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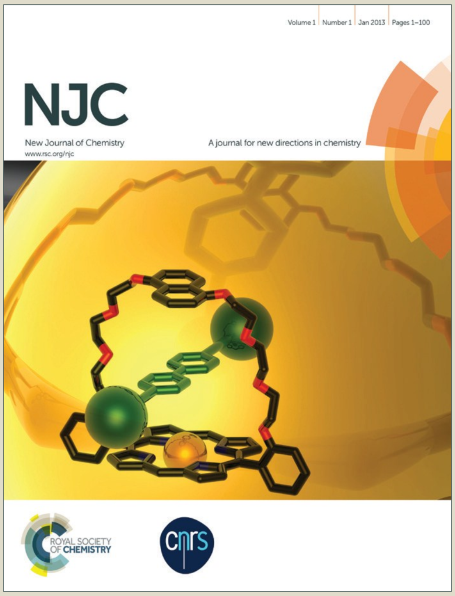

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Chemical and electrochemical grafting of polythiophene onto polystyrene synthesized *via* ‘living’ anionic polymerization

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Abstract

A novel strategy for chemical and electrochemical grafting of polythiophene onto a polystyrene backbone is reported. For this purpose, polystyrene was synthesized *via* 'living' anionic polymerization, and then brominated at *para* position of the aromatic rings of the polystyrene (PSt-Br). The bromo groups of the PSt-Br were converted to thiophene groups using the Grignard reaction, and a thiophene-functionalized PSt macromonomer (ThPStM) was synthesized. The degree of thiophene functionalization was found approximately 9% from ^{1}H NMR spectroscopy. The resultant macromonomer was subsequently used in chemical and electrochemical copolymerizations with thiophene monomer to afford a polystyrene-*graft*-polythiophene (PSt-*g*-PTh) copolymer. The number average molecular weights of PSt, chemically and electrochemically synthesized PSt-*g*-PTh graft copolymers were found to be 17300, 29700, and 25600 gmol^{-1}, respectively, from gel permeation chromatography (GPC) analysis. The electroactivity behaviors of the synthesized samples were verified under cyclic voltammetric conditions, and their electrical conductivities were measured using the four probe technique. The electrical conductivity and electroactivity measurements showed that the PSt-*g*-PTh graft copolymer has lower electrical conductivity and electroactivity than those of the pure PTh. However, these lower values can be improved at the price of solubility, and processability. Moreover, thermal behaviors of the synthesized polymers were investigated by means of differential scanning calorimetry, and thermogravimetric analysis.

1. Introduction

Since the discovery of intrinsically conductive polymers (ICPs) in 1977 a considerable research effort has been devoted on the synthesis, modification, and applications of these engineering polymers from both academia and industry committees, in part due to their unique physicochemical properties, which promotes their applications in the various practical fields such as thin-film field-effect transistors (FETs)[1], polymer rechargeable batteries[2], organic light emitting diodes (OLEDs)[3], polymeric solar cells[4], electrical memory performance[5], sensors[6], biomedical fields[7], anticorrosion and antistatic coating[8], microwave absorption[9], and many more. In the class of ICPs, the polythiophene (PTh), and its derivatives have attracted considerable attention, in part due to their high magnetic and optical properties, electrical conductivities, and environmental stabilities (both to oxygen and to moisture).[10-14]

However, the conjugated backbone of the un-substituted polythiophene is typically rigid, and the polymers tend to aggregate, resulting in poor solubility, low mechanical flexibility, and poor processability.[10, 15-17] From this point of view, modification of this conducting polymer is an immensely important in modern material science, to expand its application fields, and has been the subject of many investigations. The well known approaches towards chemically modified PTh can be listed as: (i) side chain functionalization usually at the β-carbons[18, 19], (ii) synthesis of PTh copolymers with processable polymers[20, 21], and (iii) combination of both aforementioned approaches.[22, 23] Among these procedures, synthesis of polythiophene copolymers offers a convenient way to improve its processability, as they contain conventional and conducting sequences, where conventional sequences increase the solubility and processability of the resultant copolymers. Hence, these copolymers are of prime importance as they combine the properties of two immiscible polymers and act as compatibilizer for polymer blends.[24, 25]

The most widely used methods for the synthesis of the PTh copolymers include: macromonomer technique[26], by the linkage between two different polymers through a coupling reaction[27], and the polymerization of a monomer from active sites on a polythiophene backbone.[28]

On the other hand, the polymer properties are strongly influenced by its molecular parameters such as molecular weight, molecular weight distribution (MWD), and the presence of functional groups and their spatial locations.[29, 30] From this point of view, 'living' polymerization techniques have been proposed as powerful techniques to synthesize polythiophene copolymers with well-defined molecular architectures and relatively low dispersities.[10-12] In this respect, 'living' anionic polymerization can be considered as an efficient technique offering opportunities to synthesizing monodispersed tailor-made polymers with well-defined architectures such as graft, block, star, α,ω-functional polymers and macromonomers. During the 'living' anionic polymerization, all polymer chains are created at the beginning of the polymerization, and then grown homogeneously until the depletion of the monomer.[29, 31, 32]

In the past, we have developed some novel methodologies to chemical modification of polythiophene by the incorporation of polystyrene.[11-13] Following these previous research projects, the objective of this work is to synthesize well-defined polystyrene-*graft*-polythiophene (PSt-*g*-PTh) copolymer by both chemical and electrochemical oxidative polymerization methods. For this purpose, a thiophene-functionalized polystyrene macromonomer (PStThM) was synthesized *via* a combination of 'living' anionic polymerization, and Grignard reaction. The resultant macromonomer was subsequently used in chemical and electrochemical copolymerizations with thiophene monomer to produce a PSt-*g*-PTh graft copolymer.

2. Experimental

2.1. Materials

Styrene and thiophene monomers from Merck (Darmstadt, Germany) were distilled under reduced pressure before use. Benzene and tetrahydrofuran (THF) (Merck) were dried by refluxing over sodium wire under argon atmosphere until the blue color of benzophenone was appeared, and then distilled under argon prior to use. Anhydrous ferric chloride ($FeCl_3$), bromine (Br_2), 2-thiophenecarboxaldehyde, tetraethylammonium tetrafluoroborate (TEAFB), and *sec*-butyllithium (solution in cyclohexane) (Merck) were used as received. All other reagents were purchased from Merck and purified according to standard methods.

2.2. Synthesis of polystyrene

A 100 ml flame-dried three-necked round-bottom flask was equipped with condenser, septum, gas inlet/outlet, and a magnetic stirrer. The flask was joined to the argon gas line, and cooled to -78 ºC by immersing in an ice/isopropanol bath. Then, using a syringe, 0.20 ml (0.28 mmol) of *sec*-butyllithium solution in cyclohexane (1.4 $moll^{-1}$) as an initiator was introduced into the flask under a positive flow of argon gas. Afterwards, 30 ml of dried benzene as solvent, already de-aerated by purging argon, was added into the flask, and stirred for few minutes. The styrene monomer (8 ml, 69 mmol) diluted in 10 ml of dried benzene, de-aerated by purging argon, and was introduced into the flask. While stirring, the reaction mixture was allowed to warm up to room temperature, and the reaction was continued for 8 hours at room temperature. A characteristic orange color, indicating the formation of ‘living’ polymer chains was observed. At the end of this period, the polymer was precipitated in excess methanol, filtered, and dried overnight under vacuum at room temperature

