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Synthesis and Characterization of Conducting Copolymers of Bisphenol A-Diglycidyl Ether with Thiophene Side-Groups and Pyrrole

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Copolymers of bisphenol A-diglycidyl ether with thiophene side-groups and pyrrole were synthesized by electrochemical polymerization. Bisphenol A-diglycidyl ether with thiophene side-groups (DGEBATh) was obtained from the reaction between bisphenol A-diglycidyl ether (DGEBA) and thiophene-3-acetic acid. The syntheses of copolymers of DGEBATh and pyrrole were achieved electrochemically using three different supporting electrolytes, *p*-toluene sulfonic acid (PTSA), sodium dodecyl sulfate (SDS) and tetrabutylammonium tetrafluoroborate (TBAFB). Characterizations of DGEBATh and copolymers were performed by combination of techniques including cyclic voltammetry, scanning electron microscopy, gel permeation chromatography, differential scanning calorimetry, ^{1}H-NMR and FT-IR. The conductivities were measured by the four-probe technique.

Keywords: Conducting copolymers, bisphenol A, thiophene, pyrrole, electrochemical polymerization

1 Introduction

In recent years, several studies have been reported on conducting polymers in the literature. These studies deal with the improvement of physical and mechanical properties as well as development of the electrical and optical properties of conducting polymers (1). Chemically or electrochemically synthesized polyheterocyclic polymers such as polypyrrole, polythiophene and polyaniline have important potential and practical applications (2). Some of these are non-linear optical devices (3), polymer light emitting diodes (4), gas sensors (5), organic transistors (6) and electrochromic devices (7–9).

Epoxy resins are known as thermosetting polymers for many decades. In fact, their applications range from laminated circuit boards, carbon fiber composites, electronic component encapsulations and adhesives (10,11). At the present, almost 90% of the world production of epoxy resins is based on the reaction between bisphenol A (2,2-bis(4′-hydroxyphenyl) propane and epichlorohydrin (12, 13). The resulting glycidyl terminated monomers can contain one or more bisphenol A groups, depending on the desired applications (14).

In this paper, bisphenol A-diglycidyl ether with a thiophene side-group (DGEBATh) was synthesized from bisphenol A-diglycidyl ether and thiophene-3-acetic acid. In addition, copolymers of DGEBATh and polypyrrole were synthesized by chemical and electrochemical methods using three different supporting electrolytes.

2 Experimental

2.1 Materials

Bisphenol A-diglycidyl ether (DGEBA), sodium dodecylsulphate (SDS), pyrrole, thiophene, tetrabutylammonium tetrafluoroborate (TBAFB), p-toluenesulfonic acid and N,N-dimethylformamide were purchased from Aldrich Chemical Co., Inc. (Milwaukee) and used without further purification. Thiophene-3-acetic acid (Fluka, ≥ 98 %), acetone, methanol, tetrahydrofuran, acetonitrile were purchased from Merck Co. (Darmstadt, Germany), Tetrahydrofuran (THF) was used as the eluent and polystyrene as the GPC standard.

2.2 Instruments

Electrolyses were carried out with a Wenking POS 2 potentiostat. ^{1}H-NMR spectra were recorded on a Bruker

