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### Synthesis and Characterization of Conducting Copolymers of Menthyl Ester of 3-Thiophene Acetic Acid with Pyrrole

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## Synthesis and Characterization of Conducting Copolymers of Menthyl Ester of 3-Thiophene Acetic Acid with Pyrrole

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### ABSTRACT

A new thiophene derivative containing menthyl group (MM) was synthesized and polymerized via chemical and electrochemical (constant current) methods. Polymers obtained and MM itself were used to synthesize copolymers with pyrrole under conditions of constant potential electrolyses. Cyclic voltammetry (CV), thermal analysis (DSC, TGA) and scanning electron microscopy (SEM) analyses were performed for the characterization of samples.

*Key Words:* Thiophene-functionalized monomers; Conducting copolymers; Menthyl ester.

### INTRODUCTION

Composites, graft and block copolymers are synthesized to compensate the certain deficiencies of conducting polymers such as poor mechanical and physical properties. Electropolymerization of the conducting component on an electrode previously coated

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with an insulating polymer is one of most widely used method for that purpose.<sup>[1-5]</sup> Besides producing composites and copolymers, conducting polymers consider the effect of substituents on the properties of the resulting polymer in terms of conductivity, of possible electro- or thermo-chromism and of other physical, rather than chemical properties. Actually the chemical reactivity of polymeric films on the electrodes is of great importance when considering the possible applications in amperometric or potentiometric sensors.<sup>[6]</sup> Synthesis of new polythiophene derivatives with improved conductivity and processing properties is an important part of the conducting polymer research.<sup>[7]</sup> This area has attracted great attention, since substitution of a flexible side group can improve the stability, fusibility, and processibility of thiophene without much affecting the environmental stability and electrical conductivity.<sup>[8-10]</sup>

Polythiophenes are very unique among other polyconjugated systems for two principal reasons<sup>[11,12]</sup>:

1. Their functionalization is relatively easy compared to polypyrrole, polyacetylene, poly(*p*-phenylene), and other conjugated polymers.
2. The attachment of substituents as the side groups has relatively little impact on the electronic and electrochemical properties of the conjugated polythiophene backbone.

In this study, we synthesized a new, functionalized thiophene monomer with a bulky menthyl group, in an attempt to prepare copolymers with pyrrole and thiophene.

The use of such copolymers in several applications such as enzyme immobilization will be the topic of an incoming study.

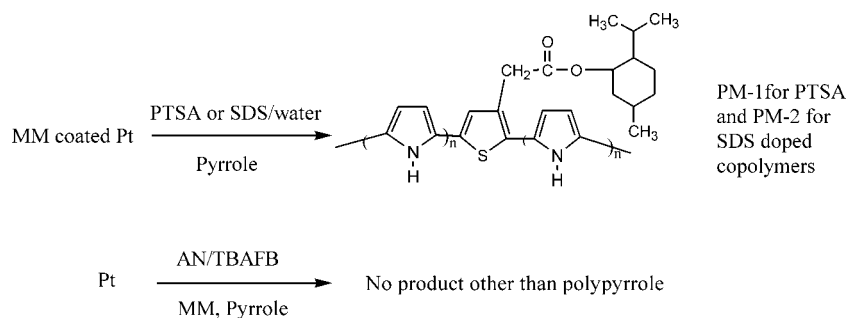
## EXPERIMENTAL

### Materials

Acetonitrile (AN) (Merck), methanol (Merck) nitromethane (NM) (Sigma), tetrabutylammonium tetrafluoroborate (TBAFB), *p*-toluene sulfonic acid (PTSA) (Sigma) and sodium dodecylsulfate (SDS) (Aldrich) were used without further purification. Pyrrole and thiophene (Aldrich) were distilled just before used. Dichloromethane was purified by the usual methods and dried over CaH<sub>2</sub> or Na wire, respectively. Thiophene-3-acetic acid (Fluka), and menthol (Fluka) were used as received.

