Conducting Copolymers of Thiophene-Functionalized Polystyrene

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The syntheses of conducting copolymers of thiophene-functionalized polystyrene and pyrrole (PS/PPy) were achieved using p-toluene sulfonic acid (PTSA) as the supporting electrolyte via constant potential electrolysis technique. Characterization of the samples was performed by a combination of techniques: cyclic voltammetry (CV), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), NMR, and FT-IR analyses. The conductivities were measured by the four-probe technique.

INTRODUCTION

The development of controlled radical polymerization in the scientific area opened the way to design many materials with new and different potential applications that can be prepared only by these methods. The control of soft materials on the nanometer size scale is becoming an increasingly important aspect of polymer science as more research is directed toward the study of nanoscopic structures and materials. The preparation of well-defined nanostructures requires

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molecular building blocks of well-defined structure; new synthetic methods for introducing functional groups at specific loci at either chain ends or along the backbone are emerging as powerful tools for construction of these architectures[1]. Considerable effort has recently been devoted to the development of viable ''living'' free radical procedures for the synthesis of well-defined polymers with controlled incorporation of functional groups.

The use of functionalized initiators yields polymer chains with a wide variety of functional groups using any of the three standard methods for ''living'' free radical polymerization: nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and radical addition fragmentation transfer polymerization (RAFT)[2]. Since the main advantage of the nitroxide-mediated system is the absence of any metal, the goal of the present approach is to synthesize and characterize a new thiophene-containing stable nitroxide initiator and use it to obtain a well-defined functionalized polystyrene.

Conducting polymers can be synthesized by either chemical or electrochemical polymerization methods. Electropolymerization has several advantages, such as simplicity, reproducibility, and thickness control[3–5]. Electrochemical initiation of polymerization reactions has been applied to the synthesis of a wide range of polymer types[6–7]. However, some difficulties appear in processing conducting polymers since they have poor mechanical and physical properties[8–11]. In order to prepare useful materials from conducting polymers, there is a need for good mechanical properties and environmental stability as well as conductivity. An obvious way to produce these polymers in a tough, processable, stable form is to make composites with stable, passive polymers. In principle, this can be achieved by block or graft copolymerization, through synthesis of the conducting polymer within the host, or by simple blending[12]. Alternatively, polymers with functional groups within or at the end of the chain can be used for the synthesis of copolymers.

Polypyrrole is one of the well-known conjugated heterocyclic polymers having high electrical conductivity and stability[13]. The electrochemical polymerization of pyrrole is usually done by electrochemical oxidation of pyrrole on a Pt electrode that is already coated with insulating polymers[14–15]. The main purpose is to obtain homogeneous composites that retain the characteristics of both polymers, at least to a certain extent.

In this study, thienyl containing TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) initiated polystyrenes were synthesized. Mn: 11.500 and 22.400 are denoted PS1 and PS2. Graft copolymers of these functionalized polystyrenes and polypyrrole were synthesized by electrochemical methods.

EXPERIMENTAL

Materials

3-Thiophene acetic acid, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO), benzoyl peroxide (BPO), and dichloro-methane (CH$_2$Cl$_2$) (all Aldrich) were used without further purification. Thionyl chloride (Fluka) and styrene (St) were distilled just before use, pyrrole (Py) was distilled before use and stored at 4°C, and p-toluene sulfonic acid (PTSA) was used as received. All solvents were purified and dried by standard techniques before use.

Preparation of the Intermediate and Initiator

3-Thiophene Acetic Acid Chloride

The acid chloride of 3-thiophene acetic acid was prepared as previously reported[16]. ^{1}H-NMR results are (δ, ppm from trimethyl silyl (TMS) in CDCl$_3$): 7.33–7.31, 7.24–7.16, 7.01–6.99 (2 m, 1d, 3H from thiophene ring); 4.16 (s, 2H, −CH$_2$).