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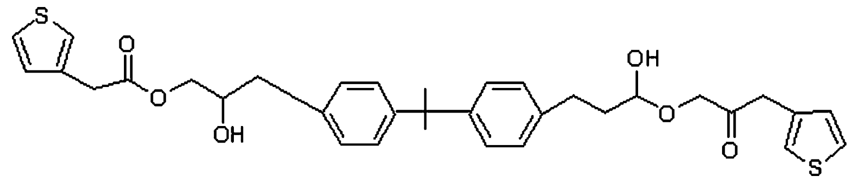
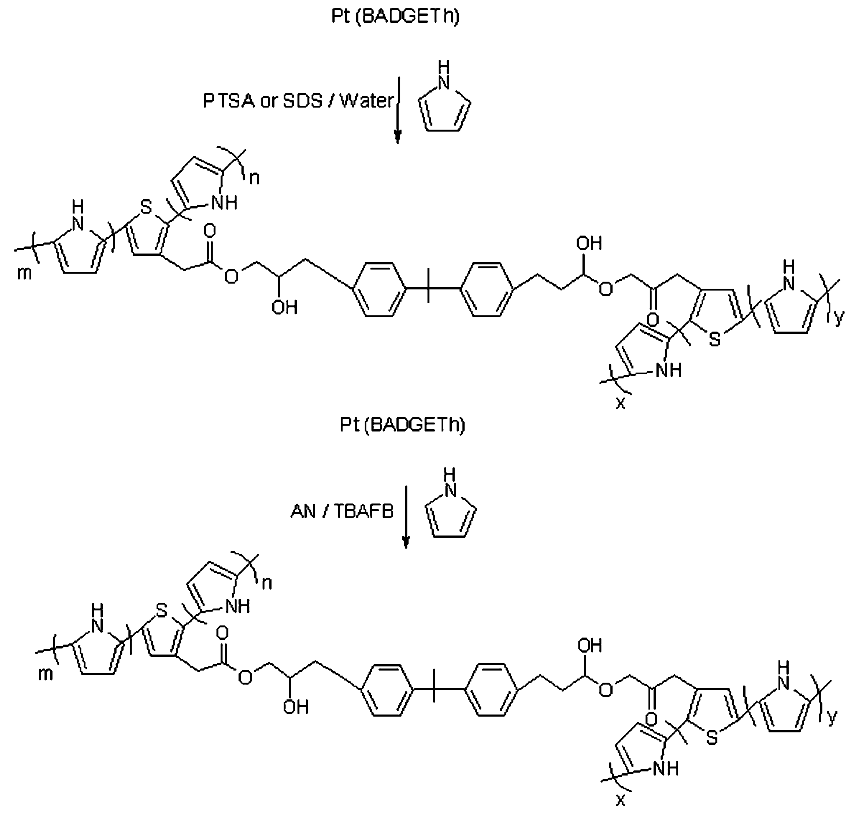


Sch. 1. Thiophene ended bisphenol A-diglycidyl ether.



Sch. 2. Synthesis of copolymers via electrochemical polymerization.

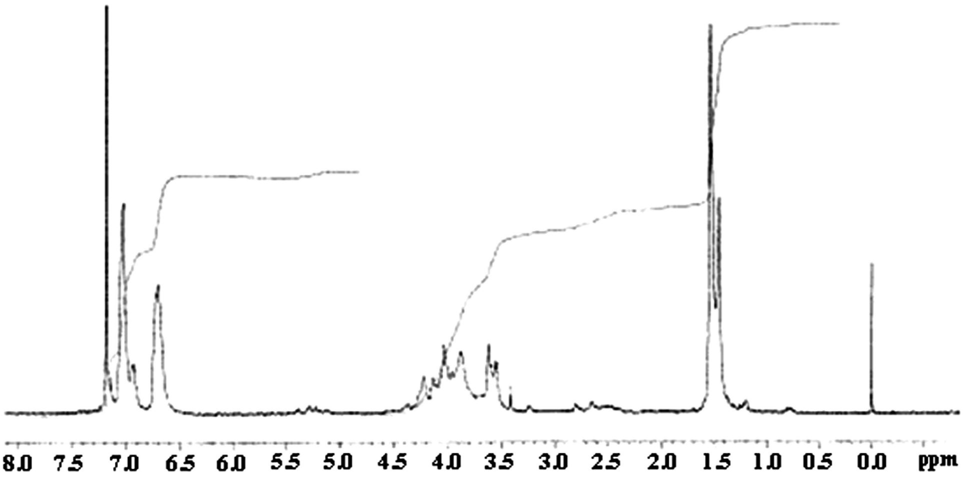


Fig. 1. ^{1}H-NMR spectrum of DGEBATh.

