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Synthesis and characterization of conducting copolymers of thiophene-3-yl acetic acid cholesteryl ester with pyrrole

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A new polythiophene containing a cholesteryl side chain in the β-position was chemically polymerised in nitromethane/carbontetrachloride using $FeCl_3$ as the oxidizing agent. Polymerisation was also achieved by constant current electrolysis in dichloromethane. Subsequently, conducting copolymers of thiophene-3-yl acetic acid cholesteryl ester (CM), PCM1 (obtained from chemical polymerisation method) and PCM4 (obtained from constant current electrolysis) with pyrrole were synthesized using *p*-toluene sulfonic acid and sodium dodecyl sulfate as the supporting electrolytes via constant potential electrolyses. Characterizations of the samples were performed by CV, FTIR, NMR, DSC, TGA and SEM analyses. Electrical conductivities were measured by the four-probe technique.

1. Introduction

Due to the increasing demand for enantiomerically pure compounds and applications requiring chiral polymers, a large interest can be anticipated in the synthesis of optically active monomers and polymers. The important application of optically active polymers is mainly as catalysts for asymmetric synthesis [1] and as chiral stationary phases for direct optical resolution of enantiomers [2, 3]. The applications of conjugated polymers in the fields of organic conductors, non-linear optics, electroluminescent materials, solar cells, high energy density batteries and modified electrodes are under active investigation. Chiral conjugated polymers represent a class of potentially useful materials and have recently received growing attention due to their potential benefits as asymmetric electrodes, polarized photo- and electroluminescence, enantioselective sensing, polarization-sensitive electro optical devices, non-linear optical materials [4–6].

Polymers containing thiophene units have been the subject of extensive research for more than 25 years. Polythiophenes are interesting not only for their electrical properties, but also others, like, electrophysical, magnetic, liquid crystalline and optical properties [7]. The processability of polythiophenes has been greatly improved by substituting a long flexible side group in the β-position [8]. This structural modification of the thiophene based polymers has resulted in the development of materials with a wide range of properties including water solubility [9], ionic conductivity [10], liquid crystalline properties [11, 12] and optical activity [13, 14].

In 1988, Lemaire *et al.* synthesized a chiral polythiophene, which has exhibited an enantioselective recognition property [15]. The high optical rotation of the polymer indicates a main chain helical conformation induced by the chiral side chain substituents present in the 3-positions of thiophene rings.

Cholesterol has been the most commonly encountered pendant chiral moiety and also is a very well known mesogenic group [12]. On the other hand, cholesterol is also interesting as an inclusion compound [16].

The aim of this attempt was the synthesis and characterization of a new monomer containing an ester group derived from 3-thiophene acetic acid and cholesterol (Scheme 1). In addition, both chemical and galvanostatical polymerisations of CM were studied. Copolymers of both monomer and chemically or galvanostatically synthesized polymers with pyrrole were synthesized by using two different supporting electrolytes in aqueous medium, namely, *p*-toluene sulfonic acid (PTSA) and sodium dodecyl sulfate (SDS).

2. Experimental

2.1. Materials

Acetonitrile (AN) (Merck), methanol (Merck) nitromethane (NM) (Sigma), tetrabutylammonium tetrafloroborate (TBAFB), *p*-toluene sulfonic acid (PTSA) (Sigma) and sodium dodecylsulfate (SDS) (Aldrich)

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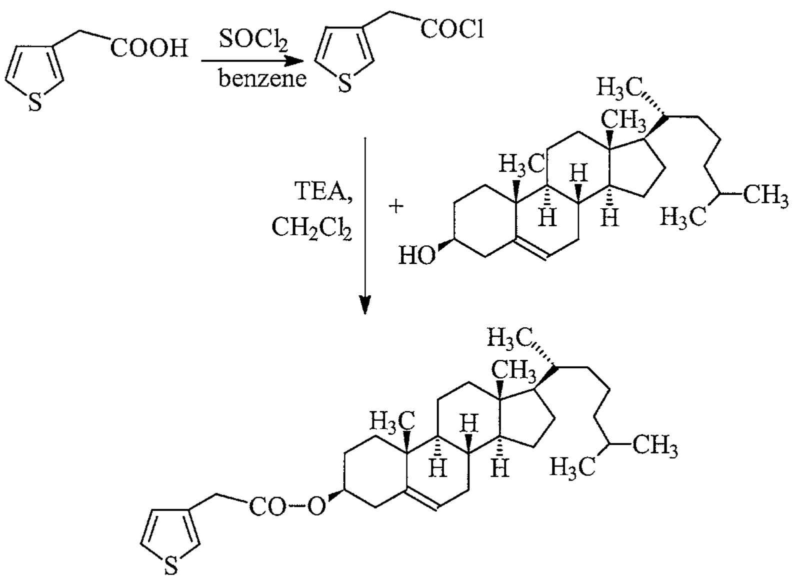


Scheme 1

were used without further purification. Pyrrole and thiophene (Aldrich) were distilled just before used. Dichloromethane and benzene were purified by usual methods and dried over CaH_2 or Na wire, respectively. Thiophene-3-acetic acid (Fluka), triethylamine (TEA) (Baker) and cholesterol (Fluka) were used as received. Thionyl chloride (Fluka) was distilled under reduced pressure just before use.

2.2. Synthesis of cholesteryl containing thiophene monomer (CM)

a. A mixture of 3-thiophene acetic acid (14.217 g, 0.1 mol) in 50×10^{-6} m^3 dry benzene and thionyl chloride (35.69 g, 0.3 mol) was refluxed for 16 h. The solvent and unreacted thionyl chloride were removed by distillation. The residual liquid product was purified by distillation under reduced pressure.

