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ORIGINAL PAPER

One-pot two-step lipase-catalyzed synthesis of α,ω-thiophene-capped poly(ε-caprolactone) macromonomers and their use in electropolymerization

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Abstract Macromonomers based on poly(ε-caprolactone) (PCL) with α,ω-thiophene functional end groups were prepared in bulk by enzymatic polymerization using immobilized *Candida Antarctica* lipase B (Novozym 435) as the catalyst. In the synthesis strategy, 3-thiophenemethanol was used to initiate the enzyme-assisted ring-opening polymerization of ε-caprolactone (ε-CL) to yield PCL with α-thiophene end group (initiation reaction, ThPCL) and then 3-thiopheneacetic acid was added to prepolymerized ε-CL to introduce ω-thiophene functionality in termination step (ThPCLTh). Macromonomers were characterized by ^{1}H and ^{13}C NMR, FTIR, and GPC. Moreover, the obtained macromonomers were employed in electropolymerization experiments and copolymers with thiophene or pyrrole were synthesized through their end thiophene groups. These polymers were characterized by cyclic voltammetry (CV), FTIR, and scanning electron microscopy (SEM). Conductivity measurements were carried out by the four-probe technique.

Keywords Macromonomer · Enzymatic polymerization · Novozym 435 · Conductive polymers · Thiophene · Electrochemical polymerization

Introduction

Polymers with end functional groups, such as macromonomers, telehelics end-functionalized macromolecules, are of good synthetic utility and commercial interest [1]. Macromonomers have been employed for synthesis of block and graft copolymers, star polymers, and polymer networks. They can be synthesized via

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various methods including anionic [2], cationic [3], free radical, step-growth polymerizations [4, 5], and chemical modifications of polymer ends [6].

As an environmentally friendly method of polymer synthesis, enzymatic polymerization have been the focus of intense research in scientific community, in contrast to the chemical ones, which generally require harsh conditions and metallic catalysts that must be completely removed especially for medical applications. Furthermore, enzymatic polymerization can offer a novel method for the preparation of polymers, which are difficult to be synthesized by conventional polymerization methods [7, 8].

Polyester is one of the most important synthetic polymers and always synthesized by ring–opening polymerization of cyclic lactones. The polymerization of lactones is of major interest due to the properties such as biodegradability, biocompatibility, no toxicity, and miscibility with other polymers [9–13]. Enzymes have been employed successfully to synthesize various kinds of lactones such as small-size (4-membered) lactones [14], medium-size (6- and 7-membered) lactones [15–18], and large-size (12-, 13-, 16-membered) lactones [19, 20]. Novozym 435, immobilized on macroporous acrylic resin, has been proven to be an effective catalyst in the ring-opening polymerization of ε-CL [16–18].

Conductive polymers as a new class of materials combine chemical and mechanical properties of the polymers with the electronic properties of the metals and semiconductors. They have been gaining more and more attention due to their potential use in many applications such as light emitting diodes [21], batteries [22], electrochromic devices [23–27], sensors [28], electromagnetic shielding [29], and corrosion inhibition [30]. Among them, polythiophenes (PThs) have a special place due to their electrical properties, environmental stability in doped and undoped states, non-linear optical and highly reversible redox switching properties [31–33].

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 possessing electrochemically polymerizable thiophene or pyrrole moieties within or at end of the chains and performing electropolymerization in the presence of an electroactive comonomer. Thus, new chemical and physical properties can be imparted to conducting polymers [34–38].

We previously reported the synthesis of α-thiophene-capped PCL with 3-thiophenemethanol as the initiator and tin(II) 2-ethylhexanoate (Sn(Oct2)) as the catalyst in bulk at 115 °C [39]. Then, the copolymerizations of α-thiophene-capped PCL with thiophene and pyrrole were achieved via constant potential electrolysis. As an extension, we report the one-pot two-step synthesis of macromonomers based on PCL possessing α,ω-thiophene end functional groups using immobilized *Candida antarctica* lipase B (Novozym 435) and show that the enzymatic way provides direct and much easier route for the synthesis of thiophene-functionalized polyesters. The obtained macromonomers were also employed in electropolymerization with pyrrole and thiophene via their thiophene end groups.

Experimental

Materials

Commercial solvents were purified according to usual procedures. Immobilized *Candida Antarctica* lipase B (Novozyme 435) was a gift from NovoNordisk (Denmark). It was washed with excess hexane and then ether and dried under vacuum at room temperature for 72 h. The ε-Caprolactone (ε-CL) (Aldrich, 99%), 3-Thiophenemethanol (Aldrich, 98%), 3-Thiopheneacetic acid (Fluka, 98%), Tetrabutylammonium tetrafluoroborate (TBAFB) (Fluka, 99%), and acetonitrile were used as received. Thiophene (Thi) (Aldrich, 98%) and Pyrrole (Py) (Aldrich, 98%) were distilled prior to use.