2.3. Synthesis of brominated polystyrene (PSt-Br)

The procedure for the synthesis of the PSt-Br involves the reaction of polystyrene with bromine in the presence of ferric chloride as the catalyst. A typical procedure as follows: a 100 ml three-necked round-bottom flask containing polystyrene (2.5 g, 24 mmol), anhydrous $FeCl_3$ (0.1 g, 0.6 mmol), and dried chloroform (60 m1) was equipped with condenser, septum, gas inlet/outlet, and a magnetic stirrer, under an argon atmosphere. The reaction mixture was de-aerated by purging argon for 10 minutes, and the flask was placed in an oil bath at 60 °C. In a separate container 0.4 ml (7.2 mmol) of bromine was dissolved in 30 ml chloroform, and was introduced to the polymer solution using a syringe through the septum under an argon atmosphere. The reaction mixture was refluxed at 60 °C under an argon atmosphere for about 4 hours in darkness to prevent a light-induced free radical reaction that would induce bromination at the polymer main chain (benzylic positions). At the end of this period, the reaction was terminated by pouring the contents of the flask into a large amount of methanol, filtered, washed several times with methanol, and dried in vacuum at room temperature. It is well established that by this methodology bromination occurs exclusively in the *para* position of the aromatic ring.[33-37]

2.4. Synthesis of ThPStM

A typical procedure for the synthesis of the ThPStM macromonomer is as follows. A 100 ml flame-dried three-necked round-bottom flask (flask 1) containing 0.12 g (5 mmol) magnesium, 0.025 g (0.1 mmol) iodine, 2 g of the brominated polystyrene (PSt-Br), and dried THF (60 ml) was equipped with condenser, septum, gas inlet/outlet, and a magnetic stirrer, under an argon atmosphere. The reaction mixture was refluxed at 65 °C for about 24 hours.

At the end of this time, a separate 100 ml flame-dried three-necked round-bottom flask (flask 2) containing 0.70 ml (7.5 mmol) of 2-thiophenecarboxaldehyde in 40 ml of dried THF was equipped with a condenser, septum, gas inlet/outlet, and a magnetic stirrer. The flask was joined to the argon gas line, and cooled to -78 ºC by immersing it in an ice/isopropanol bath. The solution was de-aerated by bubbling highly pure argon for 10 minutes, and then the Grignard reagent (flask 1) was introduced with a syringe through the septum. The reaction mixture was stirred at -78 °C under an argon atmosphere for about 4 hours. At the end of this period, the flask was warmed up to room temperature, and the reaction mixture was stirred for another 8 hours at room temperature. The thiophene-functionalized polystyrene macromonomer (ThPStM) was separated by precipitation in excess acidic methanol, filtered, washed several times with methanol, and dried in vacuum at room temperature.

2.5. Synthesis of PSt-*g*-PTh *via* chemical oxidation polymerization

A 250 ml three-necked round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer, was charged with ThPStM macromonomer (1 g)**,** and dried CH_2Cl_2 (90 ml). The reaction mixture was stirred to completely dissolving of the ThPStM macromonomer, and then thiophene monomer (1.5 ml, 19.1 mmol) was added to the solution. The reaction mixture was de-aerated by bubbling highly pure argon for 15 minutes.

In a separate container 12.4 g (76.4 mmol) of anhydrous ferric chloride ($FeCl_3$) was dissolved in 30 ml of dried acetonitrile (CH_3CN). The solution was de-aerated by bubbling highly pure argon for 10 minutes, and was slowly added to the reaction mixture at a rate of 5 ml min^{-1} under an argon atmosphere. The mixture was refluxed for about 24 hours at room temperature under inert atmosphere. The reaction was terminated by pouring the contents of the flask into a large amount of methanol. The crude product was filtered and washed several times with methanol.

The crude product was extracted with THF in a Soxhlet apparatus for 24 hours in order to remove pure polythiophene (PTh is not soluble in THF). The polymer solution was filtered, concentrated by a rotary evaporator, and precipitated into excess methanol. Afterwards, the product was added into cyclohexane, and refluxed at 40 ºC to remove any residual un-grafted polystyrene chains. It is important to note that, the synthesized PSt-*g*-PTh is not soluble in hot cyclohexane, while un-grafted polystyrene is completely soluble in cyclohexane at 40 ºC. The purified dark red solid was dried in vacuum at room temperature.

2.6. Synthesis of PTh *via* chemical oxidation polymerization

The general procedure for synthesis of pure PTh was as follows. A 100 ml three-necked round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer, was charged with 1.5 ml (19.1 mmol) of thiophene monomer and 90 ml of dried CH_2Cl_2. The solution was de-aerated by bubbling highly pure argon for 20 minutes. In a separate container 12.4 g (76.4 mmol) anhydrous ferric chloride was dissolved in 30 ml of dried CH_3CN. The oxidant solution was de-aerated by bubbling highly pure argon for 10 minutes, and was slowly added to the reaction mixture under an argon atmosphere. The reaction mixture was refluxed for about 24 hours at room temperature. At the end of this period, the precipitate was filtered off and washed several times with excess CH_3CN followed by acetone. The final black $FeCl_3$-doped polythiophene powder was obtained after drying at room temperature for 24 hours under reduced pressure.

2.7. Synthesis of PSt-*g*-PTh *via* electrochemical oxidation polymerization

The electrochemical synthesis of PSt-*g*-PTh graft copolymer was performed *via* constant potential electrolysis using potentiostat and a three-compartment cell. For this purpose, a 2% (w/v) solution of insulating ThPStM macromonomer was dissolved in CH_2Cl_2 and both sides of working electrode (Pt) were coated with ThPStM by drop-coating, and used as the working electrode. The electrolysis cell was prepared by dissolving tetraethylammonium tetrafluoroborate (0.2 $moll^{-1}$) in acetonitrile, and introducing 50 µl thiophene monomer. Constant potential electrolysis was performed at 2.00 V *versus* reference electrode (Ag/AgCl) for 1 hour at room temperature under argon atmosphere. After electropolymerization the film obtained was washed with CH_3CN several times.