### Synthesis of Menthyl Containing Thiophene Monomer (MM)

To a solution of thiophene-3-acetic acid (3.55 g) and (–)-menthol (3.9 g) in 40 mL dry THF, *N,N'*-dicyclohexylcarbodiimide (DCCI) (3.09 g) dissolved in 15 mL of THF was added at ice bath temperature. The solution was stirred for 1 h and then the reaction mixture was allowed to come to room temperature. The stirring was continued for 24 h; the precipitated dicyclohexyl urea was filtered off (55% of the theoretical quantity). THF was removed by rotaevaporatory. The crude product was purified by passing through a silica



**Scheme 1.** Synthesis of copolymers of MM with pyrrole.

gel column using a mixture of hexane/ethyl acetate 3/2 (v/v) as the eluent, followed by recrystallization from the same mixture. The process was repeated for two more times to obtain the ester as white crystals (yield, 35%).

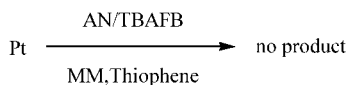
### Potentiostatic Polymerization of MM

#### Synthesis of Copolymers of MM with Pyrrole (PM-1, PM-2)

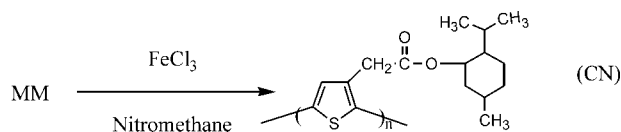
Working electrode (Pt, 2 cm<sup>2</sup>) was coated with 1% w/v MM–dichloromethane solution. Electrolyses were performed in the presence of 0.02 M pyrrole (Py), 0.05 M *p*-toluene sulfonic acid (PTSA), or 0.05 M sodium dodecyl sulphate (SDS) in water. 1.0 V was applied for 90 min. The same procedure was repeated for Acetonitrile (AN)/Tetrabutylammonium tetrafluoroborate (TBAFB) system, where 50 mg MM was dissolved in the solution (Sch. 1).

#### Synthesis of Copolymers of MM with Thiophene

Copolymerization of thiophene must take place in acetonitrile since thiophene is completely insoluble in water. 0.05 M TBAFB in acetonitrile was used as the supporting electrolyte and a constant potential of 2.0 V was applied for 2 h to a solution containing 50 mg MM (Sch. 2).



**Scheme 2.** Synthesis of copolymers of MM with thiophene.



**Scheme 3.** Chemical polymerization of MM.

#### Chemical Polymerization of MM (CN)

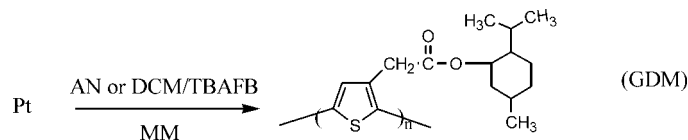
100 mg MM was dissolved in 5 mL CCl<sub>4</sub> and put in a three-necked flask. A nitromethane solution of FeCl<sub>3</sub> (2 M) was added dropwise to the solution of MM at 0 °C (Sch. 3). The reaction was carried out for 24 h under a constant flow of nitrogen and continuous stirring. After 24 h, this mixture was poured onto methanol, and then water was added until a precipitate was observed. The precipitate was washed several times with water and methanol and dried under vacuum. The oligomeric product was named as CN. The yield was 40% (CN).