Polymerization

Synthesis of α-thiophene capped PCL by initiation (ThPCL)

3-Thiophenemethanol (56.0 μL, 0.60 mmol) and ε-CL (2.0 mL, 18.1 mmol) were mixed in a screw cap reaction vial. Addition of Novozym 435 (25.0 mg) started the reaction that was allowed to run with shaking for 24 h at 55 °C. It was then stopped by filtering of the enzyme. The macromonomer was obtained by precipitation in cold methanol. The precipitated macromonomer was filtered off and allowed to dry in a desiccator. ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.34 ppm (1H, 2 position in thiophene ring); 7.25 ppm (1H, 4 position in thiophene ring); 7.11 ppm (1H, 5 position in thiophene ring); 5.05 ppm (2H, ThCH_2O–); 4.00 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2$O–); 3.59 ppm (2H, –CH_2OH); 2.26 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2$O–); 1.58 ppm (4H, –$CH_2CH_2CH_2CH_2CH_2$O–); 1.31 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2$O–). ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 173.75 ppm (C=O, C-1); 62.80 ppm (ThCH_2O–, initiator), 64.30 ppm (–CH_2O–, C-6); 61.20 ppm (–CH_2OH, end group); 34.10 ppm (–CH_2–, C-2); 28.30 ppm (–CH_2–, C-5); 25.30 ppm (–CH_2–, C-3); 24.30 ppm (–CH_2–, C-4).

Synthesis of α,ω-thiophene capped PCL by initiation and termination (ThPCLTh)

3-Thiophenemethanol (60.0 μL, 0.62 mmol) and ε-CL (2.00 mL, 18.1 mmol) were placed in a screw cap reaction vial. Polymerization reaction was started by addition of Novozym 435 (25.00 mg) and allowed to run with shaking for 24 h at 55 °C. Then, 3-Thiopheneacetic acid (0.26 g, 1.80 mmol) in dry THF (0.10 mL) was added to the reaction mixture and the reaction was further kept for another 24 h with shaking to introduce ω-thiophene functionality to PCL chains. The reaction was stopped by filtering off the enzyme. The macromonomer was obtained by precipitation in cold methanol, filtered off, and allowed to dry in a desiccator. ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.08–6.93 ppm (6H, in the two thiophene rings); 5.04 ppm (2H, ThCH_2O–, initiator); 4.02 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2$O–); 3.57 ppm (2H, –CH_2OH); 3.48 ppm (2H, –CH_2Th, terminator); 2.25 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2$O–);

1.56 ppm (4H, –$CH_2CH_2CH_2CH_2CH_2O$–); 1.30 ppm (2H, –$CH_2CH_2CH_2CH_2CH_2O$–). ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 173.75 ppm (C=O, C-1 and C=O, terminator); 61.20 ppm (ThCH_2O–, initiator); 62.80 ppm (–CH_2Th, terminator); 64.30 ppm (–CH_2O–, C-6); 62.80 ppm (–CH_2OH, end group); 34.10 ppm (–CH_2–, C-2); 28.30 ppm (–CH_2–, C-5); 25.30 ppm (–CH_2–, C-3); 24.30 ppm (–CH_2–, C-4).

3-Thiophenemethanol: ^1H NMR (500 MHz, $CDCl_3$, δ in ppm at rt): 3.88 ppm (1H, –CH_2OH): 4.62 ppm (2H, –CH_2OH): 7.31 ppm (1H, 2 position in thiophene ring): 7.19 ppm (1H, 4 position in thiophene ring); 7.07 ppm (1H, 5 position in thiophene ring).

3-Thiopheneacetic acid: ^1H NMR (500 MHz, $CDCI_3$, δ in ppm at rt): 11.09 ppm (1H, –COO*H*); 3.85 ppm (2H, –CH_2COOH), 7.32 ppm (1H, 2 position in thiophene ring); 7.20 ppm (1H, 4 position in thiophene ring); 7.07 ppm (1H, 5 position in thiophene ring).

Electropolymerization of ThPCL and ThPCLTh macromonomers

Cyclic voltammetry (CV)

Oxidation–reduction behaviors of ThPCL and ThPCLTh and their copolymers in the presence of Th and Py were investigated by CV. The system composes of a Electrochemical analyzer, CHI 842B, potentiostat–galvanostat and an X–Y recorder. Whole CV measurements were obtained in an electrochemical cell consisting of Pt (Platinum) disk electrode as a working electrode, Pt wire electrode as a counter electrode and $Ag/AgNO_3$ (0.01 M in acetonitrile) as a reference electrode.

Electrochemical synthesis of copolymers of ThPCL and ThPCLTh with thiophene and pyrrole

Conducting copolymers were synthesized by constant potential electrolysis in a one compartment cell. Electrochemical polymerization was performed for 1 h at room temperature under argon atmosphere by using Pt foil and Pt wire as working electrode and counter electrode, respectively, and $Ag/AgNO_3$ (0.01 M in Acetonitrile) as a reference electrode. Copolymers of ThPCL and ThPCLTh with Py were synthesized in 10 mL ACN, using 0.03 M Tetrabutylammonium tetraflouroborate (TBAFB) as the supporting electrolyte, Py (40 μL), and 1 mg ThPCL or ThPCLTh. Electrolysis was conducted at 1.0 V. The copolymerization reactions of ThPCL and ThPCLTh with Th were performed at 2.0 V in a reaction medium made up for 0.03 M TBAFB, 40 μL Th, and 1 mg enzymatically synthesized ThPCL or ThPCLTh in 10 mL ACN. After electrolysis, the working electrodes were washed several times with ACN to remove supporting electrolyte adhered on the surface of the copolymer films. After drying the electrode at room temperature, the copolymer films were peeled off the electrodes and were allowed to stand in CH_2Cl_2 for several hours in order to dissolve and get rid of the unreacted macromonomers.