4-Thienylacetyl-oxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (thi-TEMPO)

A solution of 6.98 mmol of 3-thiophene acetic acid chloride in 2 mL dry dichloromethane was added dropwise to a solution of 5.82 mmol 4-hydroxy-TEMPO (4-HTEMPO) in 10 mL of dry dichloromethane containing 0.97 mL triethylamine (TEA) (6.98 mmol), with stirring and under cooling with ice. The esterification reaction was performed under nitrogen atmosphere. The progress of the reaction was checked by thin-layer chromatography. Upon completion of the reaction, the chloro hydrate of TEA was removed by filtration and the solution was washed three times with acidified water (1%) and then with distilled water (four times). The organic layer was dried on magnesium sulfate and then the solvent was removed by a rotaevaporator. Onto the crude thi-TEMPO methanol was added, and the black precipitated solid was filtered. The solution was evaporated and the pure product thi-TEMPO resulted as a brown-red syrup with 65% yield.

Infra-red (IR) results , cm^{-1}: 3100 (HC=CH in thiophene); 2990, 2900, 2750 (CH$_3$−, −CH$_2$−, −CH−); 1730, 1260, 1220 (ester); 1520, 760 (thiophene ring); 1380 (TEMPO moiety).

The representation of the synthesis of thi-TEMPO is presented in Scheme 1.
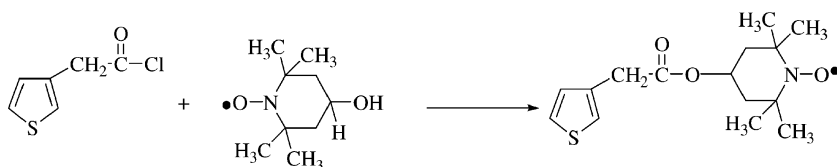
SCHEME 1 Synthesis of the thi-TEMPO initiator.

General Procedure for the Synthesis of Thiophene-Functionalized Polystyrene Prepolymers

The thienyl-containing polystyrene samples PS1 and PS2 were prepared in bulk and in solution respectively under stable free radical polymerization (SFRP) conditions using a bimolecular initiator system consisting of a mixture of BPO and thi-TEMPO. In both experiments a preheating at 95°C for 3.5 h was performed to allow BPO to decompose completely. The polymerizations were conducted at 125°C for a given time, shown as in Table I. Then the mixtures were cooled and the resulting products were purified by double precipitation in methanol. In the case of PS1 the reaction mixture was solidified. The reaction flask was cooled with liquid nitrogen, and the resultant material was dissolved in dichloromethane and purified bythe above-mentioned procedure. The reaction conditions and some characteristics of the resulting polymers are presented in Table I.

TABLE I Preparation of thienyl-containing polystyrene by using thi-TEMPO

Sample	Molar ratio of components in the reaction mixture [M]:[BPO] : [thi-TEMPO]	Reaction conditions	$M_{n,GPC}$	PD	$M_{n,NMR}$[a]
PS1	200 : 1 : 1.32	bulk, 125°C, t = 69 h	22416	1.6	Not determined
PS2	100 : 1 : 2	Xylene, 125°C, t = 24 h	11513	1.35	11336

[a]Molecular weight calculated from the integrals ratio of the peaks in the 1–2 ppm range (attributed to three protons of styrene in the main chain) and that of the peaks at 3.74 ppm belonging to two protons in thiophene moiety.

Synthesis of Conducting Graft Copolymers of PS1 and PS2

Graft copolymer films of both PS1 and PS2 with polypyrrole were synthesized in water-PTSA (para-toluene sulfonic acid) solvent-electrolyte couple in an H-shaped electrolysis cell with constant potential electrolysis technique. A Wenking POS 73 Potentiostat was used to supply the constant potential for the syntheses.

Graft copolymers were prepared by the electrochemical polymerization of pyrrole onto PS1 and PS2 precoated electrodes. The electrolyses were carried out in the presence of 0.02 M pyrrole and 0.05 M PTSA at the oxidation potential of pyrrole (1.1 V) versus Ag/Ag^+ reference electrode. Polymerization reactions lasted for 45 min for both polymer syntheses.

Finally, the films were peeled off the electrode surface and washed with electrolysis medium (water). Then, the films were immersed in the solvent of PS1 and PS2 (dichloromethane) for several hours in order to remove unreacted polymers. The representation of the synthesis is shown in Scheme 2.

Measurements

^{1}H-NMR (nuclear magnetic resonance) spectra were recorded on a Bruker 250 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer using cast films (CH_2Cl_2) on NaCl pellets. Gel permeation chromatography (GPC) analyses were performed with a setup consisting of an Agilent1100 RI apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with tetrahydrofuran (THF) as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights were calculated with the aid of polystyrene standards.