#### Galvanostatic Polymerization of MM (GDM)

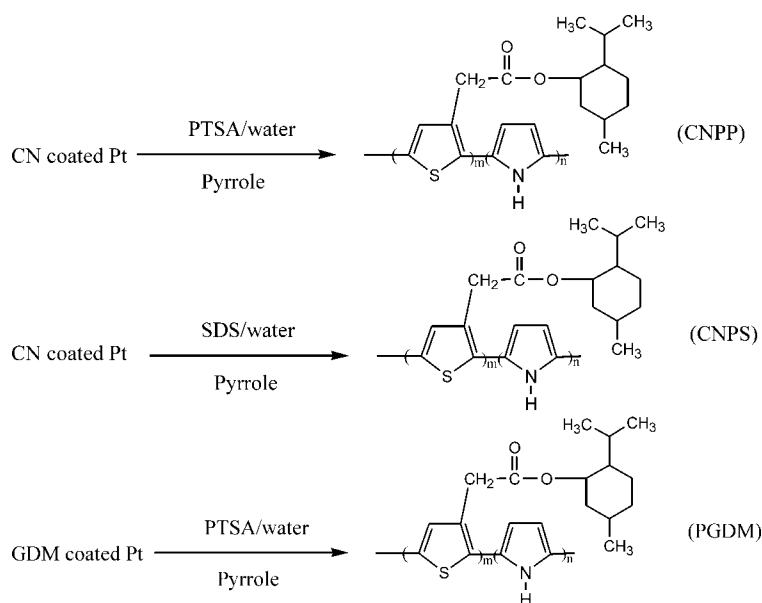
Constant current electrolyses were performed in one component cell with two Pt electrodes as the working (2 cm<sup>2</sup>) and counter electrodes (2 cm<sup>2</sup>). Acetonitrile/TBAFB and dichloromethane (DCM)/TBAFB were used as the electrolysis media. For each medium, 100 mg monomer was introduced and electrolyses were carried at 20 mA for 90 min (Sch. 4). Throughout this time, the cell was in an ice bath. A black precipitate was obtained at the end of both electrolyses. After filtering and washing with water to remove TBAFB, the precipitate (GDM) was dried under vacuum.

#### Synthesis of Block Copolymers of CN and GDM with Pyrrole (CNPP, CNPS, PGDM)

A Pt working electrode (2 cm<sup>2</sup>) was coated either with chemically synthesized polymer, CN, or galvanostatically synthesized polymer GDM from their DCM solution. CNPP and CNPS were synthesized in water using PTSA or SDS electrolytes, respectively. Since GDM is insoluble in water copolymerization with pyrrole was carried out in water/PTSA solvent/electrolyte couple (Sch. 5).



**Scheme 4.** Galvanostatic polymerization of MM.



**Scheme 5.** Synthesis of block copolymers of CN and GDM with pyrrole.

## RESULTS AND DISCUSSION

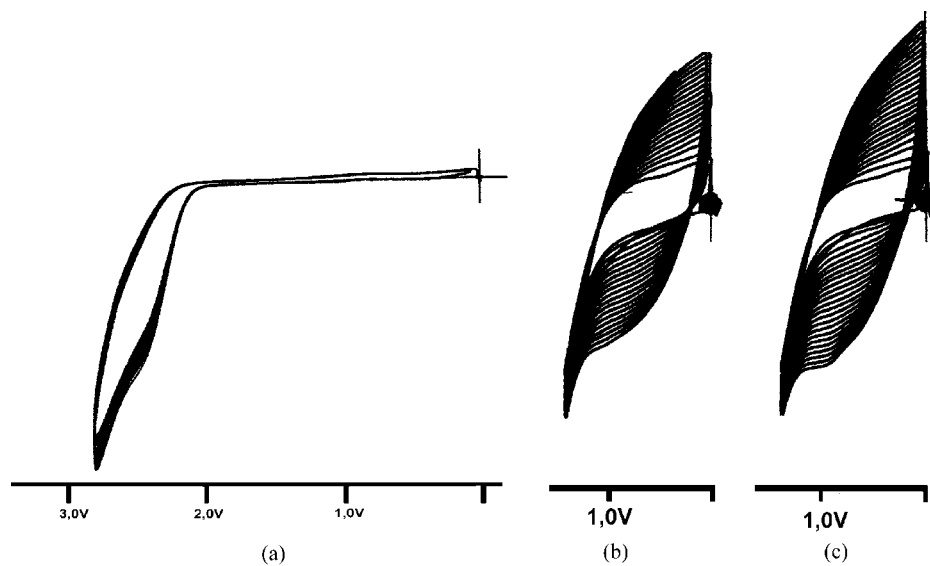
### Cyclic Voltammetry

Acetonitrile and TBAFB were used as the solvent and electrolyte, respectively for cyclic voltammetry studies. As seen from Fig. 1(a), MM has no redox peak, which implies that MM is not an electroactive material. Fig. 1(b) shows the voltammogram of pure Py and Fig. 1(c) shows the voltammogram of Py in the presence of MM. For this solvent–electrolyte couple, the addition of pyrrole to the medium makes no significant difference.