Characterization

^{1}H and ^{13}C NMR spectra were taken on a Varian 500-MHz spectrometer using $CDCl_3$ as the solvent. Infrared spectra (FT-IR) were recorded on a Bio-Rad FTS 175C spectrometer at room temperature. Molecular weights and molecular weight distributions of the macromonomers were measured on an Agilent Instrument (Model 1100) consisting of a pump, refractive index and UV detectors, and four Water Styragel columns (HR 5E, HR 4E, HR 3, and HR 2) and using THF as eluent at a flow rate of 0.3 mL/min at 30 °C and toluene as an internal standard. Molecular weights were calculated with the aid of polystyrene standards. Differential scanning calorimetry analysis (DSC) of ThPCL and ThPCLTh was carried out on a DSC 822 (Mettler Toledo) thermal analysis system under nitrogen flow (10 mL/min). All samples were first heated from 0 to 100 °C with a heating rate of 10 °C/min and held for 3 min to erase the thermal history, then cooled to 0 °C at 10 °C/min, and finally heated to 100 °C at 10 °C/min. Thermogravimetric analysis (TGA) of the macromonomers and their copolymers with thiophene and pyrrole was performed on a TGA/SDTA 851 (Mettler Toledo) thermogravimetric analyzer with a heating rate of 20 °C/min from room temperature to 700 °C under nitrogen atmosphere. Conductivities of the copolymers films are measured by a four-probe technique. The morphologies of the conjugated copolymer films were investigated by Scanning electron microscopy (SEM) (Philips XL30 SFEG Scanning Electron Microscopy).

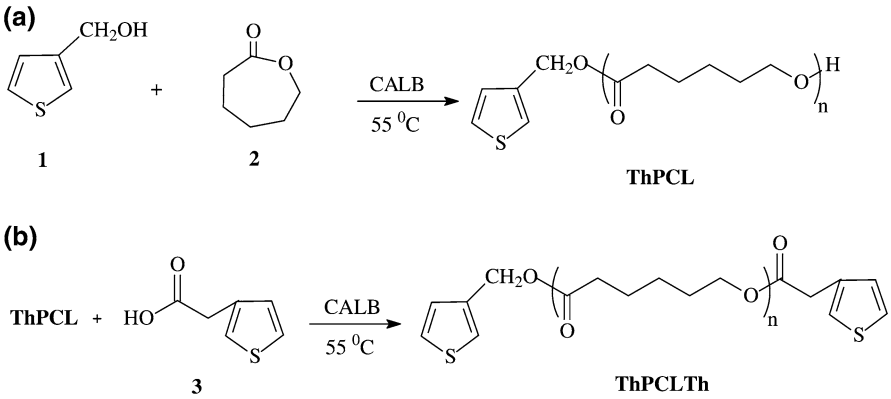
Result and discussion

Enzymatic synthesis of α and α,ω-thiophene capped PCL macromonomers

Terminal-functionalized polymers, typically macromonomers and telechelics are very useful for synthesis of functional polymers. Although various methodologies for synthesis of these polymers have been developed, most of them require elaborate and time-consuming procedures.

In the present study, the thiophene-functionalized polyesters were synthesized by enzymatic ring-opening polymerization of ε-CL in the presence of thiophene functional alcohol and acid. α- and α,ω- the thiophene functionalized of PCL were accomplished by an initiation and initiation/termination reactions, respectively, catalyzed by Novozym-435 in bulk at 55 °C.

3-Thiophenemethanol (**1**) was used to initiate the enzyme-assisted ring-opening polymerization of ε-CL (**2**) to get the desired α-thiophene functionalized polymer, ThPCL (Scheme 1a). The polymer was characterized by ^{1}H NMR and ^{13}C NMR, and GPC. In Fig. 1a, ^{1}H NMR spectrum of PCL, which was synthesized by $Sn(Oc)_2$ as a catalyst [39], is also included to indicate the identical spectra obtained from both methods. Figure 1b shows the ^{1}H NMR spectrum of ThPCL, which was prepared using Novozym 435. The characteristic ^{1}H NMR peaks of the repeating unit of PCL can be seen in both spectra. The resonance of the methylene protons adjacent to the thiophene ring of 3-thiophenemethanol shifted from 4.62 ppm (ThCH_2OH) to 5.05 ppm (ThCH_2OC(O)–, the peak d in Fig. 1b) upon



Scheme 1 Synthesis of α-thiophene capped PCL by initiation (ThPCL) (**a**) and α,ω-thiophene capped PCL by initiation and termination (ThPCLTh) (**b**)

incorporation. The aromatic protons of the thiophene ring at the chain end of PCL was observed in the NMR spectrum (a, b and c in Fig. 1b). The presence of the initiator in PCL was also confirmed by ^{13}C NMR (see the experimental part). The product possessed ~95% thiophene end-functionality. It was calculated by comparing the integral ratio of the proton signals on primary hydroxyl methylene end group, (H^g), to that of methylene group next to thiophene ring, (H^d). The ratio is found to be 1.06, which is almost the same to the theoretical value ($H^g/H^d = 1.00$). This observation confirms that ε-CL monomers have been inserted into the "–CH_2CH_2O–H" group of thiophene ring via selective acyl-oxygen cleavage of ε-CL and that α-thiophene ended PCL was successfully prepared. ^{1}H NMR spectra allowed us to calculate the $M_{n,NMR}$ of ThPCL polymer as well, assuming the DPn = 31 of ThPCL obtained from ^{1}H NMR (see the details in Table 1). Thus, $M_{n,NMR}$ was calculated by the following equations {$M_{n,NMR}$ = [31 (DPn of ThPCL) × 114.1] + M_W of 3-Thiophenemethanol}.