RESULTS AND DISCUSSION

Synthesis of Thienyl Containing Stable Radical (Thi-TEMPO)

4-Hydroxy-TEMPO (HO-TEMPO) was used as the transforming agent from living anionic and cationic polymerization to living radical polymerization[17–18] or in the production of polymeric counter radicals via polymer-analogy reaction on the N-substituted maleimide-methyl vinylisocyanate copolymer[19]. In the present approach, starting from HO-TEMPO and thiophene acetic acid chloride, a new stable

nitroxide was prepared by a classical Schotten-Bauman condensation
(Scheme 1). The structure was confirmed by both IR and ^{1}H-NMR
spectroscopy measurements.

^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectrum of thi-TEMPO in DMSO-d_6 is shown in
Figure 1. The signals at 0.92, 1.09, 1.41, and 1.75 ppm were assigned to
two types of methyl protons (axial and equatorial) and to axial and
equatorial methylene protons, respectively. For the methylene-type pro-
tons derived from thiophene acetic acid, a doublet at 3.6–3.74 ppm was
also observed. To the methyne proton of TEMPO moiety, the broad
multiplet between 5.0–5.85 ppm with a peak at 5.75 ppm was attributed to
the methine proton of TEMPO moiety and the multiplet between
6.85 ppm and 7.7 ppm corresponds to the three protons in thiophene
rings (Figure 1).
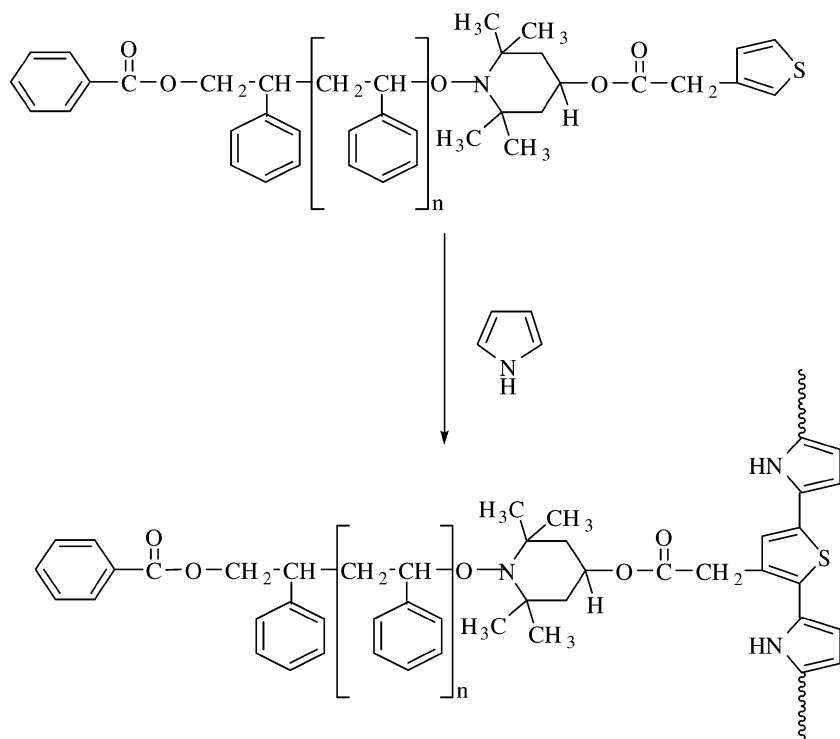
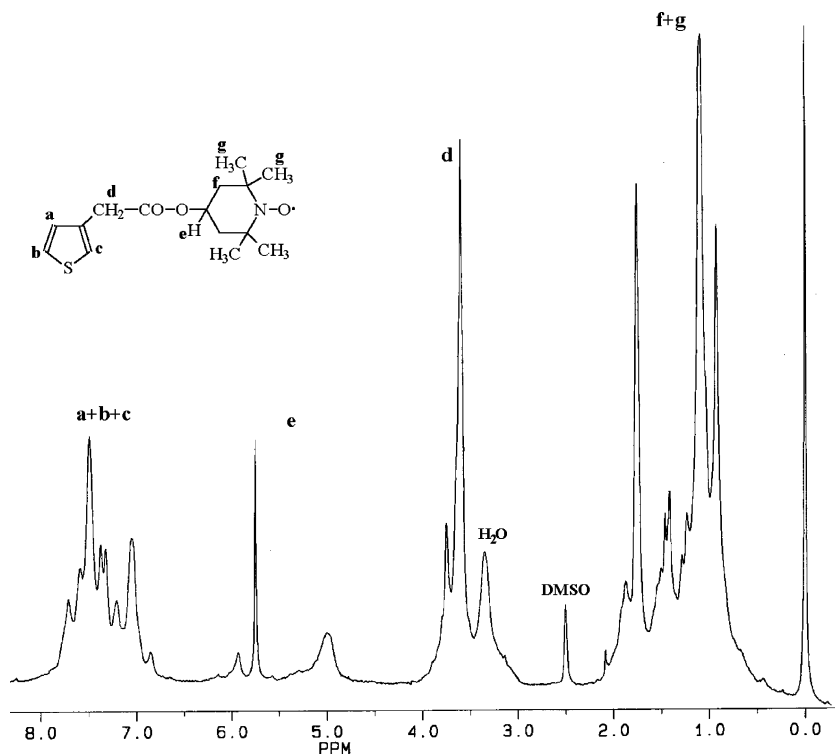SCHEME 2 Representation of the synthesis of conducting copolymers.