^1H-NMR in $CDCl_3$ (δ, ppm): 7.33, 7.21, 7.01 (3H, thiophene ring), 4.16 (2H, CH_2).

b. To a solution of 1.966 g (0.005 mol) cholesterol in $10^{-5}m^3$ dichloromethane containing 0.505 g (0.005 mol) triethylamine (TEA), was added dropwise in 0.5 h, by cooling in ice bath and nitrogen atmosphere onto 0.883 g 3-thiophene acetyl chloride (0.0055 mol). The esterification was carried out overnight at room temperature. Then the white solid of triethylamine chlorinehydrate was filtered off and the solution was washed with HCl 1% solution (three times) and water (three times). The organic layer was dried over $MgSO_4$ and the solvent was removed via rotaevaporation. The crude product was purified by chromatography through a silicagel column using a mixture of hexane/ethyl acetate (9/1 v/v) as the eluent. Twice recrystalisation from ethanol provided 1.88 g of white crystals (yield 74%).

2.3. Cyclic voltammetry (CV)

The oxidation/reduction behaviour of the monomer in the presence of pyrrole and thiophene was investigated by CV. The system consists of a potentiostat (HEKA), an X-Y recorder and a CV cell containing Pt foil working and counter electrodes, and a Ag/Ag^+ reference electrode. Measurements have been carried out under N_2 atmosphere in acetonitrile and water at room temperature.

2.4. Potentiostatic polymerisation of CM

2.4.1. Self polymerisation of CM

For the self-polymerisation of CM, an electrolysis cell was prepared by precoating the working electrode with 1 w/v% solution of CM in dichloromethane, 0.05 M PTSA and/or SDS in distilled water. Constant potential electrolyses were carried out at 1.1 V for 2 h. Electrolyses were also performed in AN-TBAFB, solvent electrolyte couple by precoating the Pt electrode with CM in 0.05 M or 0.1 M TBAFB at 2.0 V and 2.5 V for 2 h. Separate electrolyses were also performed by dissolving 50 mg of CM in dichloromethane and 0.05 M TBAFB at 2.5 V at 0°C.

2.4.2. Synthesis of copolymers of CM with pyrrole

1 w/v% solution of CM in dichloromethane was deposited onto Pt electrode. This electrode was used as the working electrode after the evaporation of the solvent. Electrolyses were performed in the presence of 0.02 M pyrrole; 0.05 M PTSA or SDS in water at 1.1 V. Separate electrolyses were also carried out 0.05 M TBAFB in acetonitrile at 1.3 V for 80 min by depositing the CM on the electrode. Then, the polymer film was peeled off from the electrode surface.

2.4.3. Synthesis of copolymers of CM with thiophene

For the synthesis of copolymers of CM thiophene was also used as the comonomer. The electrolysis cell was prepared by dissolving 0.05 M TBAFB and 0.02 M thiophene in acetonitrile was added and electrolyses were carried out at 1.9 V for 80 min.

2.5. Chemical polymerisation of CM (PCM1) and doping with iodine

Chemical polymerisation of CM was carried out in both NM/CCl_4 (3 : 1) [17] and $CHCl_3$ under constant flow of nitrogen. 100 mg of CM was dissolved in CCl_4

and placed in three-necked flask. Polymerisation was achieved by dropwise addition of $FeCl_3$ solution in NM (2.5 M) to a solution of monomer at 0°C. The reaction was run for 24 h with constant stirring. Methanol was added to precipitate the gray solid. It was washed with water and methanol several times to remove excess ferric chloride. Then, the solid (PCM1) filtered dried under vacuum. The yield is 71%.

For the polymerisation of CM in $CHCl_3$ both monomer and $FeCl_3$ were dissolved in $CHCl_3$. The reaction was performed in an inert atmosphere with constant stirring at room temperature [18].

Doping was achieved by using vapour phase doping technique. After known weight of PCM1 (20 mg) was placed into the tube, iodine was suspended to the test tube for one week. Conductivity of I_3^- doped polymer was measured by using the four-probe technique.

2.6. Galvanostatic polymerisation of CM (PCM2), (PCM3), (PCM4)

Constant current electrolyses (CCE) were carried out in AN-TBAFB, CH_2Cl_2-TBAFB and water-PTSA, solvent-electrolyte couples in one-compartment cell equipped with two electrodes; the working and counter electrodes. For water-PTSA system, stainless steel was used as the working (40 × 50 mm^2) and a steel mesh as the counter electrode (40 × 50 mm^2). 1 w/v% solution of monomer was deposited on the working electrode and electrolysis was performed by passing constant current of 100 mA. Electrolysis was also carried out in AN-TBAFB at room temperature at 300 mA. After electrolyses, a black precipitate (PCM2) was obtained from the solution by filtering. It was washed with acetonitrile several times and dried under vacuum. CCE was also performed in dichloromethane-TBAFB system at 0°C at 200 mA with 50 mg monomer and 0.05 M TBAFB in 60×10^{-6} m^3 of dichloromethane. A green product (PCM3) was obtained from the solution. CCE was also performed for the same system by using Pt foils (10 × 10 mm^2) as the working and counter electrodes. 0.2 M TBAFB and 50 mg of CM were dissolved in 15×10^{-6} m^3 dichloromethane. In this case, gray product (PCM4) was obtained both from the electrode surface and the solution.