Moreover, α,ω-thiophene end functionalities were also introduced successfully by using **1** in the initiation step and 3-Thiopheneacetic acid (**3**) in the termination step. In the initiation step, PCL synthesis was carried out by initiating **2** using Novozym 435 (CALB) as catalyst. The PCL chains were allowed to grow for 24 h before addition of the terminator group. In the termination step, the incorporation of 3-thiopheneacetic acid at the end of ThPCL was achieved by the esterification reaction of hydroxyl functional chain ends and 3-thiopheneacetic acid and resulted in polymer, ThPCLTh (Scheme 1b). The methylene protons adjacent to the carbonyl in 3-thiopheneacetic acid shifted from 3.85 to 3.62 ppm when incorporated into ThPCL. The singlet of the methylene protons closest to the thiophene ring of 3-thiopheneacetic indicated that ω-thiophene functionality was intact. Of the product polymer chains, ThPCLTh, 97% were initiated by 3-thiophenemethanol and 65% were terminated by 3-thiopheneacetic acid as calculated by comparing integrals of the terminator protons, g, (Fig. 1c) and the methylene protons (–CH_2OH) at 3.58 ppm of the end hydroxyl groups of the unterminated polymer chains. The protons of thiophene ring from 3-thiopheneacetic acid coincide with

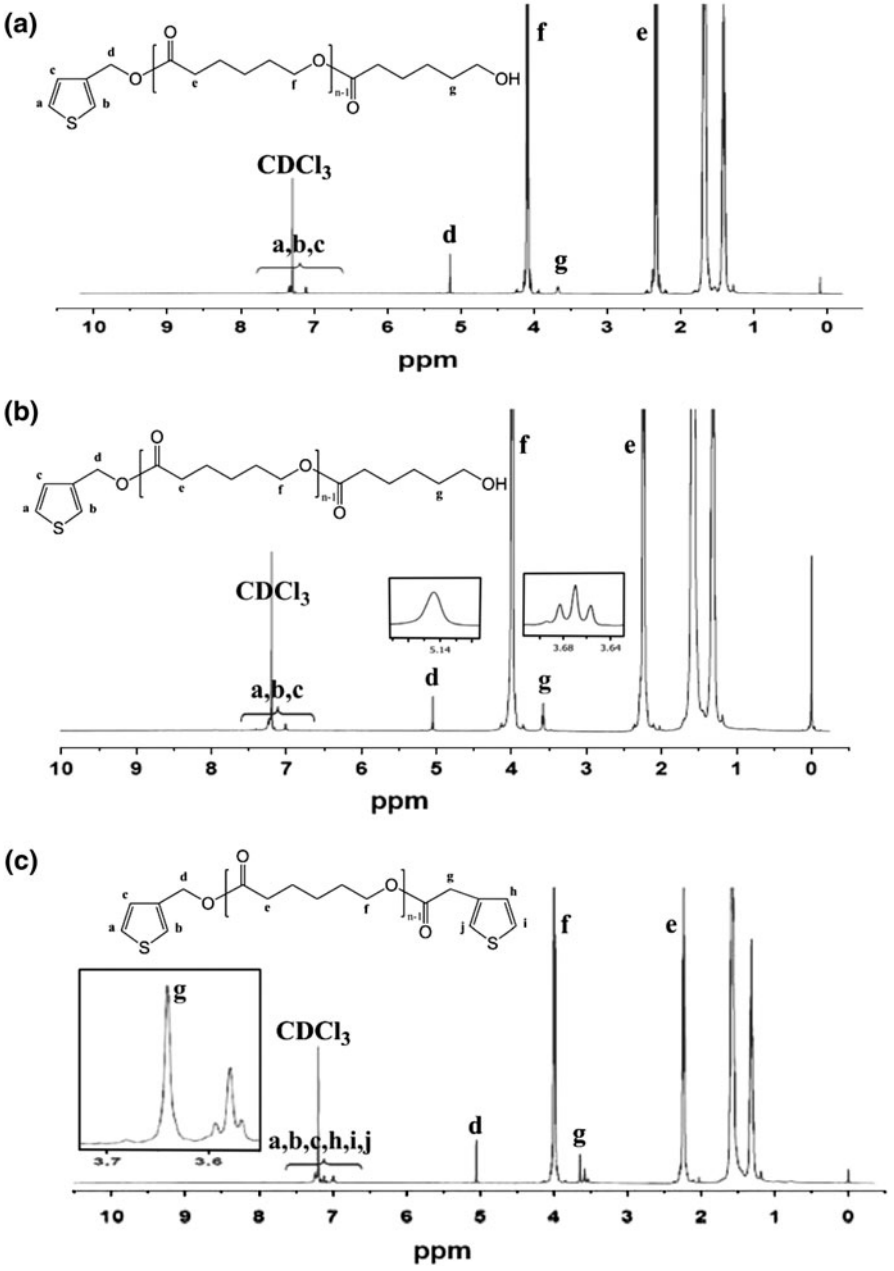


Fig. 1 ^{1}H NMR spectra of α-thiophene capped PCL synthesized by **a** $Sn(Oc)_2$ [39], **b** Novozym 435 and α,ω-thiophene capped PCL synthesized using Novozym 435 (**c**). *Inlet boxes* magnify the spectra between 3.50 and 3.70 ppm for clarity

Table 1 Synthesis of thiophene-functionalized PCL in bulk

Polymer product	I or T[b]	I:M[b]	T:M	Polymers with		Time (h)	M_n^e (NMR)	M_n^f (GPC)	M_w/M_n	Conversion (%)
				α-Th[c] (%)	ω-Th[d] (%)					
ThPCL[a]	1	1:20	–	~97	–	140	2,395	2,100	1.37	100
ThPCL	1	1:30	–	~95	–	24	3,648	3,150	1.29	99
ThPCLTh	3	–	1:10	~97	~65	48	3,289	3,050	1.43	99