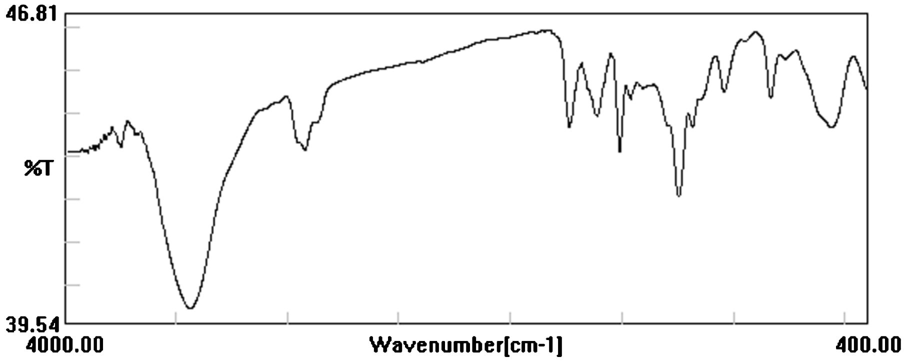


Fig. 2. FT-IR spectrum of DGEBATh.

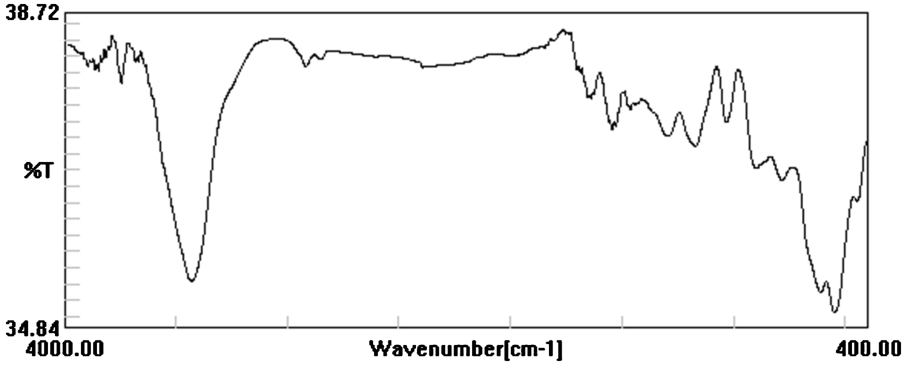


Fig. 3. FT-IR spectrum of DGEBATh/PPy.

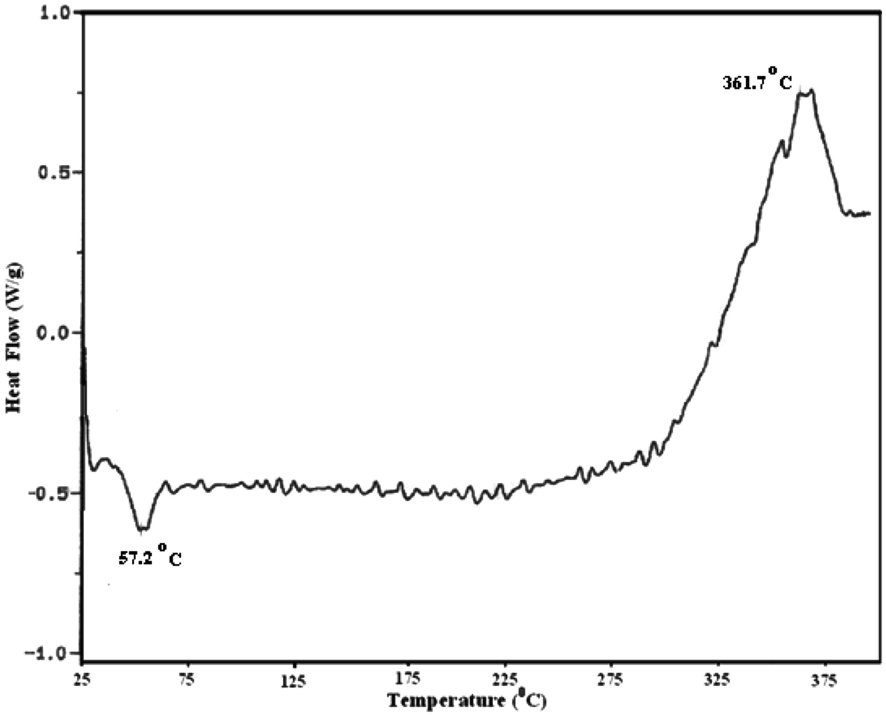


Fig. 4(a). DSC of DGEBATh.