2.7. Synthesis of block copolymers of PCM1 with pyrrole and thiophene (PCM1/PPy and PCM1/PTh)

For the copolymerisation, chemically synthesized polymer (PCM1) was deposited on the electrode and electrolyses were carried out in acetonitrile-TBAFB, water-PTSA and water-SDS systems.

2.8. Synthesis of block copolymers of PCM4 with pyrrole and thiophene (PCM4/PPy and PCM4/PTh)

The synthesis of block copolymers of PCM4, were achieved in 1 w/v% PCM4 solution prepared in dichloromethane by coating the both sides of the electrode with PCM4. Electrolyses in the presence of pyrrole were done at +1.1 V for water-PTSA and water-SDS media since excess potentials applied cause the electrolysis of water, which leads to the loss of PCM4 on the anode. Application of +1.3 V in acetonitrile-TBAFB system, however, is possible and enhances the rate of production of the resultant copolymer.

As to the polymerisation of thiophene on PCM4 electrode, +1.9 V was applied (oxidation potential of thiophene) in AN-TBAFB solvent-electrolyte couple.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry experiments were performed in acetonitrile-TBAFB, solvent-electrolyte couple. In the cyclic voltammogram of CM, no detectable redox peaks were observed (Fig. 1a). Thus, it was concluded that

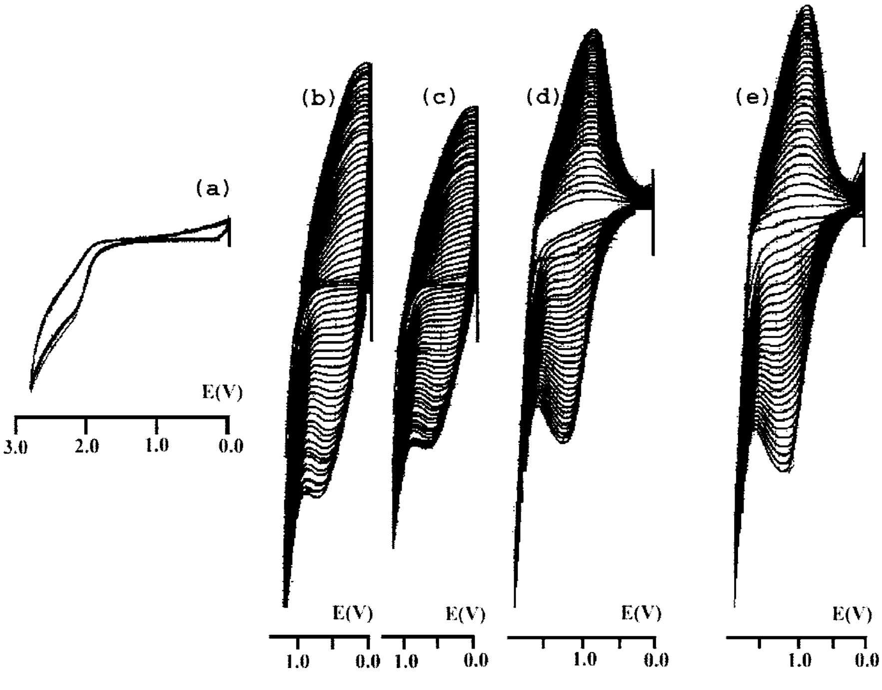
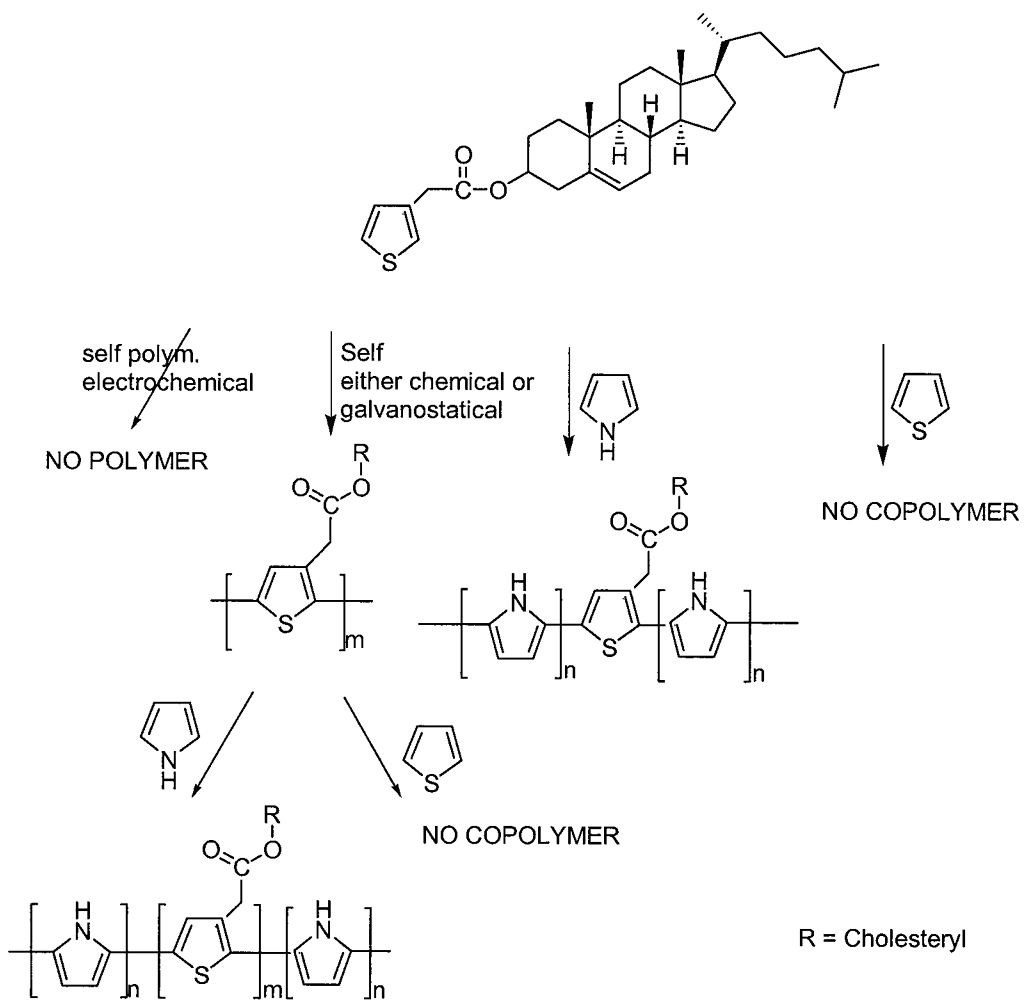