[a] PCL was synthesized by $Sn(Oc)_2$ as a metal catalyst in bulk [39]

[b] *I* Initiator, *T* Terminator, *M* Monomer. Ratio in mol/mol

[c] The fraction of the polymer that was α-thiophene functionalized. Calculated by comparing the integrals of the peaks from the methylene protons (ThCH_2O–, H^d) adjacent to the thiophene ring of 3-Thiophenemethanol with the methylene protons (–CH_2OH, H^g) of the hydroxyl groups of the polymer

[d] The fraction of the polymer that was ω-thiophene functionalized. Calculated by comparing the area of the methylene protons (–CH_2Th) adjacent to the thiophene ring of 3-Thiopheneacetic acid with that of the methylene protons (–CH_2OH) of the hydroxyl groups of the polymer

[e] $M_{n,NMR}$ was determined by ^{1}H NMR spectroscopy. Degree of polymerization was calculated by comparing the intensities of the methylene protons (–CH_2OH or (–CH_2OH + –CH_2Th)) with respect to methylene protons (–$CH_2CH_2CH_2CH_2CH_2$O–, H^f) at 4.05 ppm

[f] Determined by GPC according to polystyrene standards

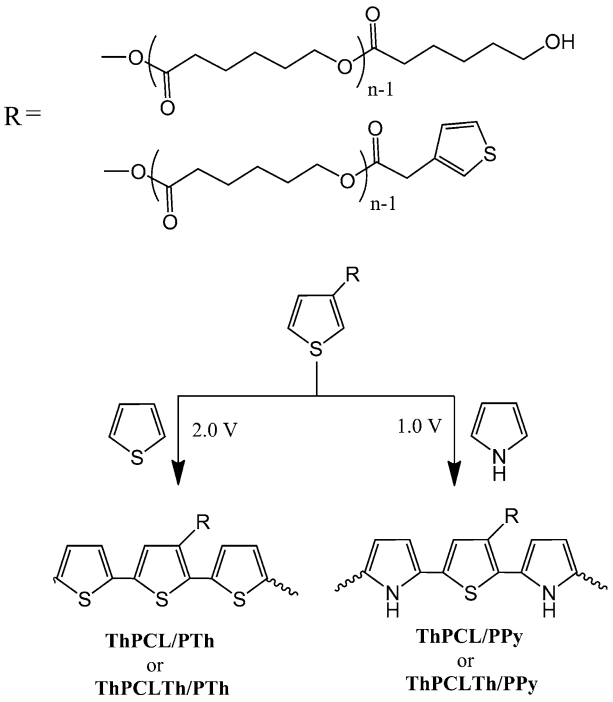
that of 3-thiophenemethanol in 6.98–7.34 ppm. The structure of ThPCLTh was also confirmed by ^{13}C NMR. We also carried out α,ω-thiophene end-functionalization reactions of PCL in toluene and THF. However, the introduction of α,ω-thiophene end functionalities into PCL polymer in solution was much lower than those obtained in bulk (data not shown).

Electropolymerization of α- and α,ω-thiophene capped PCL macromonomers

The synthesized polymers are macromonomers since they have polymerizable thiophene end groups. Therefore, they were employed in electropolymerization. Electropolymerization of ThPCL and ThPCLTh was achieved in the presence of pyrrole and thiophene by constant potential electrolysis (Scheme 2). The reaction products were black and because of their insoluble nature, the characterization was not possible by NMR technique. Therefore, FTIR spectroscopy was used as a tool to characterize the copolymers. Figure 2 shows the spectra of ThPCL and ThPCLTh macromonomers.

As can be seen in Fig. 2, the band due to the carbonyl group of ε-CL, which appears at 1,732 cm^{-1} in the spectra of ThPCL and ThPCLTh, indicates the incorporation of ε-CL monomer in the lipase-catalyzed ring-opening polymerization. The peak at around 2,948 cm^{-1} belong to aliphatic methylene stretchings. The peaks between 1,296 to 1,046 cm^{-1} can be attributed to C–O–C ester group vibrations.

In the IR spectra of ThPCL/PTh and ThPCLTh/PTh, the presence of carbonyl stretching at 1,725 cm^{-1} and C–O–C ester group vibrations between 1,295 to 1,052 cm^{-1} proves the presence of PCL in the resultant copolymers since the



Scheme 2 Electrochemical copolymerization processes of ThPCL and ThPCLTh

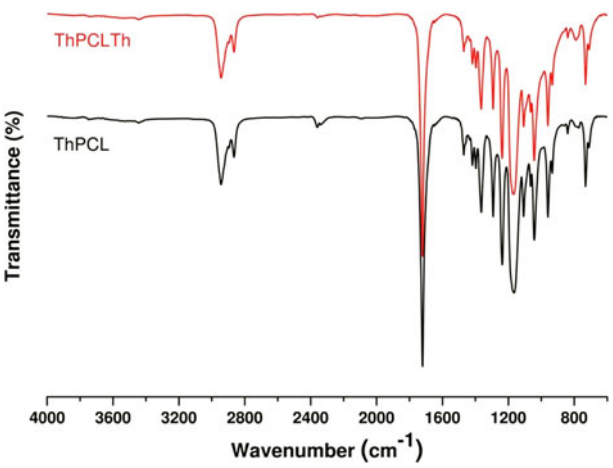


Fig. 2 FT-IR spectra of ThPCL and ThPCLTh

carbonyl is specific to the precursor polymer. The most intense band at 1,041 cm^{-1} is related to the dopant anion, BF_4^-, indicating the conductivity of the polymer (see Table 2). Additionally, the appearance of C–H_β stretching peak at 882 cm^{-1} is the result of polymerization through 2–5 positions of thiophene ring. Another peak