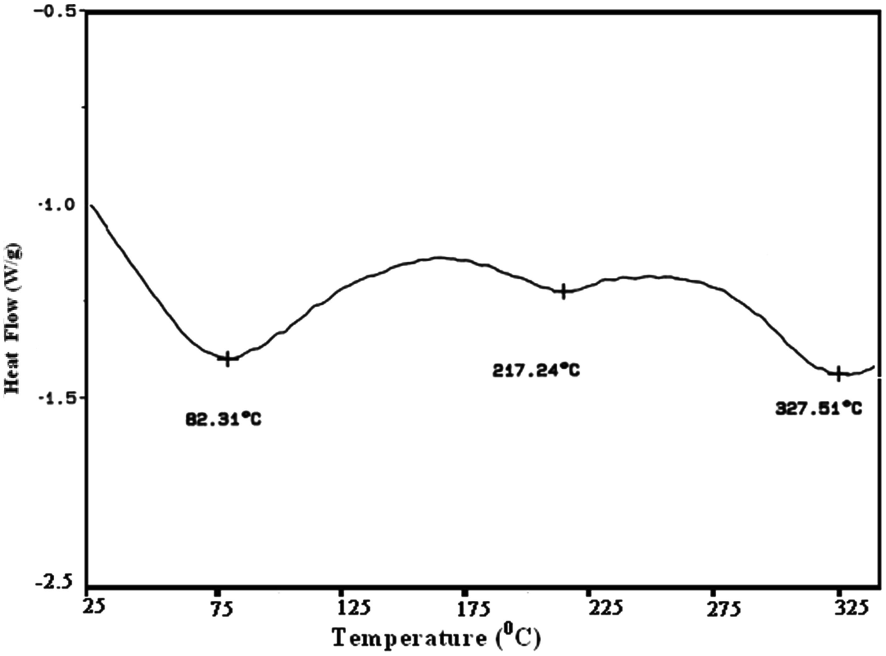


Fig. 4(b). DSC of PTSA doped DGEBATh/PPy.

400 MHz spectrometer with dimethylsulfoxide (DMSO)-*d*6 as the solvent and tetramethylsilane as the internal standard. FTIR spectra were recorded on a JASCO FT/IR-300E spectrophotometer. Gel permeation chromatography (GPC) analysis was carried out by using a Perkin-Elmer Series 200 apparatus with a refractive index (RI) detector under the following conditions: TSK gel AM GPC Gel column and N,N-dimethylformamide eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using polystyrene standards. The conductivity of the copolymers was measured by the four-probe technique. The thermal behaviors of the samples were investigated by a differential scanning calorimeter, under nitrogen atmosphere, with a scan rate of 10°C min^{-1}. The morphology of the copolymer films was investigated by scanning electron microscopy (SEM) studies (Leon 440). CV studies were carried out with CH Instruments CHI 600 model electrochemical analyzer.

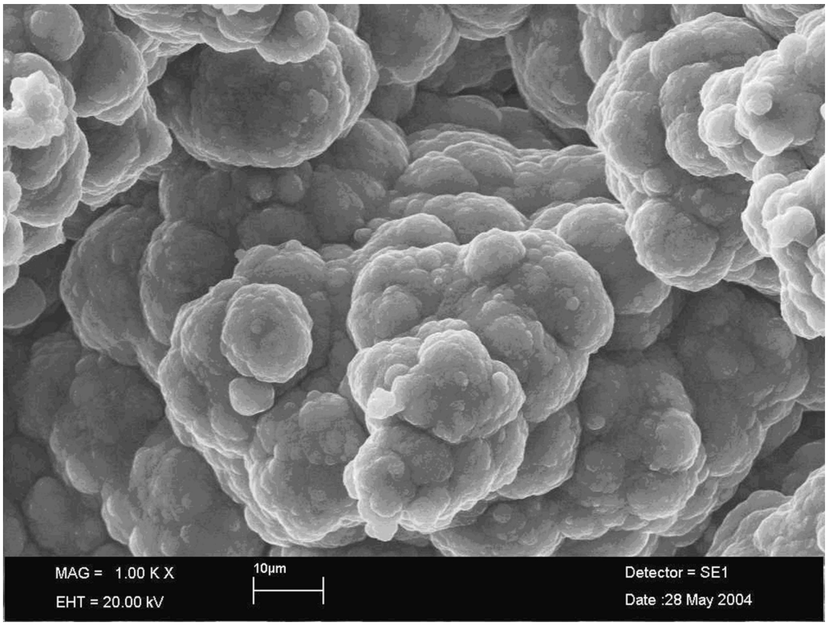


Fig. 5. SEM of polypyrrole.