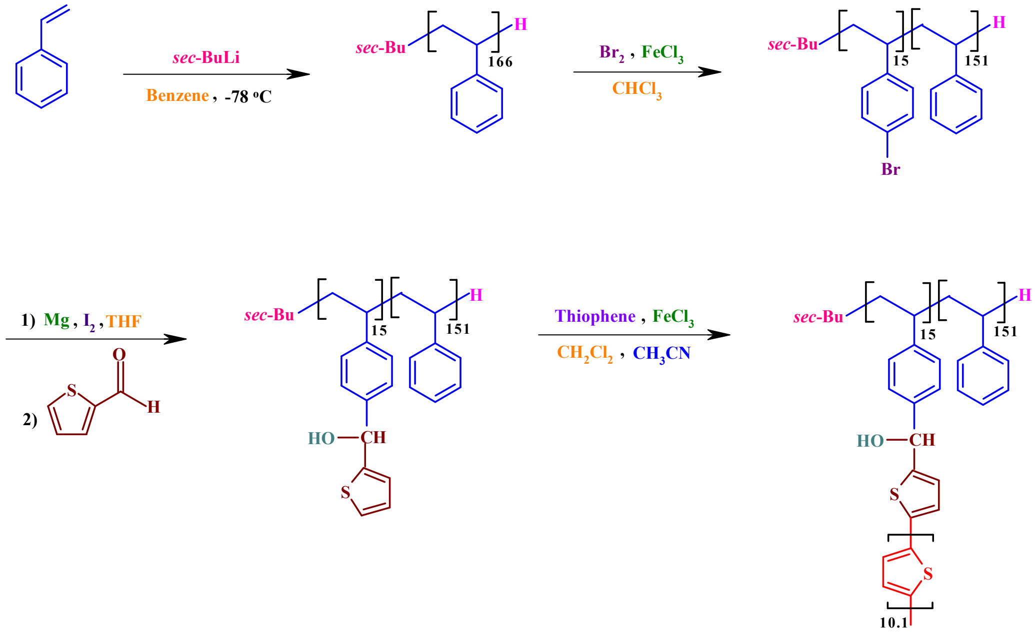
2.8. Characterization

Fourier transform infrared (FTIR) spectra of the samples were collected on a Shimadzu 8101M FTIR (Shimadzu, Kyoto, Japan) between the frequency range of 4000 to 400 cm^{-1}, with an attenuated total reflection facility. The samples were prepared by grinding the dry powders with potassium bromide (KBr), and compressing the mixture into disks. The spectra were recorded at room temperature. ^1H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C using an FT-NMR (400 MHz) Bruker spectrometer (Bruker, Ettlingen, Germany). The sample for NMR spectroscopy was prepared by dissolving about 10 mg of samples in 1 ml of deuterated chloroform ($CDCl_3$), and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. The molecular weights of the obtained polymers were determined by gel permeation chromatography (GPC) analysis with a Maxima 820 GPC Analysis Report (Ventura, CA, USA), using a polystyrene(s) (M_n=189300, 59950, 30150, 9910, 3760, 1660, and 650 $gmol^{-1}$) calibration standard.

Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 ml min^{-1} and column temperature of 25 °C. The thermal properties of the synthesized samples were investigated by thermogravimetric analyzer (TGA-PL STA 1640 equipment (Polymer Laboratories, Shropshire, UK)). The TGA experiments were conducted under nitrogen atmosphere from room temperature to 700 °C with heating rate of 10 °C min^{-1}. Differential scanning calorimetric analyses were performed with a NETZSCH (Selb, Germany), DSC 200 F3 Maia. The sample was first heated to 200 °C, and then allowed to cool for 5 minutes to eliminate the thermal history. Thereafter, the sample was reheated to 200 °C at a rate of 10 °C min^{-1}. The entire test was performed under nitrogen purging at a flow rate of 50 ml min^{-1}. Ultraviolet-visible (UV-vis) spectroscopy was conducted using a Shimadzu 1601 PC UV-vis spectrophotometer (Shimadzu, Kyoto, Japan) in the wavelength range 300 to1000 nm. Electrochemical experiments were conducted using Auto-Lab PGSTA T302N. The electrochemical cell contained five openings: three of them were used for the electrodes (working, counter, and reference), and two for argon bubbling in the solutions during all experiments. The conductivity of the synthesized samples was determined using the four-probe technique (Azar Electrode, Urmia, Iran) at room temperature.

3. Results and discussion

As mentioned in introduction, scenic the discovery of conductive polymers, the technology for the modification of these polymers have progressed significantly. It is well established that the side chain functionalization of polythiophene and synthesis of its copolymers with processable polymers are two main strategies for exploiting the PTh and overcoming its deficiencies.[10, 38] Thus, we report here an efficient method to synthesis of processable and well-defined polythiophene copolymer *via* both chemical and electrochemical oxidation polymerization methods. The chemical methodology is shown in Scheme 1.



Scheme 1. Synthesis of the ThPStM macromonomer, and PSt-*g*-PTh graft copolymer *via* chemical oxidation polymerization method.

3.1. Characterization of macromonomer

As mentioned the thiophene-functionalized polystyrene macromonomer (ThPStM) was synthesized by a combination of ‘living’ anionic polymerization, and Grignard reaction. The FTIR spectra of the PSt, PSt-Br, and ThPStM macromonomer are shown in Figure 1. The FTIR spectrum of the polystyrene shows the characteristic absorption bands due to the stretching vibrations of aliphatic and aromatic C–H at 3100–2800 cm^{-1} region, C=C stretching vibrations at 1601 and 1488 cm^{-1}, weak aromatic overtone and combination bands in the1900 to 1650 cm^{-1} region, $–CH_2$ bending vibration at 1446 cm^{-1}, and γ(C–H) in the aromatic ring at 754 cm^{-1}. However, in comparison with the FTIR spectrum of the PSt the FTIR spectrum of the

PSt-Br does not exhibit any distinct bands due to the overlapping of the C–Br band with polystyrene sharp bands. The most distinctive features in the FTIR spectrum of the ThPStM macromonomer are the appearance of new bands at 3517 and 1253 cm^{-1}, corresponding to the stretching vibrations of hydroxyl and C–O groups, respectively. Additional evidence for the syntheses of the PSt-Br, and ThPStM macromonomer was obtained from ^1H NMR data. The ^1H NMR spectra of the PSt, PSt-Br, and ThPStM macromonomer are shown in Figure 2. In ^1H NMR spectrum of the PSt the chemical shifts at 1.20-2.20 and 6.20-7.50 ppm are related to the aliphatic and aromatic protons of the polystyrene, respectively. In ^1H NMR spectrum of the PSt-Br from the ratio of aliphatic to aromatic protons, it was deduced that approximately 9 % of the styrene units were brominated.

The ^1H NMR spectrum of the ThPStM macromonomer show similar signals with minor differences. The most distinctive features in the ^1H NMR spectra of the ThPStM macromonomer and brominated polystyrene are the appearance of two new peaks at 2.70-2.80 and 5.30-5.45 ppm, corresponding to hydroxyl and –CH-OH protons, respectively. In addition, the ratio of aliphatic to aromatic protons indicates that the functionalization degree in the ThPStM macromonomer is approximately 9%, and thus all of bromine groups were converted to the thiophene groups.

It should be pointed out that, in calculation of the functionalization degrees the contributions of $CHCl_3$ at 7.24 ppm and water at 1.56 ppm (as impurities in NMR solvent) can be affected the calculations.[39, 40] However, this affects are venial due to following reasons:

1. The purity of the $CDCl_3$ as ^1H NMR solvent in this study is very high (≤99.8%), thus the $CHCl_3$ has not significant integral intensity in comparison with integral intensities of polymeric samples (10 mg ml^{-1}).

2. In the case of this study the ^{1}H NMR spectrum of the $CDCl_3$ exhibited that the integral intensities of the $CHCl_3$ and water are approximately the same, thus these signals does not significantly affect the calculations.