Table 2 Conductivities of the films

Films (BF_4^- doped)	Solution side (S/cm)
ThPCL/PPy	8.3×10^{-1}
ThPCLTh/PPy	1.3×10^{-1}
ThPCL/PTh	3.3×10^{-2}
ThPCLTh/PTh	1.4×10^{-2}

appeared at 1,615 cm^{-1} is the proof of conjugation [24, 25]. IR spectrum of ThPCL/PPy and ThPCLTh/PPy films revealed a carbonyl peak at 1,730 cm^{-1}, signifying the presence of PCL segments in the resultant films. The peaks at 1,291 to 1,027 cm^{-1} are related to C–O–C stretchings and dopant anion. The peak at 905 cm^{-1} belongs to N–H wagging, proving the presence of Py in the structure [39].

Cyclic voltammetry

Redox behaviors of ThPCL and ThPCLTh were investigated by using CV. CV's of both polymers in an ACN-TBAFB system implied that the precursor polymers are not electroactive. Although, both ThPCL and ThPCLTh reveal two sequential oxidation and reduction peaks, the decreasing electroactivity in the multiscans can be considered as the lack of possibility of the reaction via end thiophene groups for these polymers (Fig. 3a, b).

Upon addition of Py into the reaction medium, oxidation peaks of ThPCL/Py and ThPCLTh/Py were observed at 0.05 and 0.23 V, respectively. When Fig. 3d, e are compared with the voltammogram of pristine Py in Fig. 3c, the redox peaks are not at the same positions (pure PPy—$E_{p,a}$: 0.64 V), and the peak height with the same scan number is different. These shifts are known to be indications for the reaction between Py and Th end groups of the precursor polymers.

The possibility of the reaction between thiophene moieties at the chain end(s) of the precursor polymers and Th is also clearly shown in Fig. 3g, h. ThPCL and ThPCLTh showed increasing redox peaks with increasing number of scan runs at 1.23 and 1.52 V, respectively. These potential values are somewhat different from that of thiophene's cyclic voltammogram on a bare Pt electrode where an increasing redox peak was observed at 1.15 V in Fig. 3f. It implies that reaction of the precursor polymers with Th occurs through the thiophene moieties at the chain end(s).

Thermal behaviors of macromonomers (ThPCL and ThPCLTh) and their copolymers with pyrrole and thiophene

The melting and crystallization behavior of ThPCL and ThPCLTh have been examined by DSC. Fig. 4 shows the DSC curves of the polymers in the first heating run, the cooling run, and the second heating run. These curves indicate the presence of characteristic transitions such as melting and crystallization, which are the typical of semicrystalline PCL polymer. Although the polymers gave a monomodal crystallization temperature (T_c) in the cooling run, dimodal melting points in the