Figure 1 Cyclic voltammogram of (a) monomer (CM), (b) CM in the presence of pyrrole, (c) pyrrole on a bare Pt electrode, (d) CM in the presence of thiophene and (e) thiophene on a bare Pt electrode.



Scheme 2

CM was not electroactive. However, with the addition of pyrrole, a redox peak, which revealed increasing height with increasing scan number, was observed at +0.75 V (Fig. 1b). This potential value was somewhat different from the oxidation potential of pure polypyrrole, which was obtained as +0.65 V after 33 scans (Fig. 1c). The shift to higher potential value may serve as an indication for the copolymer formation.

In the presence of thiophene, a redox peak was observed at +1.25 V (Fig. 1d). The same redox peak appeared for the thiophene on a bare Pt electrode (Fig. 1e). This observation may reflect that there is no noticeable interaction between CM and thiophene.

3.2. Characterization

For the self-polymerisation of CM by constant potential electrolysis, no product formation was observed on the electrode surface for AN-TBAFB, dichloromethane-TBAFB, water-PTSA and water-SDS systems. However, self-polymerisations of CM were achieved both by chemical polymerisation ($FeCl_3$) and galvanostatic polymerisation (CCE) methods successfully. Via constant current electrolysis, desired product was obtained only in the dichloromethane-TBAFB system at 0°C by using a single compartment cell and Pt foil electrodes. As for the other systems, the target product was not obtained. Electropolymerisations of CM, PCM1 and PCM4 with pyrrole and thiophene were shown in Scheme 2. Only pyrrole seemed to be appropriate for the polymerisation.

3.2.1. ^1H NMR and FT-IR characterization

^1H-NMR spectrum of the monomer and PCM1 were taken by using a Bruker-Instrument-NMR Spectrometer (DPX-400) with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. ^1H-NMR data for the monomer: ^1H-NMR(δ, ppm): 7.27 (s, 1H), 7.15 (s, 1H), 7.05 (s, 1H), from 3-thienyl ring, 5.37 (s, 1H) C=CH from cholesteryl 4.65 (s, 1H), COO—CH— in cholesteryl), 3.62 (s, 2H), Th-CH_2—COO—, 0.67–2.40 (m, 44H), cholesteryl. In the ^1H-NMR spectra of the PCM1, a wide signal in the region of 6.75 to 7.10 ppm was assigned to thiophene hydrogens. The dominant signal at 7.00 ppm was assigned to head to tail, head to head linkage structure [19, 20]. Other signals remained unchanged but broadened due to polymerisation.

The IR spectrum was recorded on a Nicolet 510 FTIR spectrometer. The absorption bands at 768 and 3106 cm^{-1} are due to the thienylene $C-H_\alpha$ stretching modes in the monomer. As to the CM and PCM1, the bands related to the carbonyl group and to C—O—C stretching are present at about 1725 and in the 1000–1265 cm^{-1} region respectively [21]. There are several peaks, which are attributed to the cholesteryl group. These are 2933, 2863, 1462, 1377, 1010, 955, 803 and 740 cm^{-1}. After the chemical polymerisation of CM, a