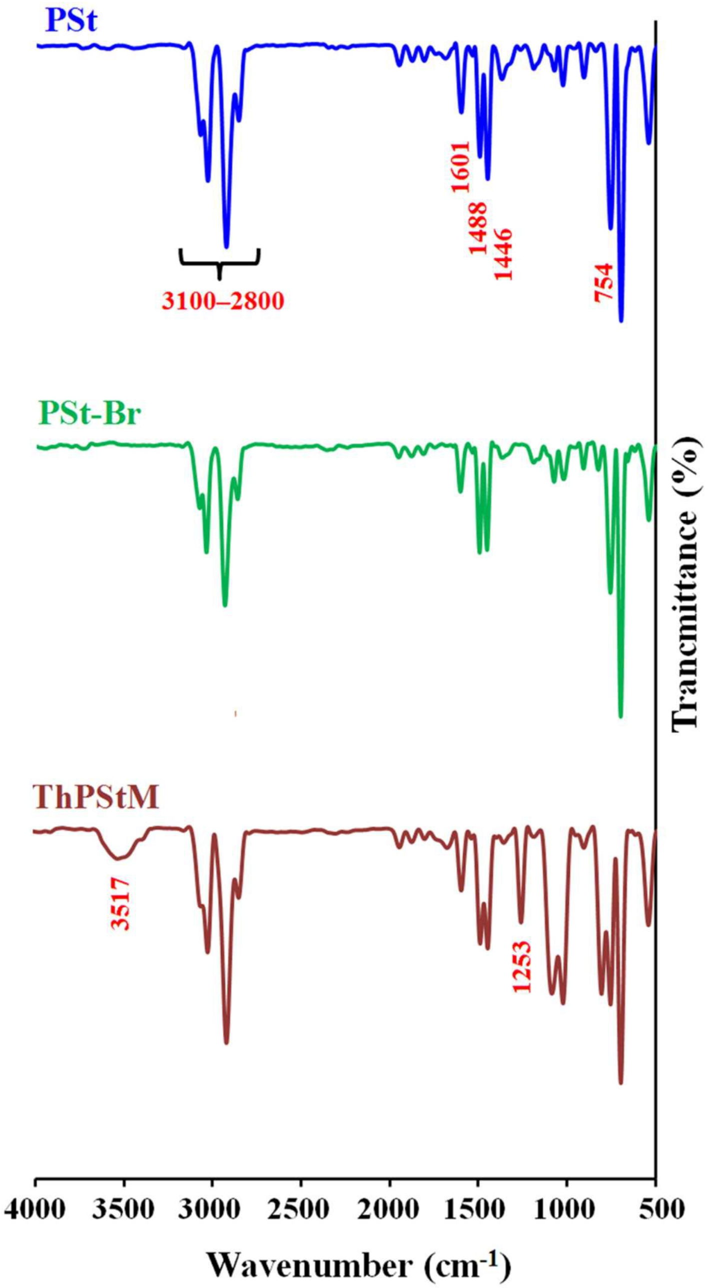


Figure 1. Fourier transform infrared spectra of the PSt, PSt-Br, and ThPStM macromonomer.

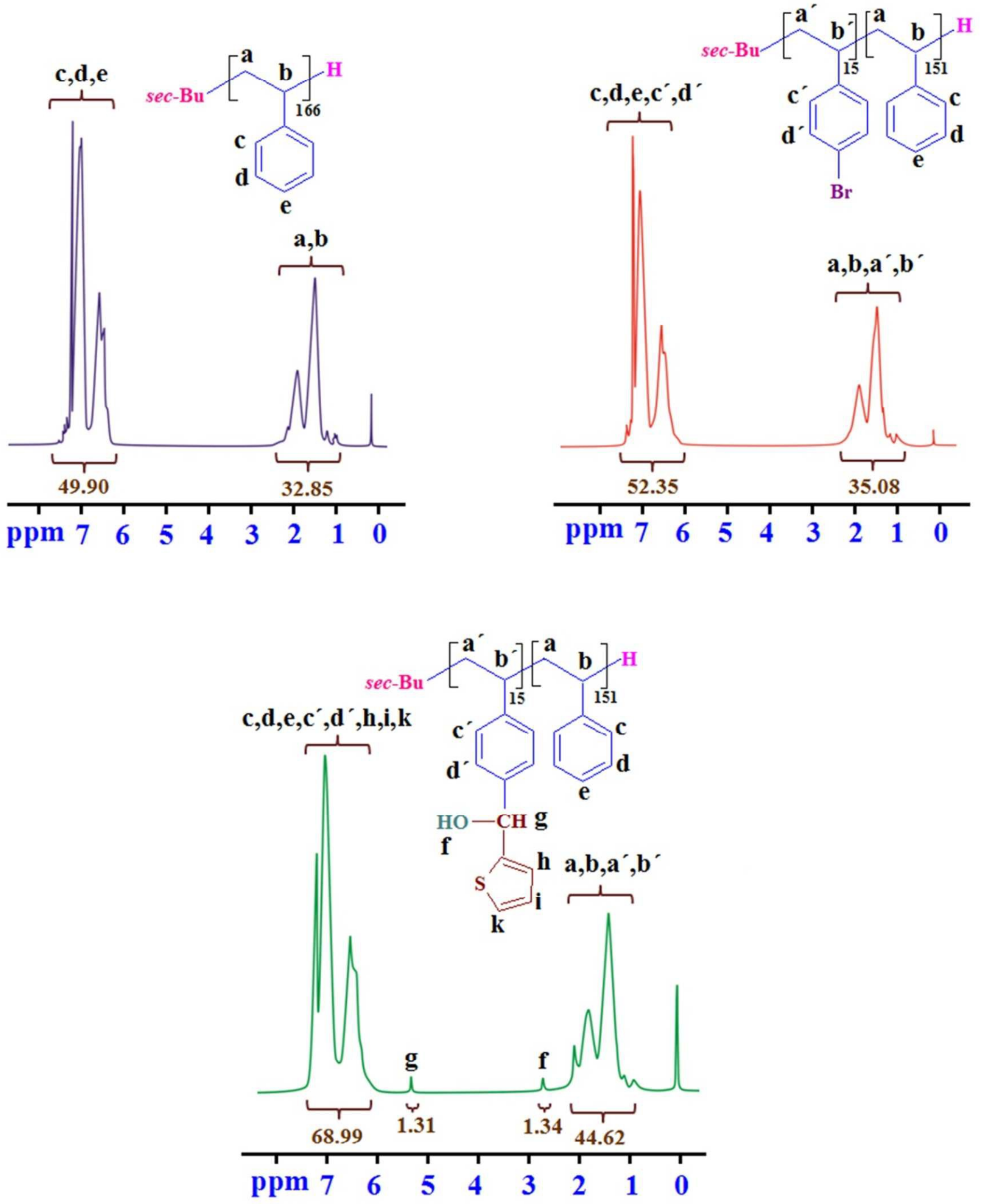


Figure 2. The ^{1}H nuclear magnetic resonance (NMR) spectra of the PSt, PSt-Br, and ThPStM macromonomer.

3.2. Characterization of chemically synthesized PSt-*g*-PTh

The FTIR spectra of the pure PTh, and PSt-*g*-PTh graft copolymer are shown in Figure 3. As seen in this figure the pure PTh shows the characteristic absorption bands due to the stretching vibrations of C=C (1647 and 1481 cm^{-1}), weak aromatic α and β hydrogen's at 3100-3000 cm^{-1}, γ(C–H) in the aromatic ring (1078 and 783 cm^{-1}), and the C–S bending band at 702 cm^{-1}. As seen in FTIR spectrum of the PSt-*g*-PTh graft copolymer this spectrum shows all the characteristic bands corresponding to the PSt and PTh segments.