In the case of thiophene, different behavior was observed. A voltammogram of thiophene in the presence of MM reveals no redox peak, not even the standard peak due to the growth of pure polythiophene. At the beginning, for a few runs, the peak increases after which it stops growing and the peak height reduces thereon. This may indicate the formation of soluble oligomers, which leave the electrode surface after a certain chain length. The presence of MM in the electrolysis medium prevents the growth of polythiophene chains (Figs. 2(a) and 2(b)).

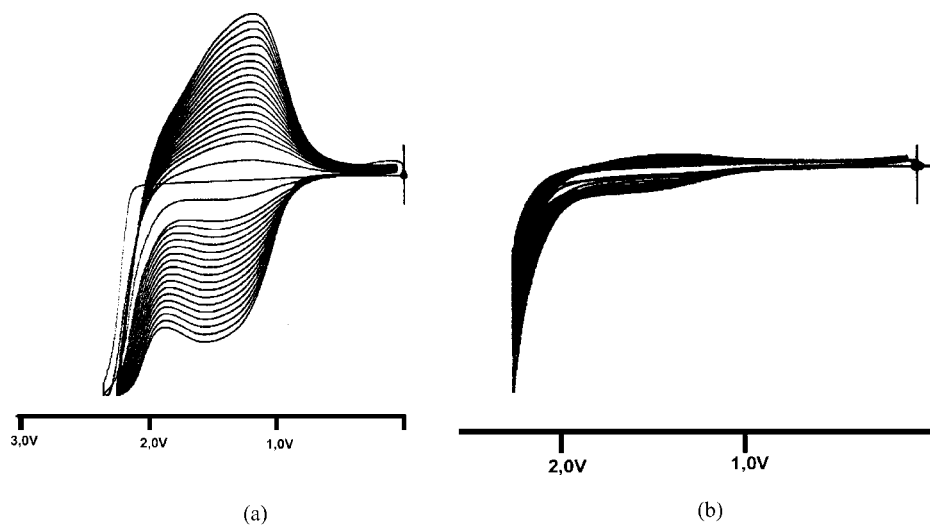
### Characterization

Homo-polymerization of MM, by constant potential electrolysis, cannot be achieved for any system tried. Chemical polymerization and constant current electrolysis were also used for homo-polymerization of MM and these methods turned out to be successful.



**Figure 1.** Cyclic voltammograms of (a) MM; (b) polypyrrole; (c) polypyrrole in the presence of MM.

With regards copolymerization of MM, experiments with pyrrole were successful as revealed by electrode coatings except the one where MM is directly introduced to the electrolysis solution. No product was obtained for all the reactions carried out with thiophene.



**Figure 2.** Cyclic voltammogram of (a) polythiophene; (b) polythiophene in the presence of MM.

### <sup>1</sup>H-NMR

<sup>1</sup>H-NMR spectrum of the monomer was taken by using a Bruker 250 MHz spectrometer with CDCl<sub>3</sub> as solvent and tetramethylsilane as the internal standard. <sup>1</sup>H-NMR data for the monomer: <sup>1</sup>H-NMR ( $\delta$ , ppm): 7.29–7.02 (m, 3H), from 3-thienyl ring 3.96 (s, 1H), COO-CH- in menthyl, 3.77 (s, 2H), Th-CH<sub>2</sub>-COO-, 1.08–1.89 (m, 18H), menthyl. (Fig. 3)

### FTIR

IR spectrum was recorded on a Nicolet 510 FTIR spectrometer. For MM, C-H <sub>$\alpha$</sub>  stretching modes which arises from thienylene are observed at 3108 cm<sup>-1</sup> and 757 cm<sup>-1</sup>. A product of chemical polymerization, CN, shows carbonyl group and C-O-C which<sup>[13]</sup> are also observed for the monomer. These bands are at 1733 cm<sup>-1</sup> and 1063 cm<sup>-1</sup>, respectively. Other peaks which belong to MM are 2944, 2863, 1456, 1390, 833 cm<sup>-1</sup>. After chemical polymerization, a peak at 757 cm<sup>-1</sup>, indicating C-H <sub>$\alpha$</sub>  stretching, disappears completely, whereas absorption peak at 840 cm<sup>-1</sup> (C-H <sub>$\beta$</sub>  vibration mode) was observed.