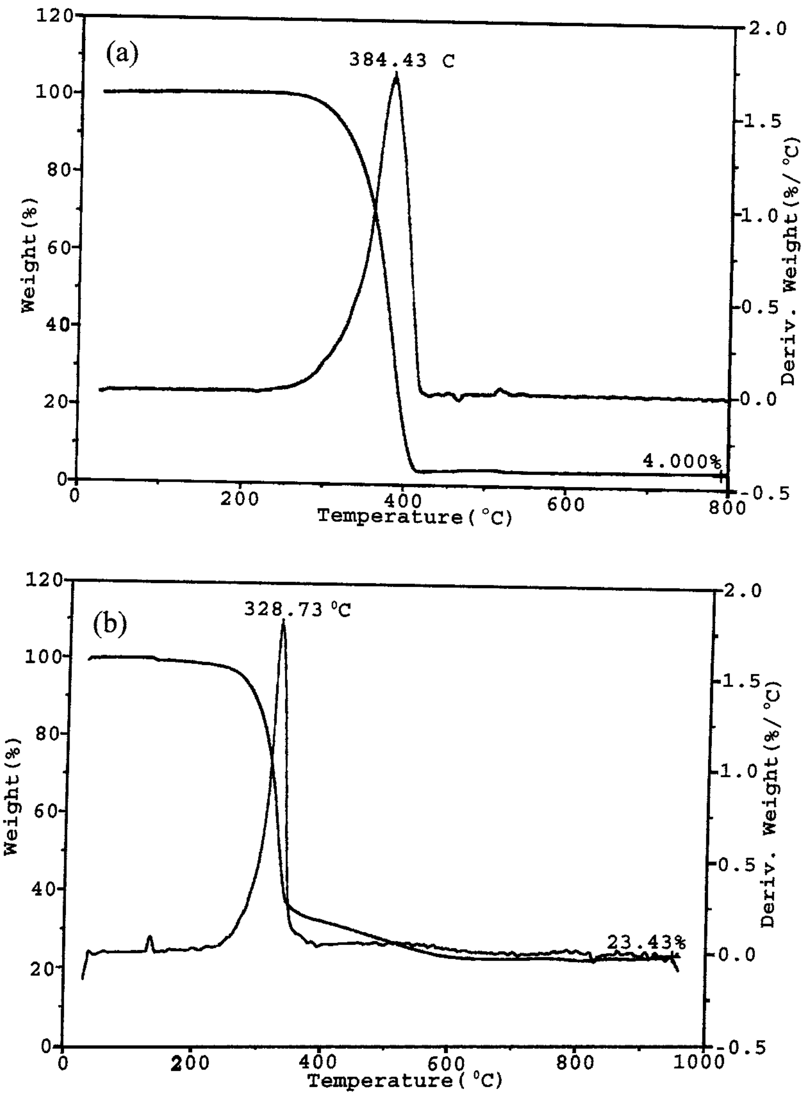


Figure 2 TGA thermograms of (a) CM and (b) PCM1.

new band appears at 1626 cm^{-1} indicating the conjugation [22]. Moreover, the band at 768 cm^{-1} is very much attenuated in the polymers (PCM1 and PCM4), which is proof of 2,5 disubstitution on the thiophene ring. Doping PCM1 with iodine, took on a noticeable change in the IR spectra. At 500–1500 cm^{-1} strong and broad doping-induced bands are present, which are related to the presence of free charge carriers.

Electrochemically synthesized copolymers; CM/PPy, PCM1/PPy and PCM4/PPy contain an absorption band at around 1710 cm^{-1} for the water-SDS and water-PTSA systems. This proves the presence of CM in the resultant polymers, since the carbonyl is specific to the monomer. The possibility of overoxidation of pyrrole, giving carbonyl on the ring, has been eliminated via studying the IR of PPy produced under the same conditions. Moreover, it was concluded that copolymerisation was not achieved in AN-TBAFB system with pyrrole and/or thiophene due to the lack of any carbonyl absorption band in the IR spectrum. In other words, in these cases pure PPy and PTh were obtained.

3.2.2. Thermal analysis

Thermal behaviour of the samples was investigated by using a Du Pont 2000 Thermal Gravimetry Analyser and Differential Scanning Calorimetry. TGA thermogram of the monomer (CM) showed one weight loss at 384.4°C (Fig. 2a) whereas for the PCM1, a weight loss was observed at 328.7°C (Fig. 2b). The most striking difference is the char residue. Only 4% of the samples remained for the monomer whereas 23.43% remnant was found for PCM1. The thermogram for the CM/PPy (PTS$^-$ doped) revealed four transitions at 73°C, 226.8°C, 362°C and 490°C (Fig. 3a). However, three thermal transitions were observed at 114°C, 235°C and 500°C for CM/PPy (SDS doped) film (Fig. 3b). PTS$^-$ doped polymer is more thermally stable than the SDS doped film. Thermograms of PCM1/PPy (PTS$^-$ doped) and PCM4/PPy (PTS$^-$ doped) are nearly the same with the CM/PPy (PTS$^-$ doped). This is due to the high percentage of the pyrrole content in the copolymer matrix. This argument is also valid for PCM1/PPy (SDS doped) and PCM4/PPy (SDS doped) samples.

The DSC thermogram of the monomer shows a sharp melting point at 106.3°C and it is stable up to 224°C (Fig. 4a). PCM1 exhibits three endothermic transitions at 172.5°C, 223.2°C and 265°C (Fig. 4b). The same experiment was performed by heating the sample up to 200°C with 10°C/min rate in the first run and cooling back to room temperature and heating again up to