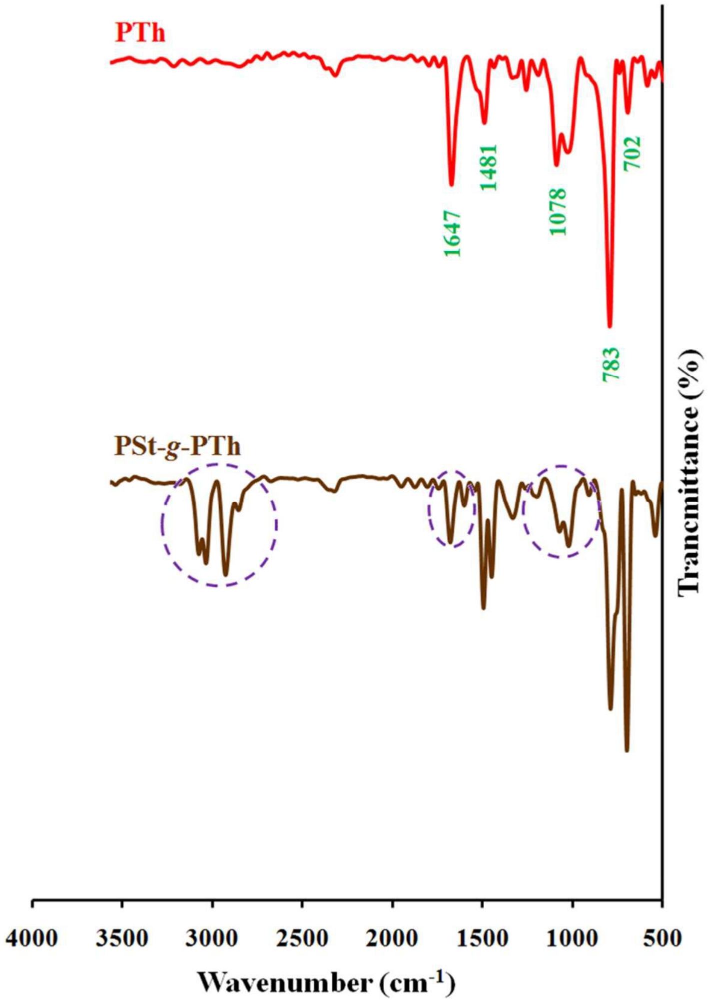


Figure 3. Fourier transform infrared spectra of the PTh, and PSt-*g*-PTh graft copolymer.

It is well known that the molecular weight, and dispersity are very important features of polymers, can be controlled in the 'living' anionic polymerization technique by the systematic variation of monomer weight to the moles of the initiator, and also the degree of conversion. As an example, the number average molecular weight of polystyrene obtained after complete conversion using *sec*-BuLi as an initiator is calculated by the following equation.

$$\text{Theortical } \mathrm{M_n}\,(\mathrm{g\ mol^{-1}}) = \frac{\text{styrene (g)}}{\text{sec}-\text{BuLi (mols)}}$$

It is important to note that, the conversion of the monomer in ‘living’ polymerization methods is often not 100%, but it still provides a methodology for the synthesis of well-defined polymer with relatively low dispersities (M_w/M_n~1.20).

The GPC chromatograms of the PSt, and PSt-*g*-PTh graft copolymer are shown in Figure 4. As seen in this figure the PSt with relatively low dispersity (1.24) was synthesized through ‘living’ anionic polymerization technique. In addition, single GPC peak with a clear shift to a higher molecular weight region suggested that polythiophene was chemically grafted onto polystyrene backbone, and there was no homopolymer contamination.

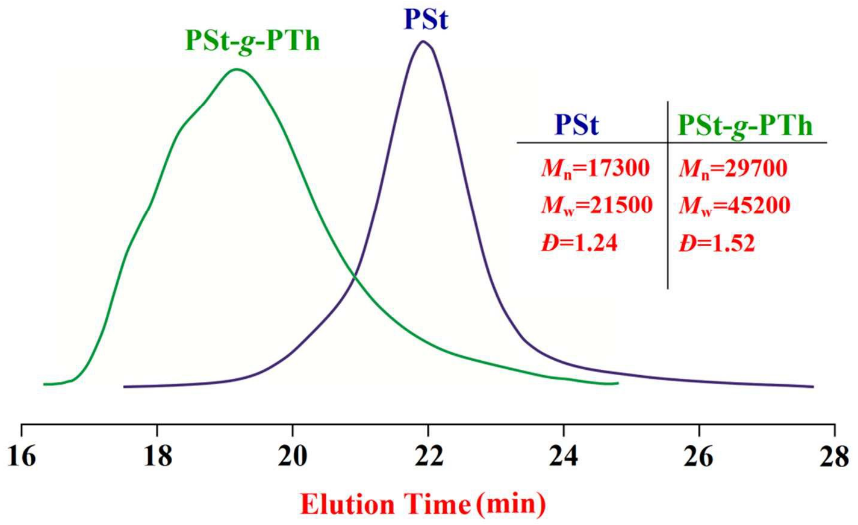


Figure 4. The GPC chromatograms of the PSt, and PSt-*g*-PTh graft copolymer (M_n; number average molecular weight, M_w; weight average molecular weight, *Đ*; dispersity).

After purification of the PSt-*g*-PTh graft copolymer (as given in Experimental section), the grafting parameters such as grafting yield, grafting efficiency, and weight gain were calculated, based on gravimetric measurements, according to the following equations: grafting yield (%G)=$(W_g\text{-}W_0)/W_g\times100$; grafting efficiency (%GE)=$W_g/(W_m+W_0)\times100$; and weight gain (%WG)=$(W_g\text{-}W_0)/(W_m+W_0)\times100$

where W_g is the mass of the grafting copolymer, W_0 is the mass of the ThPStM macromonomer, and W_m is the mass of the thiophene monomer taken for the reaction. The grafting parameters for PSt-*g*-PTh graft copolymer was calculated, and summarized in Table 1. These results provided additional evidence for successfully synthesis of the PSt-*g*-PTh graft copolymer, in accordance with the results obtained by GPC study.

Table 1. Grafting parameters for the PSt-*g*-PTh graft copolymer.

Sample	Mass of grafting (W_g)	Weight gain (%WG)	Grafting efficiency (%GE)	Grafting yield (%G)
PSt-*g*-PTh[a]	1.68	26.5	65.4	40.5

[a] In un-doped state.

3.3. Thermal property study of the chemically synthesized samples

Thermal behaviors of the obtained polymers were investigated by differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) upon heating under nitrogen atmosphere. Figure 5 shows the DSC traces of the pure PSt, and PSt-*g*-PTh graft copolymer. The DSC curve of the pure PSt exhibits an endothermic peak approximately at 83 °C, corresponding to the glass transition temperature (T_g) of the polymer. In DSC curve of the PSt-*g*-PTh graft copolymer the endothermic peak approximately at 89 °C can be designed as the glass transition temperature of the copolymer sample. In addition, in comparison with pure PSt, the T_g of the PSt-*g*-PTh graft copolymer slightly increased by impeding chain flexibility.

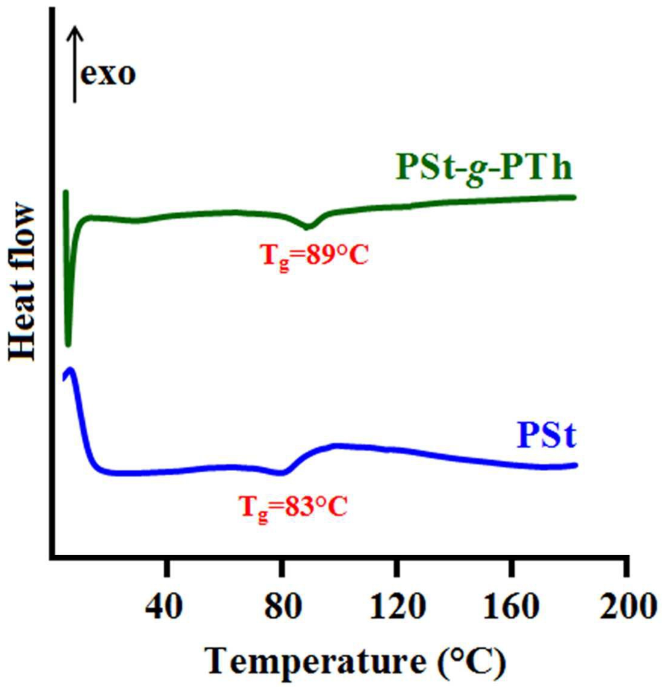


Figure 5. Differential scanning calorimeter traces of the pure PSt, and PSt-*g*-PTh graft copolymer.