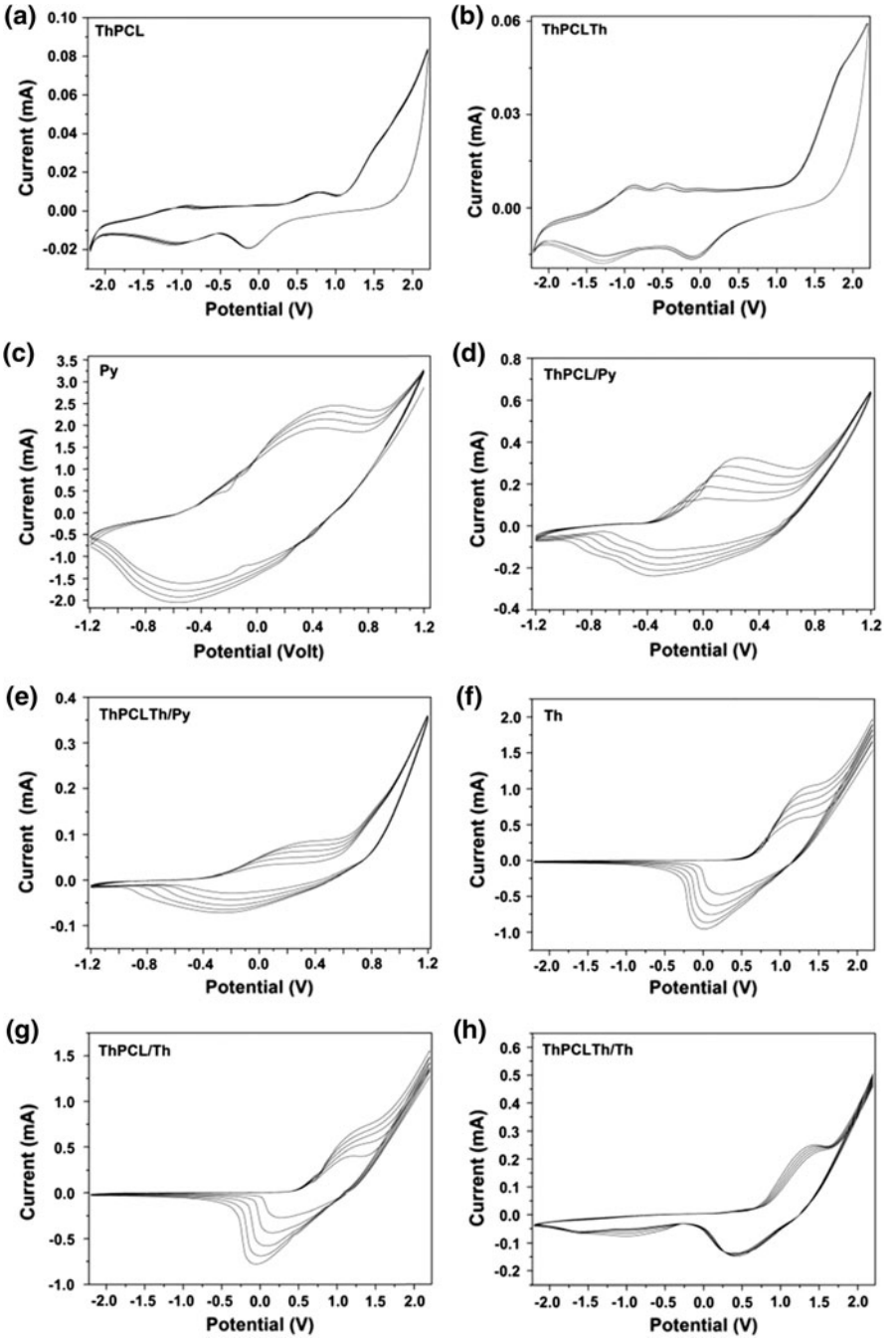


Fig. 3 Cyclic voltammograms of ThPCL (**a**), ThPCLTh (**b**), pure Py (**c**), ThPCL in the presence of Py (**d**), ThPCLTh in the presence of Py (**e**), pure Th (**f**), ThPCL in the presence of Th (**g**), and ThPCLTh in the presence of Th (**h**). Scan rate 400 mV/s

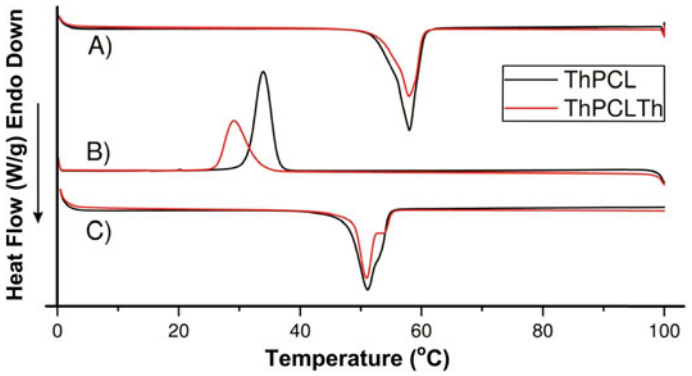


Fig. 4 DSC curves of ThPCL and ThPCLTh in the first heating run (**a**), cooling run (**b**), and second heating run (**c**)

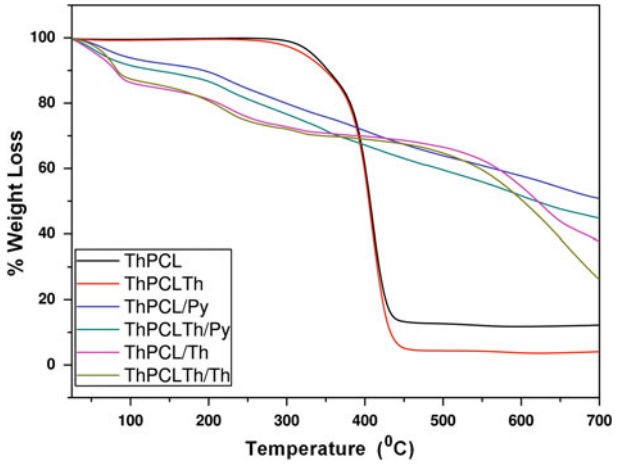


Fig. 5 TGA curves of macromonomers and their copolymers with Py and Th

first and second heating runs were observed for both polymers. Also, the polymers have the same maximal melting points in the first and second heating runs as demonstrated in Fig. 4b.

Thermal properties of ThPCL and ThPCLTh and their copolymers with pyrrole and thiophene were investigated by determining the weight loss of a sample upon linearly increasing the temperature by conventional TGA at a rate of 20 °C/min from room temperature to 700 °C under nitrogen atmosphere. Figure 5 shows the temperature dependence profiles of the polymers. ThPCL and ThPCLTh show higher T_{onset} than their copolymers prepared electrochemically via the reaction of Th and Py. TGA thermograms of both ThPCL and ThPCLTh revealed two weight losses. ThPCL gave weight loss at 407.6 °C whereas the weight loss of ThPCLTh was observed at 406.1 °C. The first weight losses of ThPCL and ThPCLTh appeared to start at around 270.5 and 249.1 °C, respectively. About 12.2 and 4.05% of the polymers remained after 700 °C indicating the higher thermal resistance of ThPCL.

By comparison with ThPCL and ThPCLTh, a large difference in the values for the char residues of the copolymers draws attention. Incorporation of either PPy or PTh into the precursor polymers yields higher char yield due to the inherent stable properties of PPy and PTh segments. As can be clearly seen from TGA curves, the copolymers of ThPCL and ThPCLTh with Py and Th show multi-weight losses starting before 100 °C as compared to the precursor polymers. Initial weight losses are attributed to extraction of solvent and followed by dopant (TBAFB) removal.

Conductivities of the films

A standard four-probe technique was used to estimate the conductivities of the copolymers (ThPCL/PPy, ThPCLTh/PPy, ThPCL/PTh, and ThPCLTh/PTh) which were all doped with BF_4^-. Their conductivities are given in Table 2. After washing with CH_2Cl_2, the conductivities of the films did not show any considerable change. The conductivities of both the electrode and solution sides were also of the same order of magnitude, implying the homogeneity of the films at least in terms of conductivity [24, 40].