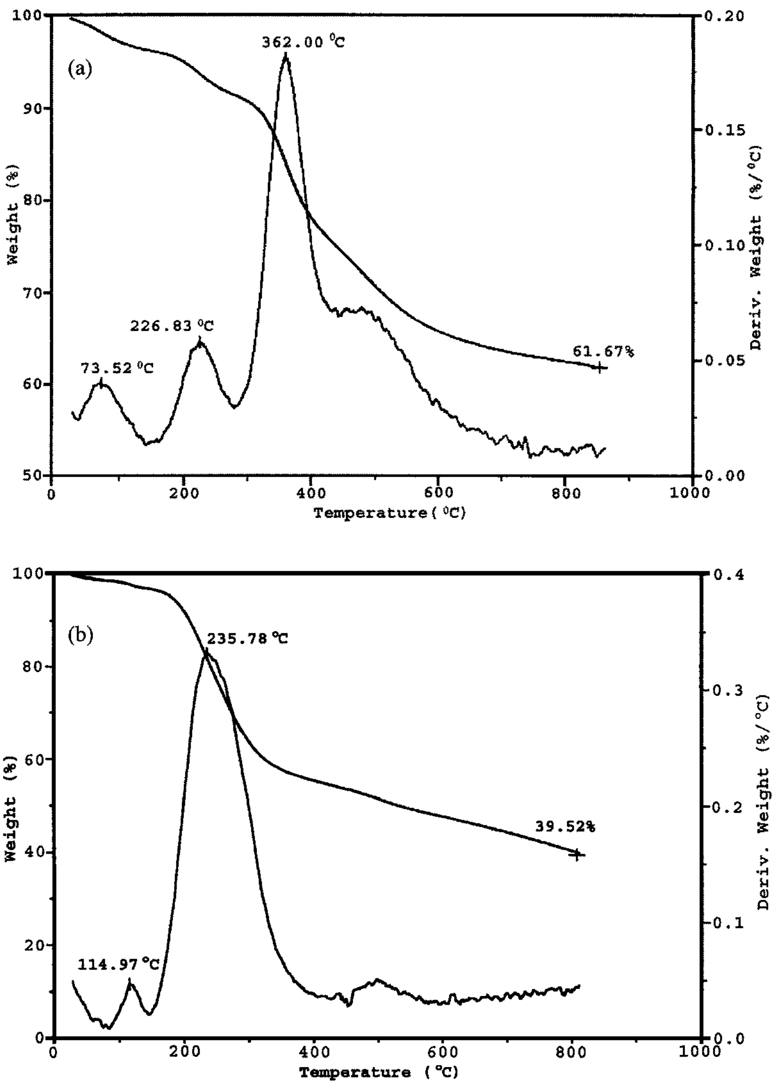


Figure 3 TGA thermograms of (a) PPy/CM (PTSA doped) and (b) PPy/CM (SDS doped).

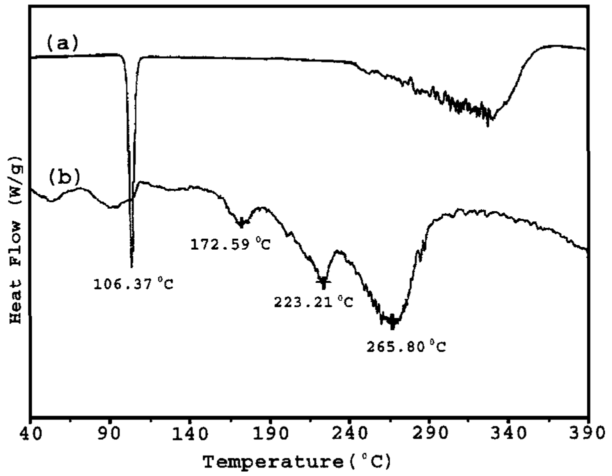


Figure 4 DSC thermograms of (a) CM and (b) PCM1.

400°C. Only two transitions were observed at 223.2°C and 265°C. These are due to the decomposition of the samples. For the copolymers, CM/PPy (PTS$^-$ doped) and CM/PPy (SDS doped) thermograms are shown in Figs 5a and b respectively (Fig. 5). Two transitions were observed for CM/PPy (PTS$^-$ doped) at 91.1°C and 334.4°C. The first transition is due to the removal of the water from the polymer matrix. The second one corresponds to the decomposition of the sample. DSC curves of PCM1/PPy (PTS$^-$ doped) (two transitions at 82.4°C and 334.7°C) and PCM4/PPy (PTS$^-$ doped) (at 101.3°C and 344°C) are nearly the same as CM/PPy (PTS$^-$ doped), which is probably due to the long chains of PPy in the copolymer matrix. The SDS doped CM/PPy shows also two transitions at 89.2°C and 265.1°C. Similarly, the first one is attributed to the removal of the adsorbed water and second one is related to the dopant ion leaving the matrix. It can be concluded that PTS$^-$ doped copolymers are thermally more stable than SDS doped copolymer. Thermograms of PCM1/PPy (SDS doped) (85.2°C and 260.1°C) and PCM4/PPy (SDS doped) (72.91°C and 251.2°C) are similar to that of CM/PPy.

3.2.3. Conductivity measurements

Electrical conductivity measurements were carried out by using the standard four-probe technique. Conductivities of the copolymers doped with either PTS$^-$ or SDS, were 0.2–6 S/cm. There was no significant difference between the conductivity of washed and unwashed samples. The conductivities of both the electrode and solution sides were also in the same order of magnitude, that reveals the homogeneity of the films (Table I). To impart electrical conductivity to the PCM1, the vapour