The characteristic TGA curves of the pure PSt, and PSt-*g*-PTh graft copolymer are shown in Figure 6. As seen in this figure the decomposition of the pure polystyrene was occurring in one step around 240–370 °C, after which the loss rate slows down. The residue at 800 °C for pure PSt is 4 wt%. However, the decomposition of the PSt-*g*-PTh graft copolymer was initiated from 180 °C corresponding to the early decomposition of the polythiophene segment(s), and the weight loss increases rapidly from this temperature to about 470 °C, after which the loss rate slows down. The residue at 800 °C for this sample is 34 wt%.

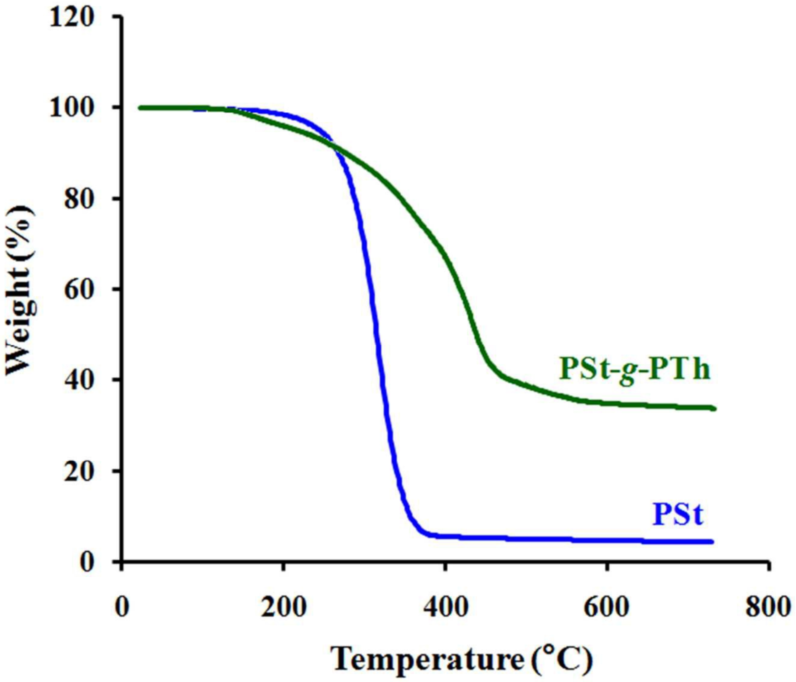


Figure 6. Thermogravimetric analysis of the pure PSt, and PSt-*g*-PTh graft copolymer.

3.4. Characterization of electrochemically synthesized PSt-*g*-PTh

The electrochemically synthesized PSt-*g*-PTh film was characterized by FTIR spectroscopy, and GPC analysis. After electropolymerization the film obtained was washed with CH_3CN and CH_2Cl_2 several times, in order to remove adsorbed tetraethylammonium tetrafluoroborate, and un-grafted ThPStM chains, respectively. The FTIR spectra of the electrochemically synthesized PSt-*g*-PTh and pure PTh are shown in Figure 7. As can be seen the pure PTh shows the characteristic absorption bands due to the stretching vibrations of C=C at 1628 and 1482 cm^{-1}, weak aromatic hydrogen's at 3100-3000 cm^{-1}, γ(C–H) in the aromatic ring at 1023 and 785 cm^{-1}, and the C–S bending band at 684 cm^{-1}. The FTIR spectrum of the electrochemically synthesized PSt-*g*-PTh graft copolymer shows all the characteristic bands corresponding to the PSt and PTh segments.

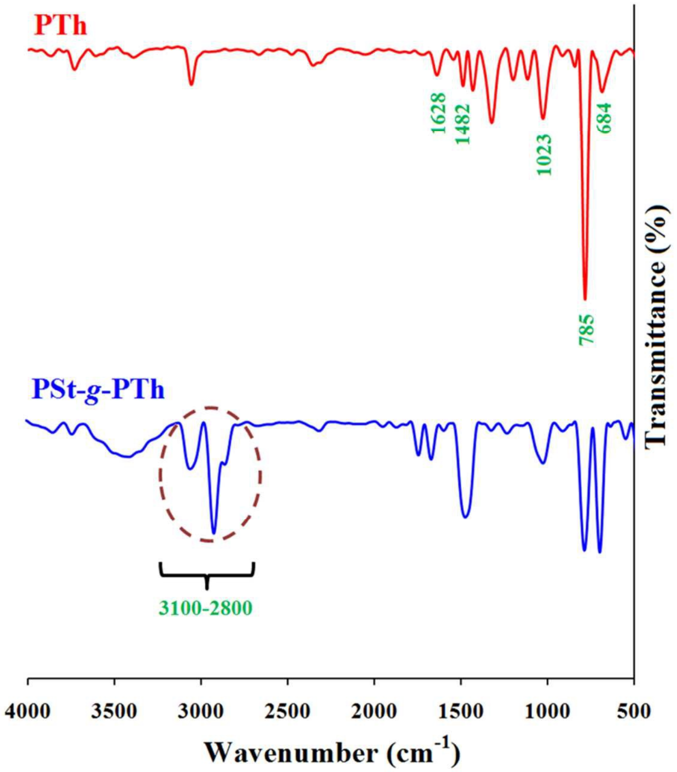


Figure 7. Fourier transform infrared spectra of the electrochemically synthesized PTh, and PSt-*g*-PTh.

The GPC chromatogram of the electrochemically synthesized PSt-*g*-PTh graft copolymer is shown in Figure 8. In comparison with GPC chromatogram of the PSt (Figure 4), the GPC chromatogram of the electrochemically synthesized PSt-*g*-PTh was shifted to a higher molecular weight region suggested that polythiophene was grafted onto polystyrene backbone. In addition, the single peak of the chromatogram indicates that there was no homopolymer contamination.

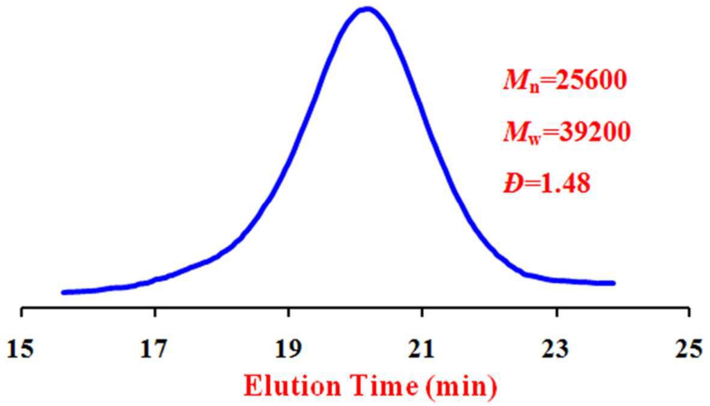


Figure 8. The GPC chromatogram of the electrochemically synthesized PSt-*g*-PTh graft copolymer.

