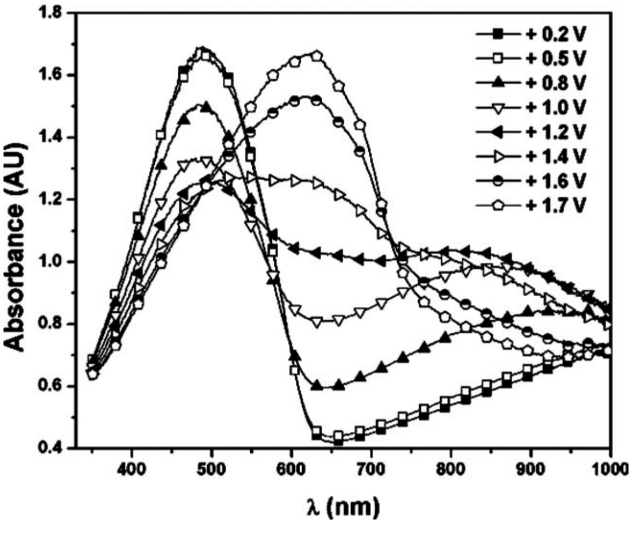


FIGURE 10 Spectroelectrochemistry of PCL-Th/PTh||PEDOT device at applied potentials between +0.2 and +1.7 V.

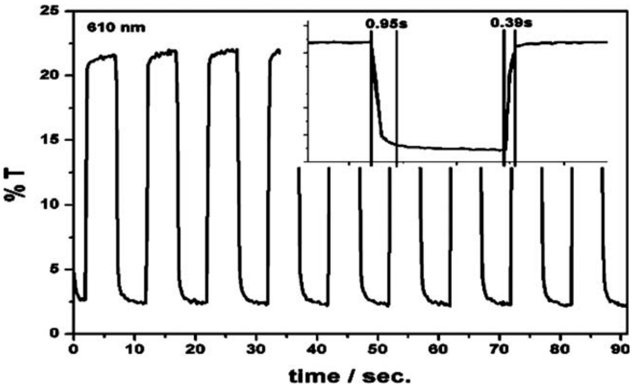


FIGURE 11 Switching histogram between −0.2 V and +1.7 V.

CONCLUSIONS

A novel thiophene monomer with miktofunctional initiator groups (primary hydroxyl and tertiary bromide) at the third position of the thiophene ring was successfully prepared in a four-step reaction sequence. Investigation of the accurate prediction of geometry and IR spectroscopic characteristic for the thiophene monomer in the gas phase was carried out by DFT. DFT calculated bond lengths, angles, and vibrations were predicted in good agreement with available experimental data and experimental vibrational spectra. Primary hydroxyl initiating site of the thiophene monomer for ε-CL gave α-Th end-capped PCL homopolymer via ROP. In addition, copolymerizations of PCL-Th with Py and Th via constant potential electrolyses indicated the possibility of the reaction between Py or Th and α-Th end group of PCL-Th. Spectroelectrochemical analysis of PCL-Th/PTh copolymer film supports the idea that an electrochromic copolymer was obtained. The copolymer obtained from the electropolymerization reaction between PCL-Th and Th on ITO-coated glass electrode was employed as an anodically coloring material in ECD application. Reversible and distinctive color changes of PCL-Th/PTh film showed that it can be used in the construction of electrochromic devices. Further study related to the preparation of block copolymer having thiophene functionality at the junction point via the ATRP of MMA using PCL-Th as the macroinitiator and its ECD application are now in progress.

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