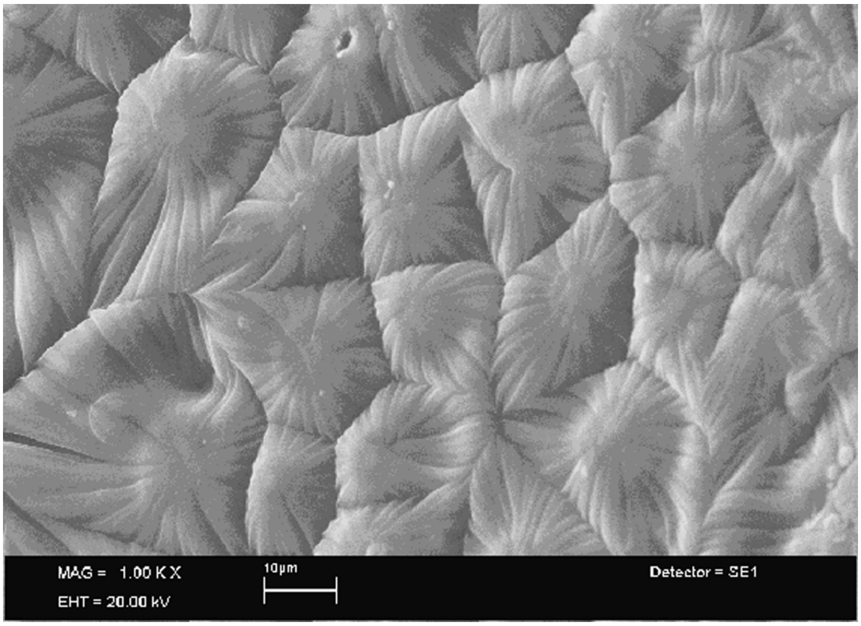


Fig. 6. SEM of PTSA doped DGEBATh /PPy.

2.3 Synthesis of DGEBA Containing Thiophene Side-Groups (DGEBATh)

Bisphenol A-diglycidyl ether (1 g) was dissolved in 15 mL acetone in 50 mL flask. Thiophene-3-acetic acid (0.5 g) was introduced into the flask combined with a magnetic stirrer and a condenser. The mixture was heated at 60°C for 24 h. The reaction mixture was heated for 20 h. The hot solution was poured into a large amount of methanol. This procedure was repeated several times. The monomer was dried under vacuum (Scheme 1).

2.4 Synthesis of Copolymers with Pyrrole by Electrochemical Polymerization

DGEBATh/Py copolymers were prepared by electrochemical polymerization of pyrrole on DGEBATh-coated electrodes in distilled water/PTSA, water/SDS, and acetonitrile/TBAFB media containing 0.05 M pyrrole at the oxidation potential of pyrrole (1.0V vs. Ag/Ag+ reference electrode). The electrolyses were continued until films with sufficient thickness (ca 50 μm) were obtained. Anode was removed from the cell and left in dichloromethane for