FIGURE 1 [^1]H-NMR spectrum of thi-TEMPO.

FT-IR Spectrophotometer

By comparing the IR spectra of HO-TEMPO and thi-TEMPO, the disappearance of the peaks at 3400 cm^{-1} and 1062 cm^{-1} characteristic of the hydroxyl group in the first reagent concomitantly with the appearance of the new ones at 1730 cm^{-1}, 1260 cm^{-1}, and 1220 cm^{-1} owing to the newly formed esteric linkage in the thi-TEMPO product were observed. The peaks at 3100 cm^{-1} (ν_{CH}), 1675 cm^{-1} ($\nu_{C=C}$), 1520 cm^{-1} (ν_{ring}), 832 and 760 cm^{-1} (ν_{C-H}) proved the presence of a thiophene ring in thi-TEMPO and at 1360 cm^{-1} the presence of the nitroxyl radical ring.

Synthesis and Structural Characterization of Thiophene-Capped Polystyrene and Conducting Copolymers

For the synthesis of thiophene-functionalized polystyrene, the thi-TEMPO was used in two attempts in bulk and solution, respectively. In

the case of bulk polymerization, the viscosity of the reaction mixture was increased and the mixture was eventually solidified. Even if the GPC trace of polymer PS1 was unimodal, the value of the polydispersity (1.6) was near to the theoretical limit that is characteristic of the "living-controlled" radical polymerization. In the second attempt, xylene as the solvent in a volume of twice the monomer weight (mL/g) was used. Taking into account that the high TEMPO/BPO ratio results in a decreased molecular weight accompanied by a narrow polydispersity[20], this ratio was increased in the solution polymerization. As seen in Table I, this parameter has an effect on both M_n and PD.

^{1}H-NMR Spectroscopy

^{1}H-NMR spectra of polystyrenes were taken using a Bruker-Instrument-NMR Spectrometer (DPX-400) with CDCl$_3$ as the solvent and tetramethlysilane as the internal standard.