Another difference between CN and MM spectra arises from the absorption peak at 1646 cm<sup>-1</sup> which is observed for CN spectrum indicating the conjugation.

Copolymers, which are synthesized via electrochemical polymerization, were also analyzed. PM-1 and PM-2 systems contain an absorption band at 1730 cm<sup>-1</sup>. This carbonyl band reveals that copolymerization takes place between the two components.

In the case of GDM, a peak showing the presence of carbonyl group and the presence of conjugation at around 1730 and 1656 cm<sup>-1</sup>, respectively, indicate that polymerization does occur.

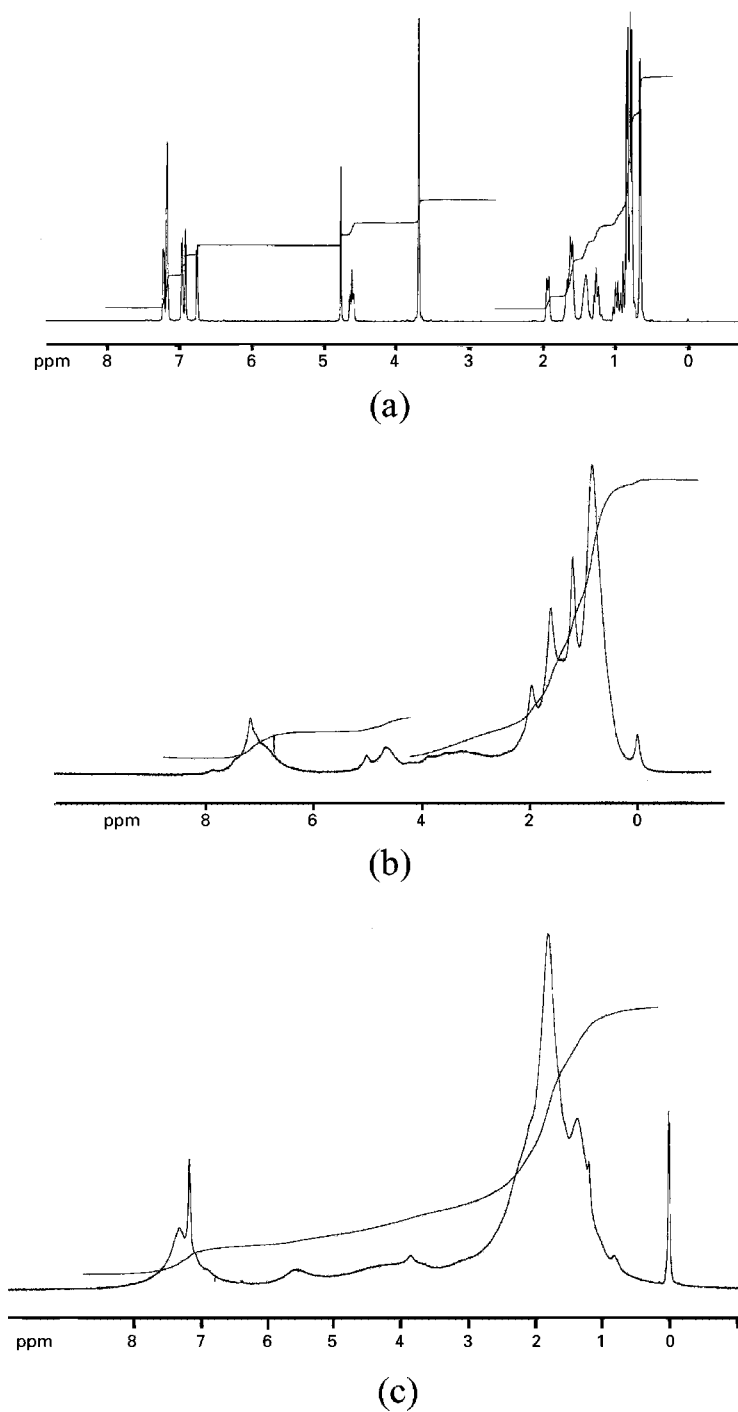
Also for CNPP, CNPS and PGDM, FTIR spectrum contains peaks indicating the presence of a carbonyl group, which is a proof of copolymerization.