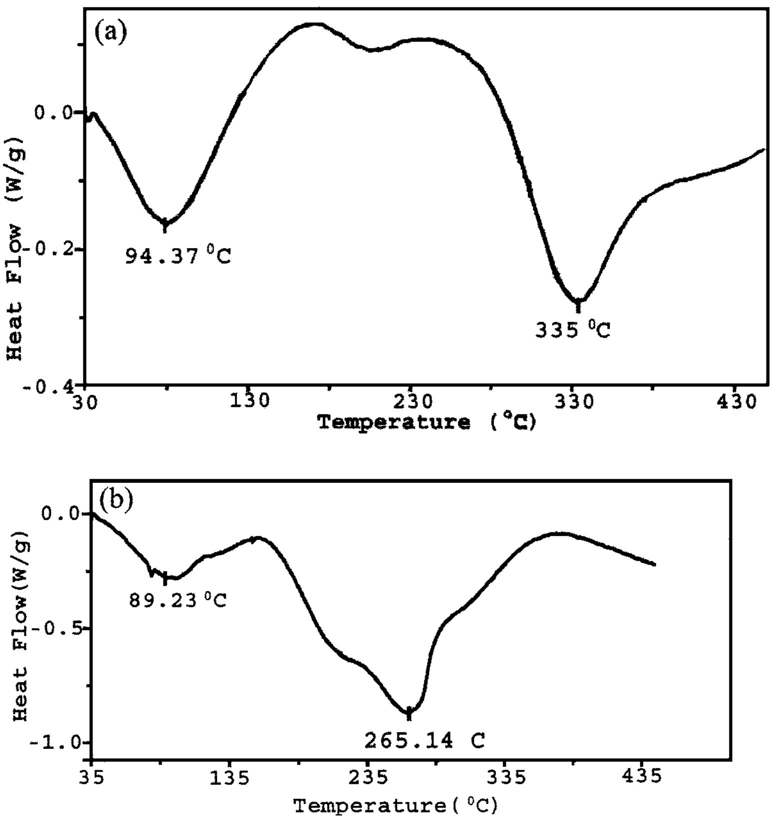
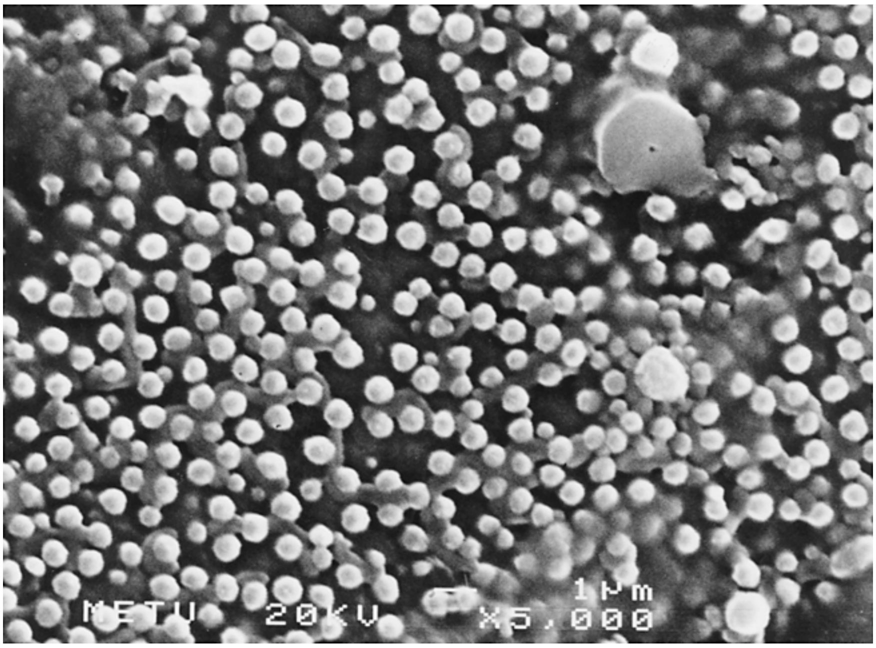


Figure 5 DSC thermograms of (a) PPy/CM (PTSA doped) and (b) PPy/CM (SDS doped).



(a)

Figure 6 SEM micrographs of (a) electrode side of washed PPy/CM (PTSA doped), (b) electrode side of washed PPy/CM (SDS doped), (c) electrode side of unwashed PPy/PCM4 (SDS doped) and (d) electrode side of washed PPy/PCM4 (SDS doped) (*Continued*).

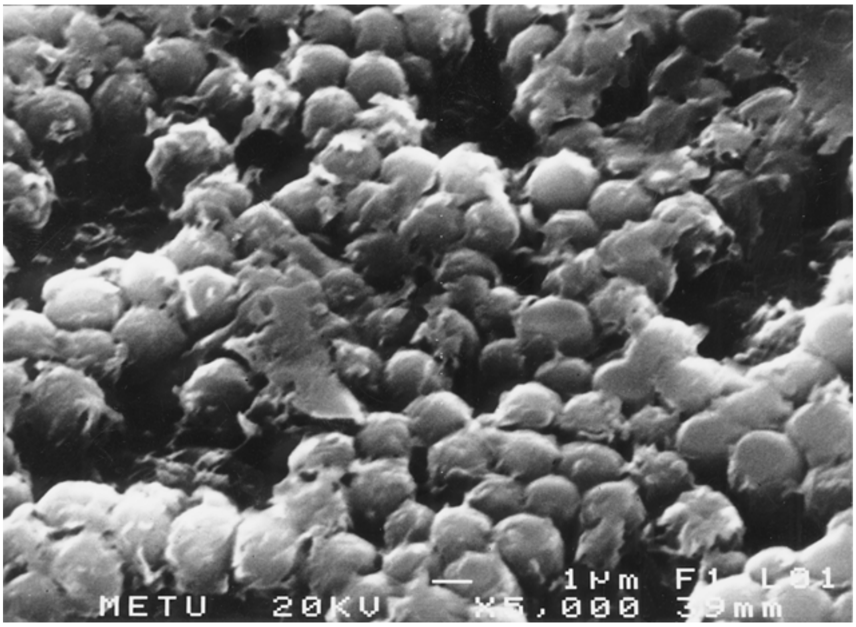
TABLE I Conductivities of the films (S/cm)