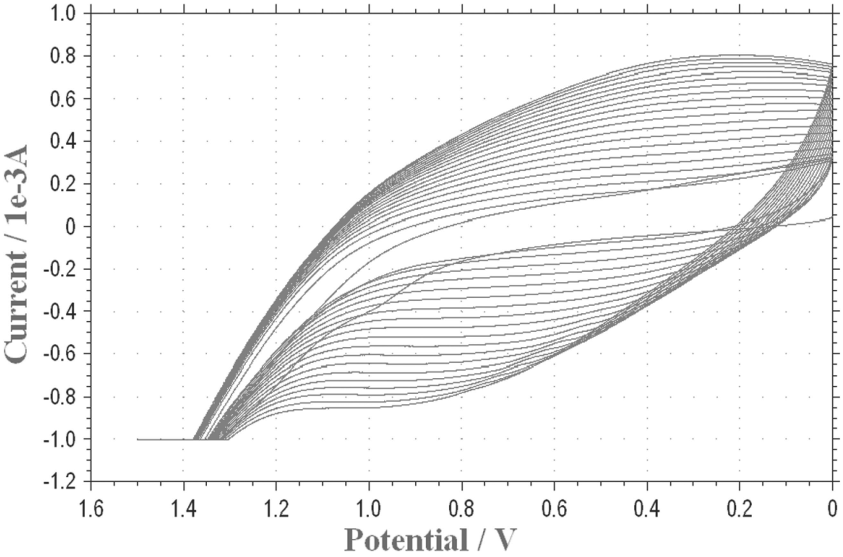


Fig. 7. Cyclic voltammogram of pure polypyrrole.

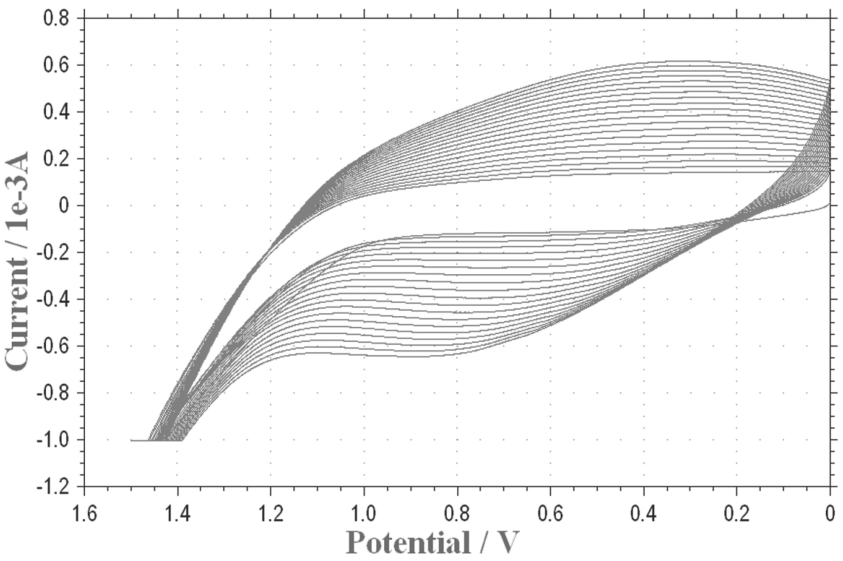


Fig. 8. Cyclic voltammogram of DGEBATh /PPy.

several hours to remove the ungrafted precursor polymer (Scheme 2).

3 Results and Discussion

3.1 ^{1}H-NMR Spectrometry

^{1}H-NMR spectrum of DGEBATh was taken on a Bruker-Instrument-NMR Spectrometer (DPX-400) with dimethylsulfoxide (DMSO)-*d*6 as the solvent and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard. The DGEBATh presented ^{1}H-NMR peaks at 1.3–1.67 ppm (doublet of CH_3), 2.6 ppm (OH protons), 3.42–4.49 (CH_2 protons in DGEBATh chain), 3.6 ppm (multiple CH protons), 6.7 ppm (CH protons of thiophene) and 7.02 ppm (CH protons of benzene ring) (Fig. 1).

3.2 FTIR Spectrometry

The FTIR spectrum of DGEBATh (Fig. 2) presents the usual OH absorption peak at 3440 cm^{-1} (OH stretching), aromatic and aliphatic CH peaks are between 3100 and 2867cm^{-1} (CH stretching), 1742 cm^{-1} (CO carbonyl), typical aromatic ring absorbance peaks are between 1650 and 1472 cm^{-1}. Characteristic peaks at 1370 cm^{-1}and at 1250 cm^{-1} belong to CH_3 and C-S single bond respectively. Typical absorptions for thiophene ring are at 3100, 842, 780 cm^{-1} and 1046 cm^{-1} stands for C-O single bond.