### Thermal Analysis

Dupont 2000 Thermal Gravimetry Analyzer and Differential Scanning Calorimetry were used to obtain thermal behavior of polymers and copolymers synthesized. TGA showed weight losses for MM and CN at 265°C and 196°C, respectively (Fig. 4(a)). No residue was observed for MM, whereas it was 16.2% for CN.

Copolymers synthesized with MM in the presence of pyrrole (PM-1 and PM-2) show four transitions. For PM-1, obtained by using PTSA as the supporting electrolyte, these transitions are at 85°C, 240°C, 353°C, and 480°C. 85°C and 353°C are the temperatures for the removal of water and the dopant ion, respectively. For PM-2, transitions at 80°C, 129°C, 254°C, and 512°C are observed (Figs. 4(b) and 4(c)). Similarly, removal of water and dopant ion is observed at 80°C and 254°C. There is a difference in the point of decomposition temperature, which is 480°C for PM-1 and 512°C for PM-2, indicating that thermal stability of the latter is a bit better.

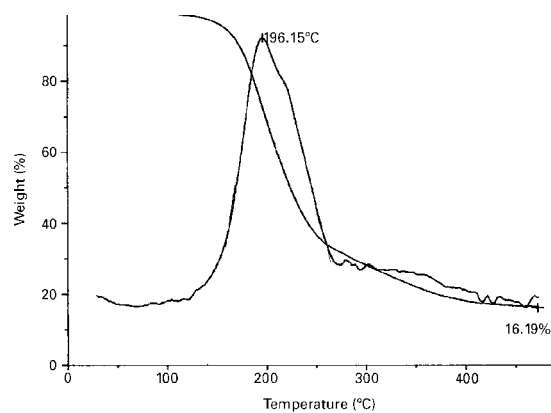




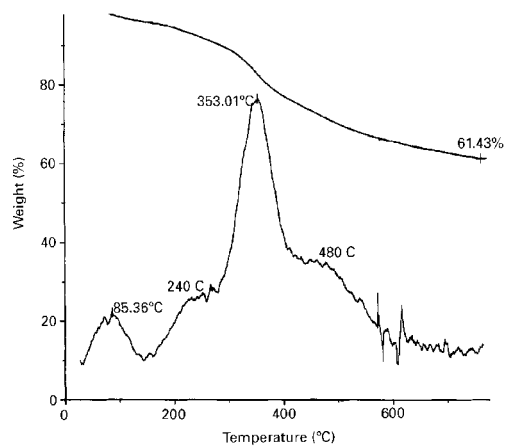
**Figure 3.** NMR spectra for (a) MM; (b) CN; and (c) GDM.

## Copolymers of Menthyl Ester

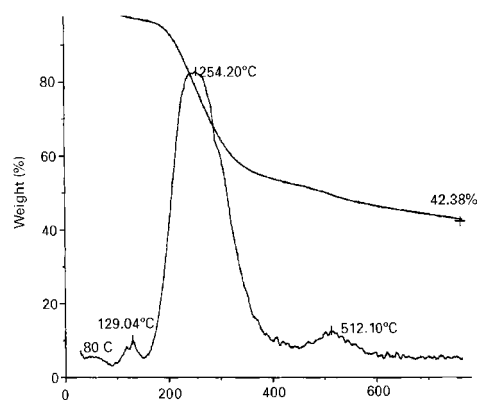
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(a)



(b)



(c)