In the ^{1}H-NMR spectrum of PS1, the characteristic peaks belonging to the thiophene moiety were not detectable owing to the high molecular weight. In the spectrum of PS2, the characteristic peaks of both thienyl and TEMPO moieties were observable, which also allows evaluating the molecular weight. In Figure 2, a signal at 3.74 ppm as a broad singlet is attributed to **i** methylene protons in thienyl moiety. Also, a signal as a multiplet around 0.9 ppm is assigned to the axial methyl protons in TEMPO group as well as the **h** hydrogen. Moreover, the styrene
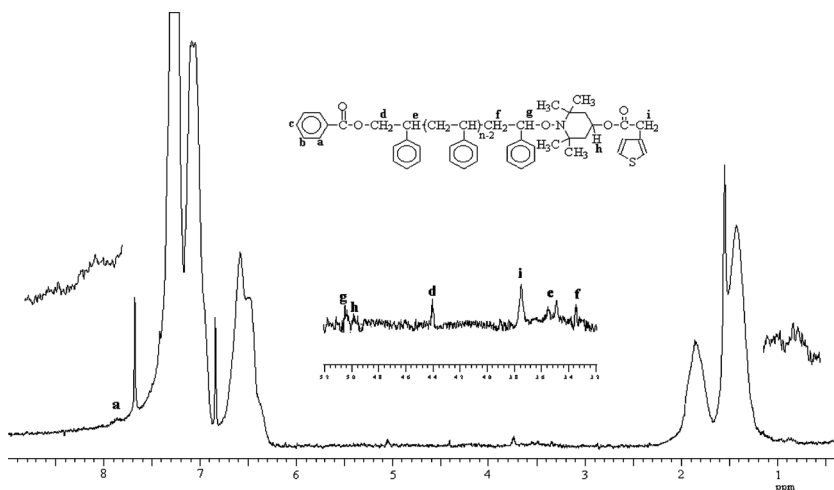

FIGURE 2 ^{1}H-NMR spectrum of thiophene-functionalized polystyrene.

structural units near the chain ends show characteristic signals for the methylene (**d, f**) and methyne (**e, g**) (Figure 2). In the aromatic region near the broad peaks of polystyrene, two peaks at 7.79–7.82 ppm and at 7.67 ppm are attributed to the aromatic protons **a** and **c** in the benzoyl peroxide moiety.

Cyclic Voltammetry

The redox behavior of the macromonomers was examined by cyclic voltammetry (Wenking POS 2 potentiostat). Platinum wires were used as the counter and working electrodes and a Ag/Ag+ was used as the reference electrode. Cyclic voltammetry experiments were performed in acetonitrile (AN)/tetrabutylammonium tetrafluoroborate (TBAFB) solvent electrolyte couple. In the cyclic voltammogram of polystyrenes, no detectable redox peak was observed. Thus, it was concluded that they are not electroactive. However, with the addition of pyrrole, a redox peak appeared at 0.40 V (Figure 3(a)). This potential value revealed a similar
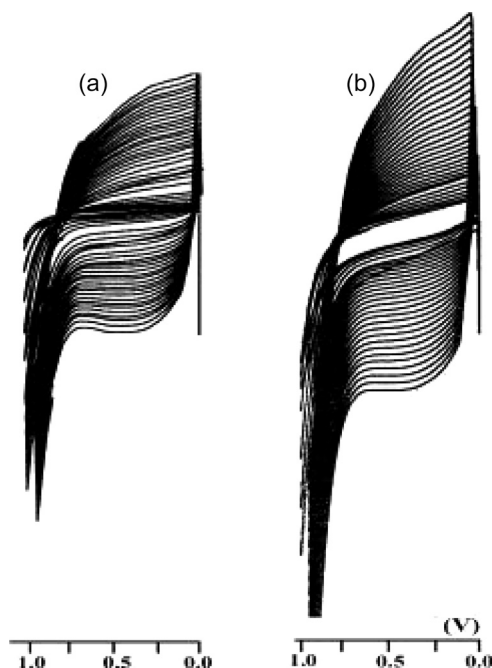

FIGURE 3 Cyclic voltammogram of (a) PS2 with pyrrole and (b) pure polypyrrole

TABLE II Conductivities of the films

Polymer	Conductivities (S/cm)	
	Solution side	Electrode side
PS1/PPy	0.2	0.7
PS2/PPy	3	2

trend with the oxidation behavior of pure PPy (Figure 3(b)). However, the initial scans for PS/PPy reveal no current, in contrast to pure PPy where the first run reveals approximately 50 μA of current. Moreover, the multiscans yield increasing current with several μA increments. In the PS/PPy case, it requires almost twice the multiscans to reach the same height of peaks. These arguments help to indicate that pyrrole chains grow through the thiophene side group of the polystyrene.

Conductivities of the Films

For PTSA-doped PS1/PPy and PS2/PPy films, the conductivities of both the solution and the electrode sides were measured by the standard four-probe technique (Table II).

PS1/PPy and PS2/PPy films have different conductivities by an order of magnitude. PS2/PPy films have higher conductivities, most probably due to high thiophene content in PS2, and thus the possibility of having longer chains of thiophene cannot be ruled out.