Table 1. Conductivity of copolymers of DGEBATh

Polymer	*Conductivity (S/cm)*
PPy	4.1
DGEBATh/PPy (PTSA)	3.0
DGEBATh/PPy (TBAFB)	17.3
DGEBATh/PPy (SDS)	9.6

FTIR spectrum of electrochemically synthesized BADGETh/PPy/PTSA (Fig. 3) shows peaks at 1555, 1470, 1315, 1180 cm^{-1} due to C–N and C–C stretchings which are characteristic for polypyrrole (PPy). A characteristic peak at 1742 cm^{-1} belonging to carbonyl group of DGEBATh was also observed. These results indicate that the polymerization of pyrrole occurred through the DGEBATh chain. N-H streching of pyrrole ring at 3430 cm^{-1} proves the presence of pyrrole on the polymer chain.

3.3 Gel Permeation Chromatography (GPC)

The yield and molecular weight of the polymer were evaluated by GPC. N,N-dimethylformamide was used as the eluent and polystyrene as the standard. Weight-average molecular weight of DGEBATh /PPy is 30800, number-average molecular weight is 29200 and polydispersity index PDI is 1.05.

3.4 Conductivity Measurements

Compact thin pellets of the copolymers doped with PTSA, TBAFB or SDS were prepared under 8–10 tons/cm^2 for the measurement of electrical conductivities. A typical sample with 13 mm in diameter and 0.5 mm thickness was prepared. Conductivity measurements of copolymers doped with PTSA, TBAFB or SDS were performed by four probe technique and calculated from the following equation: $\sigma = V^{-1} I (\ln 2/\pi dn)$ where V is the potential in volts, I is the current in amperes, and dn is the thickness of the samples in centimeters. Conductivities of the copolymers doped with PTSA, TBAFB or SDS were in the range 3.0–17.3 S/cm (Table 1).

3.5 DSC Analysis

DSC thermograms were examined in the range between 25 and 450°C at a heating rate of 10°C/min. Figure 4(a) DSC of DGEBATh shows one endothermic and one exothermic peak. Endothermic peak at 57.20°C is due to the removal of the solvent and exothermic peak is referred to the decomposition of DGEBATh at 361.70°C.

DSC thermograph of PTSA doped DGEBATh/PPy (Figure 4(b)) shows three endotherms. The first peak at 82.31°C is due to the removal of the solvent, the second one is due to the loss of PTSA ions at 217.24°C, and the last one is referred to the decomposition of DGEBATh /PPy at 327.51°C.

3.6 SEM Analysis

The surface morphology of electrochemically synthesized PTSA doped DGEBATh/PPy copolymer was investigated by Scanning Electron Microscope. Surface morphologies of the PTSA doped DGEBATh /PPy copolymer was different than the cauliflower morphology of polypyrrole (Figures 5–6).

3.7 Cyclic Voltammetry (CV) Measurements

The oxidation/reduction behavior of the polypyrrole (Fig. 7) and DGEBATh/PPy (Fig. 8) were investigated by CV. The system consists of a potentiostat and a CV cell containing platinum foil working and counter electrodes and a Ag/Ag$^+$ reference electrode. Cyclic voltammograms of polypyrrole and DGEBATh/PPy in TBAFB/acetonitrile solvent/electrolyte couple are clearly different from each other.

4 Conclusions

The syntheses of copolymers of DGEBATh and polypyrrole by chemical and electrochemical methods using three different supporting electrolytes were successfully achieved. Characterization studies were performed by using spectral techniques such as ^{1}H NMR, FTIR, GPC, DSC, SEM and CV. The conductivities were measured by the four-probe technique. Weight-average molecular weight of DGEBATh /PPy is 30800, number-average molecular weight is 29200 and polydispersity index PDI is 1.05. Conductivity measurements of the copolymers doped with PTSA, TBAFB or SDS were in the range 3.0–17.3 S/cm while the pure polypyrrole was 4.0 S/cm. Scanning electron micrographs of the PTSA doped DGEBATh /PPy copolymer was clearly different from that of polypyrrole. Cyclic voltammogram of polypyrrole was different than DGEBATh/PPy in TBAFB/acetonitrile solvent/electrolyte couple. According to results, copolymers doped with PTSA, TBAFB or SDS were successfully achieved.

Acknowledgements

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