**Figure 4.** TGA thermograms for (a) CN; (b) PM-1; (c) PM-2.

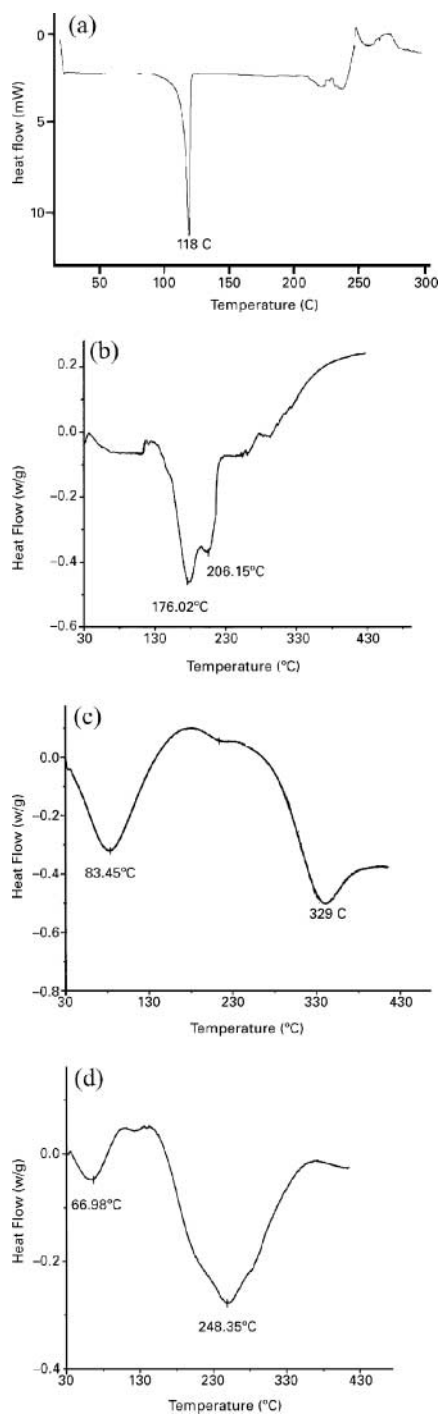


Figure 5. DSC thermograms for (a) MM; (b) CN; (c) PM-1; (d) PM-2.

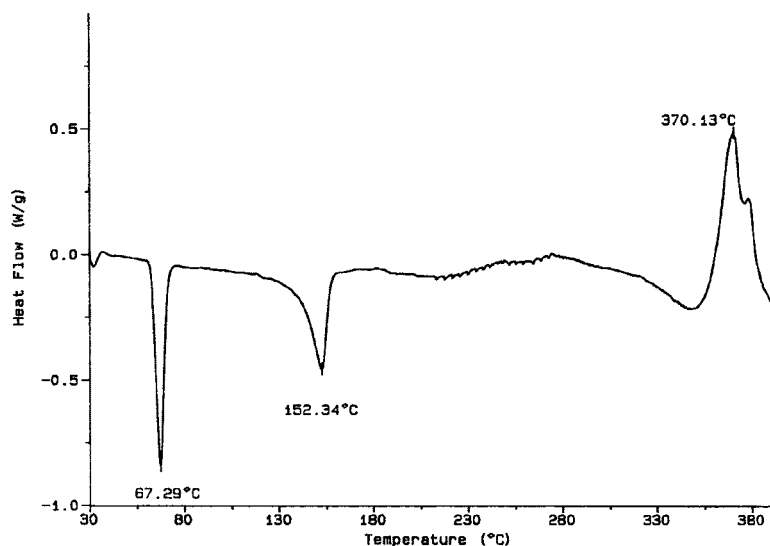


Figure 6. DSC thermogram for GDM.

A high percentage of pyrrole in the CNPP and CNPS gives rise to weight loss behavior similar to that of pristine polypyrrole.

A DSC thermogram for monomer shows a sharp melting point at 118°C (Fig. 5(a)). For CN, two transitions are observed at 176°C and 206°C (Fig. 5(b)), which are due to the decomposition of the sample. Copolymers of PM-1 and PM-2 both yield two transitions at 83°C, 329°C, and 66°C, 248°C, respectively (Figs. 5(c) and 5(d)). The same behavior was also observed for CNPP and CNPS.

Transitions about 330°C and 250°C are due to the removal of dopant ions, PTSA and SDS.