Morphologies of the films

The surface morphologies of the copolymer films (ThPCL/PPy, ThPCLTh/PPy, ThPCL/PTh, and ThPCLTh/PTh) were investigated by Scanning Electron Microscopy (SEM). SEM micrographs of the films were characterized after washing them with ACN and CH_2Cl_2 in order to dissolve and get rid of the unreacted precursor polymers and excess supporting electrolyte (TBAFB). The micrographs of the films were taken from the solution side and are given in Fig. 6. The micrographs of pure PPy and PTh are also included to show the differences in the morphologies.

At first sight, it is clearly seen that the images of the films are different from those of both pure PPy and PTh. When SEM micrographs of ThPCL/PPy and ThPCLTh/PPy films are compared to that of pure PPy film (Fig. 6a), the holes observed in pure PPy film was removed in both films (Fig. 6b, c). ThPCL/PPy has a rough surface while ThPCLTh/PPy has a smooth structure. As for SEM micrographs of ThPCL/PTh and ThPCLTh/PTh films in Fig. 6e, f, the former has similar, but more compact cauliflower structure as compared to the morphology of the pure PTh. For the case of latter, an unusual morphology was observed which is rather different than that of the pure PTh. The differences in the morphologies of the films compared to the pure PPy and PTh indicate the reactions of the precursor polymers with either Py or Th.

Conclusions

α,ω-thiophene functional groups of PCL were prepared by enzymatic polymerization using Novozym 435 as the catalyst. It was excellent catalyst for obtaining α-thiophene-functionalized PCL by alcohol-initiated ring-opening polymerization of ε-CL (initiation). It was also employed for the functionalization of the hydroxyl end group of PCL (termination reaction). When the two synthetic strategies were

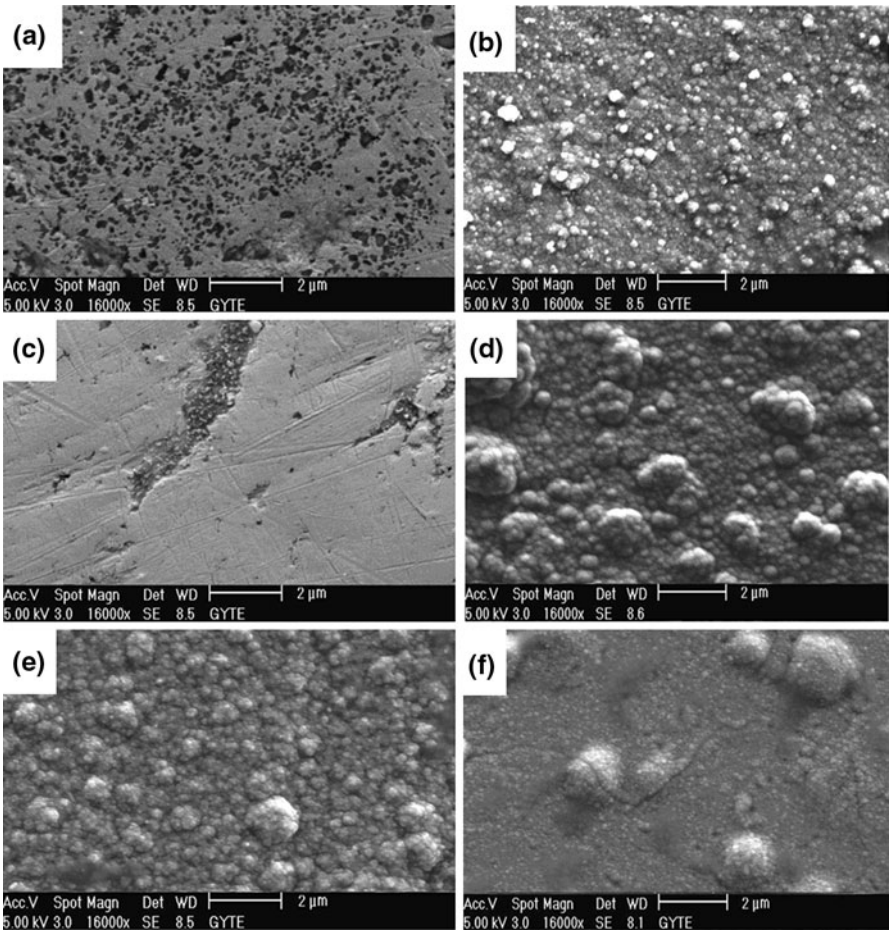


Fig. 6 SEM micrographs of pure PPy (**a**), ThPCL in the presence of Py (**b**), ThPCLTh in the presence of Py (**c**), pure PTh (**d**), ThPCL in the presence of Th (**e**), and ThPCLTh in the presence of Th (**f**). (The micrographs were taken from the solution side)

combined, Novozym 435 catalyzed the formation of α,ω-thiophene-capped PCL. In the polymerization of ε-CL, the thiophene functionality was introduced almost quantitatively at the polymer α-terminal (ca. 97% introduction of the initiator **1**), whereas the termination reaction did not give the polymer quantitatively bearing the thiophene group at the polymer ω-terminal (ca. 65% introduction of the terminator **3**). The end-thiophene functionalities that were introduced into PCL polymers were subsequently employed in electropolymerization with Py and Th. Investigation of the electrically conducting copolymers reveals that PPy or PTh grows through the thiophene moieties existing at the chain end(s) of ThPCL and ThPCLTh. The synthetic strategy employed in this study may be of considerable importance for synthesis of ε-CL based polymers with different end functionalities.

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