FT-IR Spectrophotometer

The IR spectrum was recorded on a Nicolet 510 FT-IR spectrometer. FT-IR spectra of pure PS1 and PS2 insulating polymers showed CH_2 asymmetric and symmetric C−H stretchings at 2923 cm^{-1} and 2850 cm^{-1}. The three bands at 3081, 3059, and 3025 cm^{-1} arose as a result of aromatic C−H stretching. The peaks at 1600 and 1492 cm^{-1} arose from aromatic ring modes. The absorption band of aromatic out-of-plane C−H bend was observed at 756 cm^{-1}. Also, the peak at 698 cm^{-1} is due to the aromatic ring.
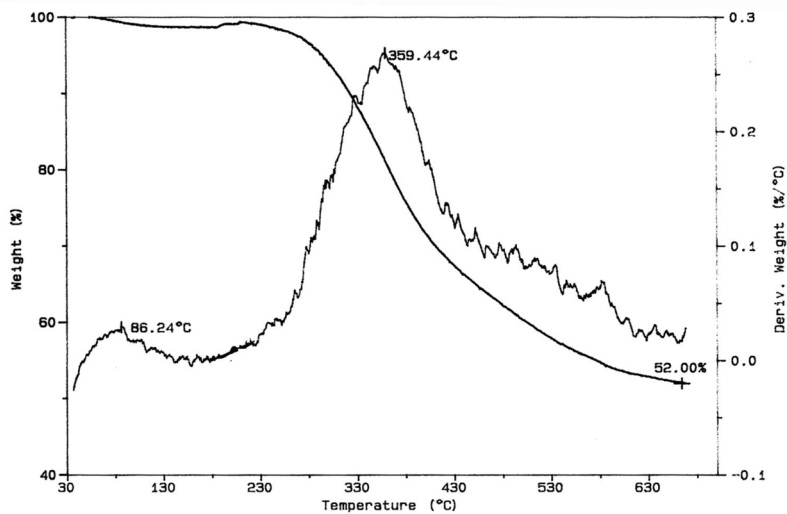
FT-IR spectra of PTSA-doped PS1/PPy and PS2/PPy showed the characteristic peaks of PS1 and PS2 at 698, 756, and 1491 cm^{-1}. The existence of these peaks proves the presence of PS moieties in the resultant polymer.

Thermogravimetric Analysis

The thermogram of PS1 (Figure 4(a)) shows that it was stable up to about 430°C. After that temperature, one weight loss was observed at
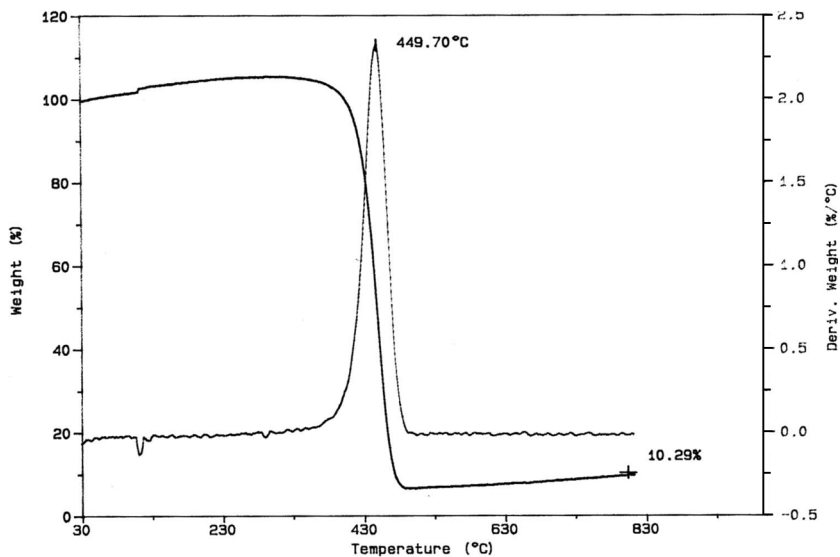
(a)

(b)

FIGURE 4 (a) TGA thermogram of PS1; (b) TGA thermogram of PS1/PPy.