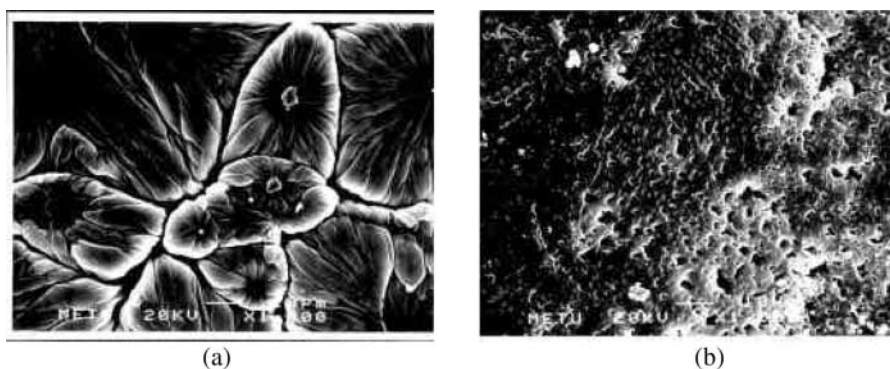
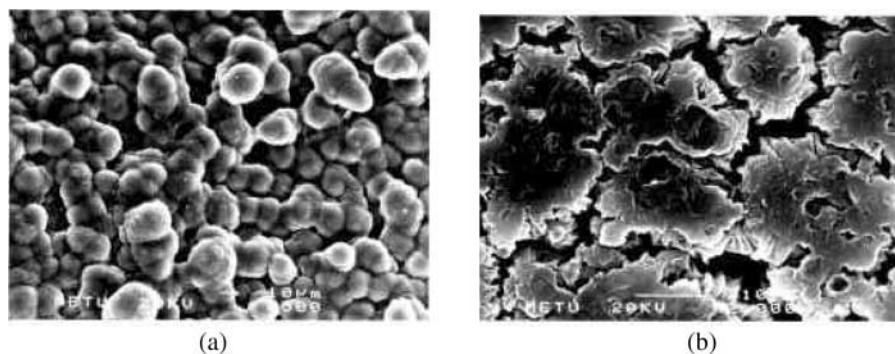


Figure 7. SEM micrographs of (a) PM-1; (b) PM-2.



**Figure 8.** SEM micrographs of (a) solution side; (b) electrode side of CNPS.

The product of galvanostatic polymerization shows a sharp transition at 152°C (Fig. 6). Copolymer of GDM/pyrrole shows similar behavior with the copolymers of MM and CN.

### Scanning Electron Microscope Analysis

Analysis of morphologies of films was done by using JEOL JSM-6400 Scanning Electron Microscope. Copolymers of MM with Py, i.e., PM-1 and PM-2, exhibit different morphologies than that of pure polypyrrole, which has a smooth surface on the electrode side and standard cauliflower structure on the solution side. For both copolymers, the solution side has the standard cauliflower structure, but the electrode sides are interesting. For PM-1, the electrode side contains regular islands, whereas PM-2 has rather a smoother surface (Fig. 7).

In the case of CNPP, the solution side has the standard cauliflower structure. For unwashed films, the electrode sides are smooth due to the CN layer that did not react with pyrrole, but when films are washed (with the solvent of MM) regular islands are observed

**Table 1.** Conductivities of polymers of menthyl monomer.

	Electrode side (S/cm)	Solution side (S/cm)
CN <sup>a</sup>	$3.7 \times 10^{-3}$	$3.7 \times 10^{-3}$
PM-1	3.4	3.2
PM-2	4.1	4.0
CNPP	0.7	0.2
CNPS	0.8	0.6

<sup>a</sup> Pellet.

indicating the removal of CN. The solution side of CNPS is totally different from the others and contains granules. Also, the electrode side presents a different picture where there exists separated irregular islands (Fig. 8).

### Conductivity Measurements

A standard four-probe technique was used for conductivity measurements. Conductivities were in the range of 0–4 S/cm and no significant difference was observed between the electrode and solution sides of the films. There is no order of magnitude difference between the electrolytic films in Table 1, although PM-2, which is doped, with SDS exhibits the best conductivity.

### CONCLUSION

Chemical polymerization and constant current electrolysis were performed to obtain polymers of menthyl monomer. MM and these polymers were used to synthesize copolymers with pyrrole. In terms of surface morphology, water/PTSA solvent/electrolyte couple is the most interesting medium for copolymerization. In terms of conductivity, the best films were obtained in water/SDS medium. Hence, copolymers of MM are prepared with an appreciable conductivity.

### ACKNOWLEDGMENTS

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