3.5. Eectroactivity behaviors

As mentioned in Experimental section, similar to other conducting polymers the polythiophene and its copolymers can be synthesized *via* both chemical and electrochemical oxidation polymerization methods in the presence of a catalyst. The electrochemical process is more advantageous since film properties such as thickness and conductivity can be controlled by the synthesis parameters such as current density, substrate, pH, nature and concentration of electrolyte. In addition, in electrochemical method the polymer is enabling to simultaneous doping, and entrapment of molecules.[10]

After electropolymerization the effect of the potential scanning rate (V) on the peak currents for the synthesized samples (PTh and PSt-*g*-PTh) were studied in the range of 25 to 150 mV s^{-1} scan rate, in the acetonitrile–tetraethylammonium tetrafluoroborate (TEAFB), solvent–electrolyte couple (0.1 $moll^{-1}$) between 0.00 and +1.70 V *versus* the Ag/AgCl electrode (Figure 9).

As shown in Figure 9**a**, the cyclic voltammograms (CVs) of the bare Pt electrode does not exhibit any detectable redox peak in the potential range of 0.00 to +1.70 V *versus* the Ag/AgCl electrode. In contrast, the cyclic voltammograms (CVs) of the pure PTh (Figure 9**b**) shows a typical redox couple with anodic peak at approximately 1.1 V *versus* Ag/AgCl electrode, and the anodic peaks shifts in the direction of positive potential with increasing scan rate, which indicates the electrochemical oxidation/reduction (doping/dedoping) of the deposited PTh film was chemically reversible. As can be seen in the Figure 9**c**, the CVs of the PSt-*g*-PTh graft copolymer exhibit some qualitative similarities to those of the pure PTh. The CVs of the PSt-*g*-PTh exhibited that the grafted PTh onto PSt backbone still retained good redox activity in the resulting graft copolymer, and the resulting graft copolymer was highly stable. In addition, similar to CVs of the pure PTh for PSt-*g*-PTh graft copolymer the anodic peak current is linearly increased (0.95 to 1.4 V) with increasing of scan rate.

To evaluate the electroactivity further the relationship between the peak current sizes *versus* scan rate was determined. The linear relationships between the current and scan rate in the range of 25 to 150 mV s^{-1} for the electrochemically synthesized pure PTh, and PSt-*g*-PTh samples are shown in Figure 9**d**. This linear relationship is typical of redox-active polymers attached to the electrodes and also exemplifies the stability of the synthesized samples toward doping/dedoping.

In addition experimental section, the electroactivity behaviors of the chemically synthesized pure PTh and PSt-*g*-PTh graft copolymer were investigated under cyclic voltammetric conditions. As can be seen in Figure 10, the cyclic voltammetry (CVs) curves of both pure PTh and PSt-*g*-PTh graft copolymer samples shows a typical redox couple with anodic peaks at approximately 1.3, and 1.4 V *versus* Ag/AgCl electrode, respectively, and the anodic peaks shifts in the direction of higher currents with increasing scan rate. Moreover, the linear relationships between the current and scan rate in the range of 25 to 125 mV s^{-1} for the chemically synthesized pure PTh and PSt-*g*-PTh graft copolymer are shown in Figure 11.

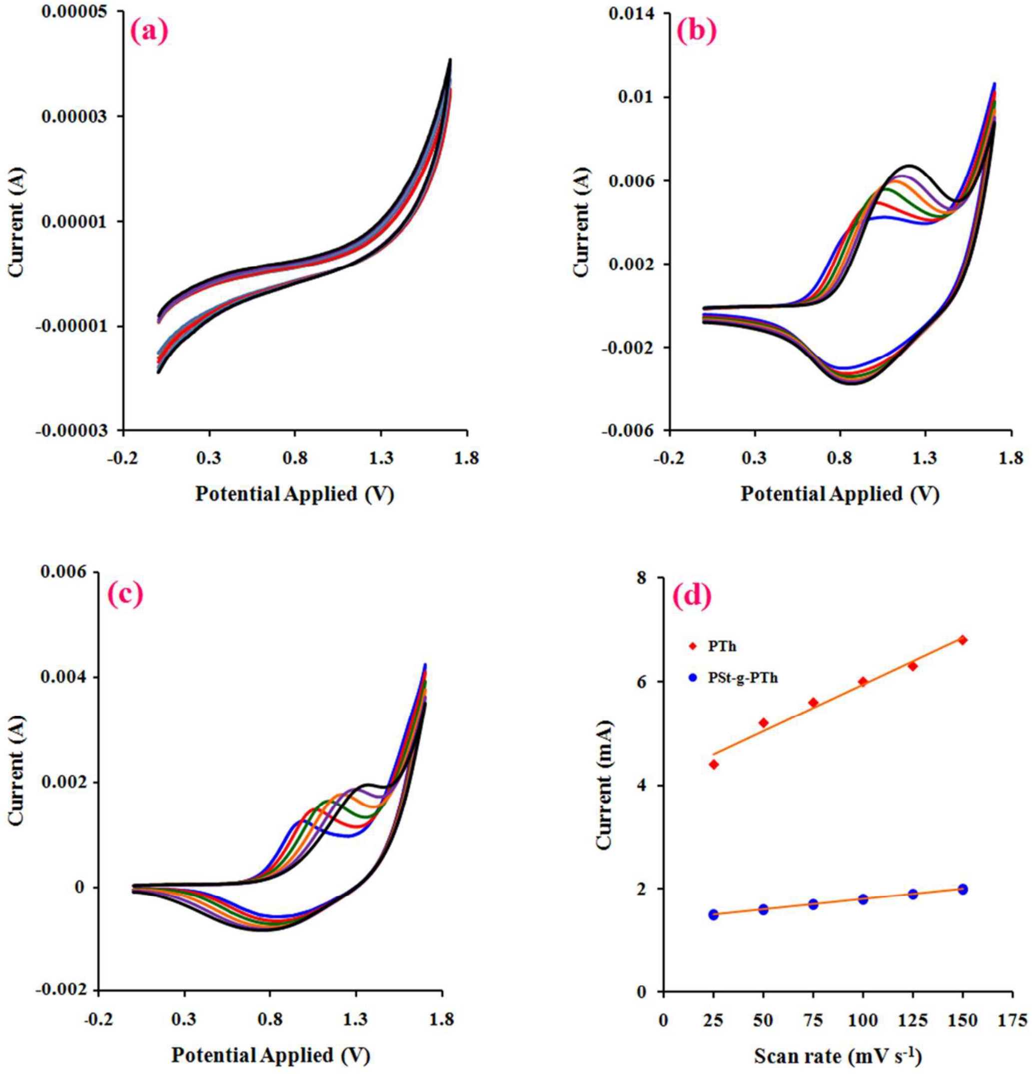


Figure 9. Cyclic voltammetry (CVs) curves of the bare Pt electrode (a), electrochemically deposited pure PTh (b), electrochemically grafted thiophene onto ThPStM macromonomer (c) in a acetonitrile–tetraethylammonium tetrafluoroborate (TEAFB), solvent–electrolyte couple (0.1 moll^{-1}), and the effect of the potential scanning rate (V) on the

peak currents for the electrochemically synthesized PTh and PSt-*g*-PTh in the range of 25 to 150 mV s^{-1} scan rate.