449°C. The thermogram of PS2 revealed the same behavior as that of PS1. Ten percent of PS1 remained at 730°C, whereas 14% remainder was found for PS2.

The thermogravimetric analysis of PS1/PPy (Figure 4(b)) showed two weight losses at 86°C and at 359°C. The first one was due to the removal of solvent from the polymer matrix. The second one was the main weight loss, indicating the decomposition of the sample. The trend was the same for PS2/PPy. Thermal transitions of PS2/PPy were observed at 83°C and at 390°C, 52% PS1/PPy remained, whereas this value was 62% for PS2/PPy.

Differential Scanning Calorimetry (DSC)

The DSC curve of PS1 exhibited a glass transition temperature (T_g) at 104°C. The endothermic transition was observed at 416°C, which was due to the decomposition of PS1. In the case of PS1/PPy copolymers, thermograms revealed two endothermic transitions at around 91°C and 332°C. The first one was due to the removal of the solvent from the polymer matrix, and the second one represented the evacuation of the dopant ion. DSC thermogram of PS2 showed a glass transition temperature at 97°C and decomposition peak at 414°C (Figure 5(a)). PTSA-doped PS2/PPy had two endothermic peaks at 85°C and 342°C. The first peak indicated the solvent removal and the second one arose from the removal of the dopant ion (Figure 5(b)).

Morphologies of the Films

Scanning electron microscopy (SEM) studies were carried out to investigate the morphologies of the films by JEOLJSM-6400. Graft copolymers doped with PTSA were washed in CH_2Cl_2. There was no significant difference between the micrographs of washed and unwashed PS1/PPy and PS2/PPy films. The surface appearances of the films reveal that the solution side (Figure 6(a)) and electrode side (Figure 6(b)) of PS1/PPy films are different. The solution side of PS1/PPy (Figure 6(a)) film has a cauliflower-like structure. Smooth surface was observed at the electrode surface of PS1/PPy (Figure 6(b)). Appearances of PS2/PPy films are nearly the same when compared with PS1/PPy films.