Polymer	Electrode side	Solution side
PCM1 (pellets)	5×10^{-2}	5×10^{-2}
CM/PPy (PTS^- doped)	0.2	3.3
CM/PPy (SDS doped)	0.3	0.4
PCM1/PPy (PTS^- doped)	5.0	6.0
PCM1/PPy (SDS doped)	0.3	0.5
PCM4/PPy (PTS^- doped)	0.4	1.0
PCM4/PPy (SDS doped)	0.3	0.6

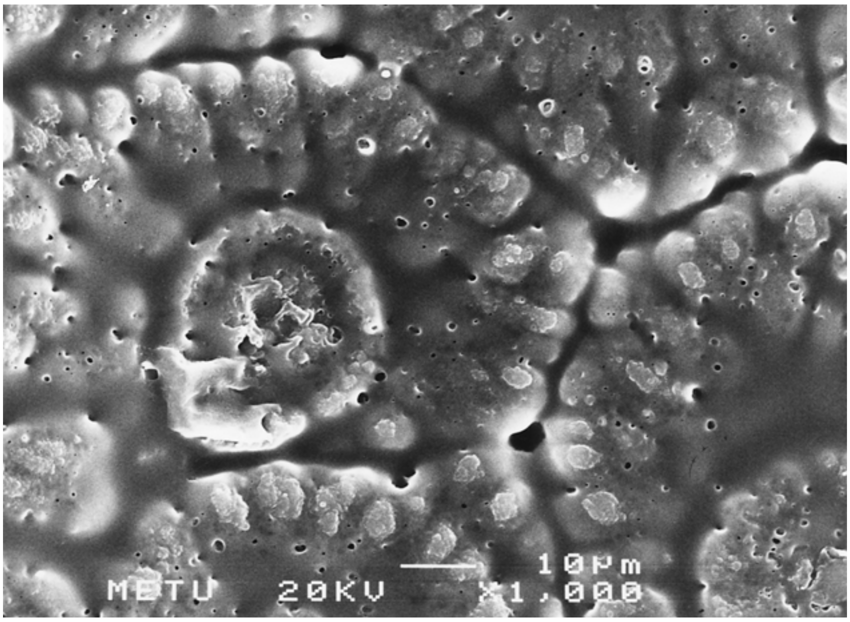
phase doping process was applied (I_2 : acceptor). The conductivity was measured as 5×10^{-2} S/cm.

3.2.4. Scanning electron microscopy (SEM)

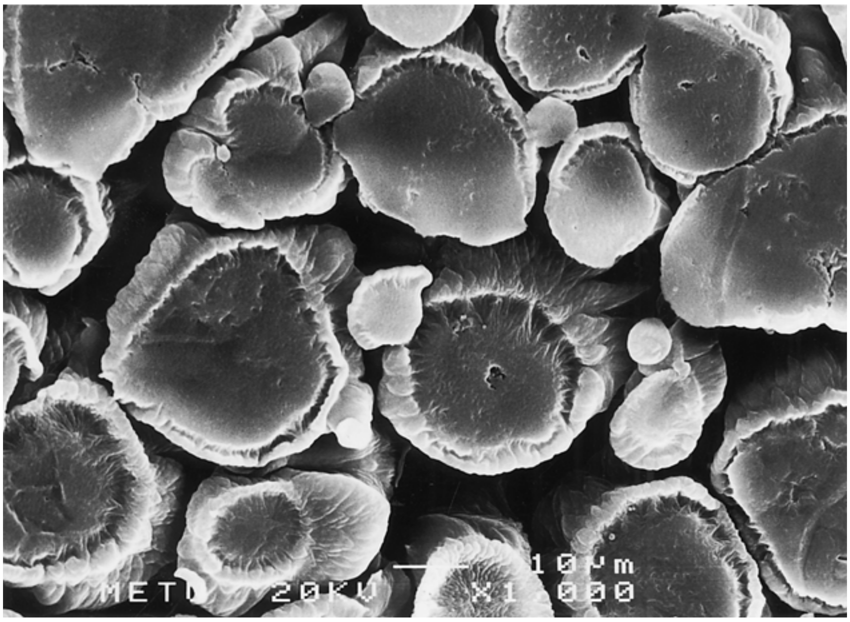
The morphologies of the copolymer films were investigated by SEM studies (JEOL JSM-6400). As far as the SEM micrographs of PPy/CM films are concerned, electrode side morphologies of both PTS^- doped (Fig. 6a) and SDS doped (Fig. 6b) species are significantly different from that of pure PPy. This may be



(b)



(c)



(d)

Figure 6 (*Continued*).

yet another indication of the polymerisation of pyrrole on CM. PTS^- doped PPy/CM's electrode side had small globule like droplets, on the other hand, SDS doped one had larger and more denser globules. Micrographs of SDS doped unwashed PPy/PCM4 (Fig. 6c) and washed (Fig. 6d) electrode sides of PPy/PCM4 films revealed that the surface appearance of films was altered by the washing process. However, washed PPy/PCM4 film had quite different morphology compared to pure PPy, indicating interaction between PCM4 and pyrrole.

4. Summary

Chemical polymerisation of CM via controlled addition of $FeCl_3$ was achieved at low temperature. Moreover, polymerisation of CM was also accomplished by CCE. The syntheses of copolymers of thiophene-3-yl acetic acid cholesteryl ester (CM), PCM1 and PCM4 with pyrrole were achieved by using two different solvent-electrolyte pairs (water-PTSA and water-SDS).

Since the polymerisation of pyrrole is feasible through the thiophene moiety of the cholesteryl containing monomer, we plan the physical entrapment of cholesterol enzyme during polymerisation. If this is possible, construction of a biosensor will be accomplished.

Acknowledgments

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