CONCLUSION

Incorporation of thienyl moiety into polystyrene chains was achieved by the polymerization of styrene in the presence of thi-TEMPO in both solution and bulk polymerization conditions. The synthesis of graft copolymers of thienyl containing PS1 and PS2 with pyrrole was achieved
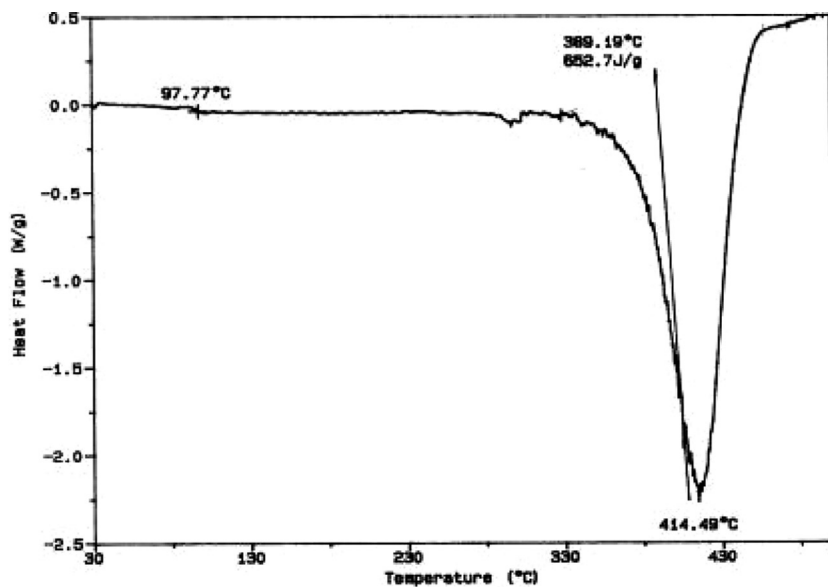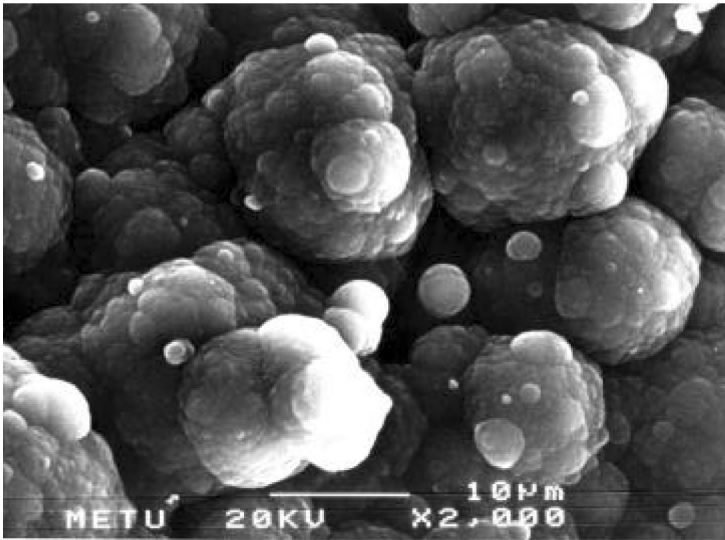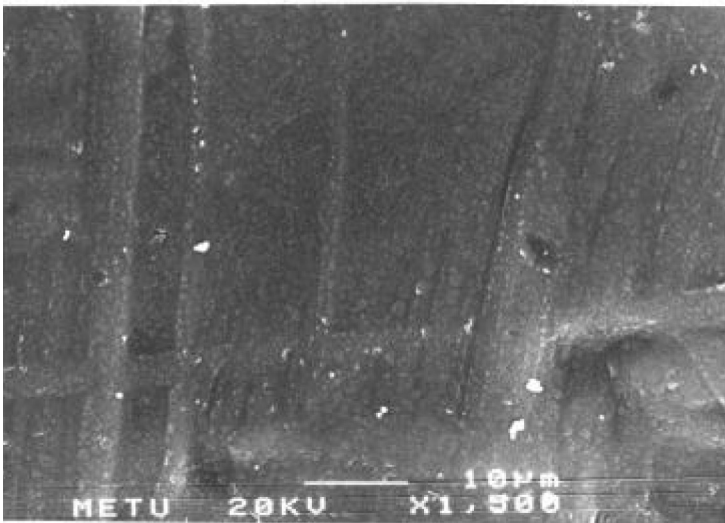
(a)
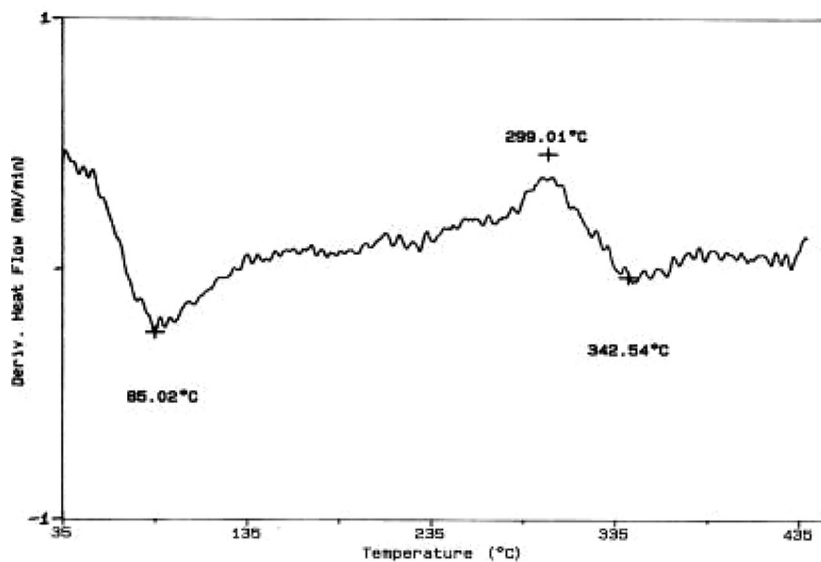
(b)

FIGURE 5 (a) DSC curve of PS2; (b) DSC curve of PS2/PPy.

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(a)

(b)

FIGURE 6 (a) SEM micrograph of solution side of washed PS1/PPy; (b) SEM micrograph of electrode side of washed PS1/PPy.

in the presence of PTSA-supporting electrolyte. Results obtained in the characterization of the graft copolymers support the idea of achieving the growth of polypyrrole chains through the thiophene moieties present in PS1 and PS2.

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