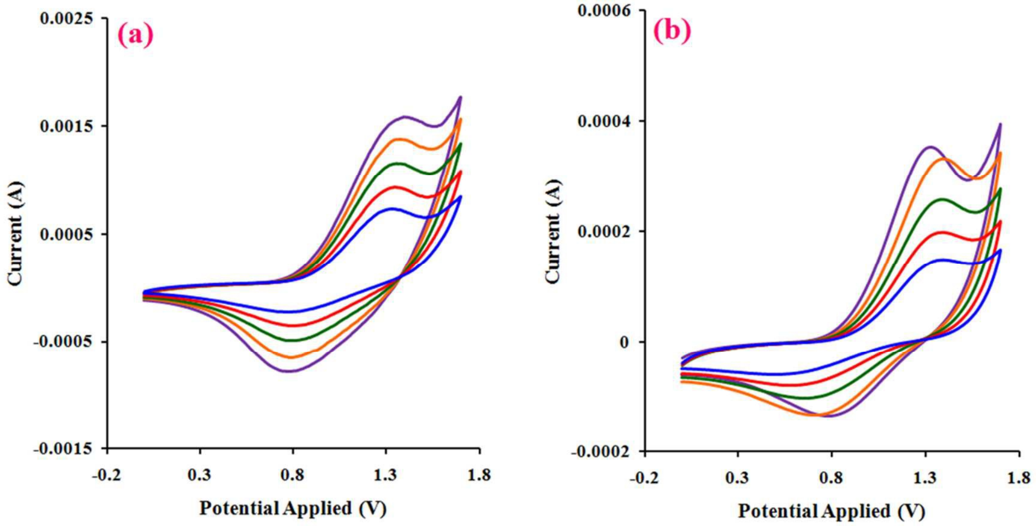


Figure 10. Cyclic voltammetry (CVs) curves of the chemically synthesized pure PTh (a), and PSt-*g*-PTh graft copolymer (b) in a acetonitrile–tetraethylammonium tetrafluoroborate (TEAFB), solvent–electrolyte couple (0.1 moll^{-1}).

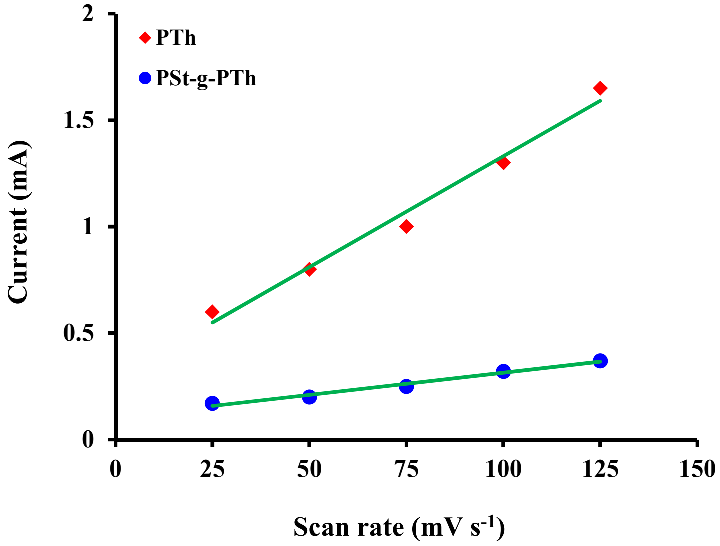


Figure 11. The effect of the potential scanning rate (V) on the peak currents for the chemically synthesized PTh and PSt-*g*-PTh graft copolymer in the range of 25 to 125 mV s^{-1} scan rate.

3.6. Electrical conductivity measurement

It is well established that the conducting polymers such as polythiophene and its copolymers could intrinsically carry, and transport electric charge in the semiconducting-to-metallic region. Thus, these polymers can be considered as prospective materials for industrial, technological, and biomedical applications.[41, 42] In this study, the electrical conductivities of the synthesized samples were measured by the four-probe technique in air at room temperature. The experimental determination was repeated 5 times for each sample to evaluate the sample accuracy. In addition, the conductivities were preserved for at least 100 hours post fabrication. Using the values of voltage (V), current (I), and thicknesses (d) of the samples, the volume specific resistivity (ρ; Ω cm), and subsequently, the electrical conductivities (σ; S cm^{-1}) were calculated using the following formula.

$$\rho = (V/I)\,(\pi/\ln 2)d$$

$$\sigma = 1/\rho$$

Table 2 summarizes the electrical conductivities of the samples were synthesized by both chemical and electrochemical approaches. As shown in this table the electrochemically synthesized samples posse's higher electrical conductivities than those of the chemically synthesized samples.

On the bases of the electrical conductivity, and electroactivity studies results the conclusion could be drawn that the PSt-*g*-PTh graft copolymer has lower electrical conductivity, and electroactivity than those of the pure PTh. However, the lower electrical conductivity, and electroactivity levels can be improved at the price of solubility, and processability.

Table 2. The electrical properties of the synthesized samples.

Sample	Volume specific resistivity (ρ; Ω cm)	Electrical conductivity (σ; S cm^{-1})
Electrochemically synthesized PTh	0.78	1.30
Chemically synthesized PTh	0.87	1.15
Electrochemically synthesized PSt-*g*-PTh	1.54	0.65
Chemically synthesized PSt-*g*-PTh	2.00	0.50

3.7. Optical properties

The optical properties of the chemically synthesized samples were studied using ultraviolet-visible (UV-vis) spectroscopy. The samples for UV-vis spectroscopy were prepared by dissolving the same amount of the samples in THF followed by ultrasonic treatment for 15 minutes. As can be seen in Figure 12, the UV-visible spectrum of the pure PTh was characterized by an electronic transitions at about 511 nm, while the UV-visible spectrum of the PSt-*g*-PTh graft copolymer was characterized by an electronic transitions at about 496 nm, being lower than the pure PTh. This shift to shorter wavelength (blue shift) is originated from the lower concentration of conjugated units in the case of PSt-*g*-PTh graft copolymer in comparison with pure PTh.

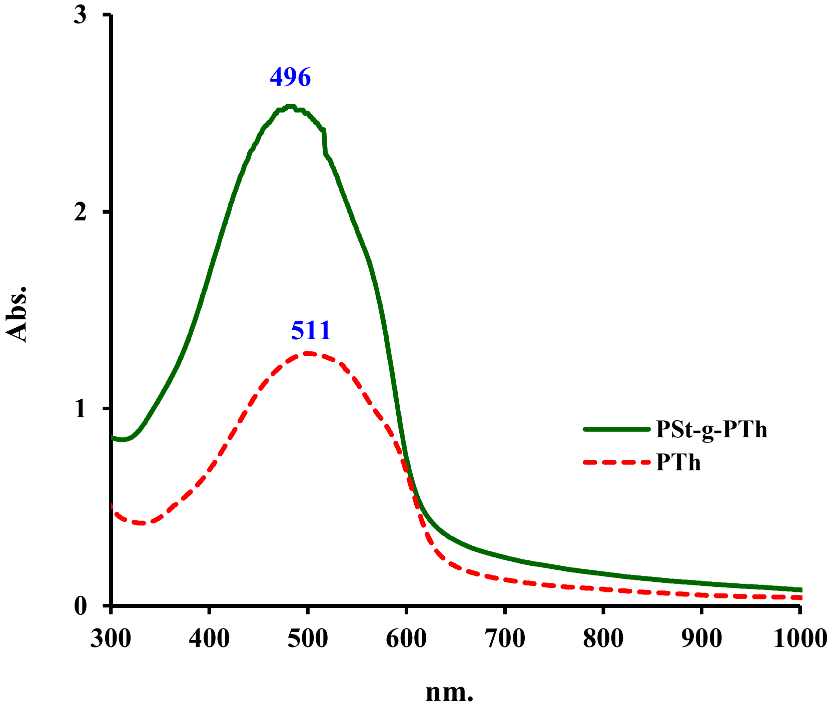


Figure 12. Electronic spectra of the pure PTh and PSt-*g*-PTh graft copolymer in tetrahydrofuran (THF) solution.

4. Conclusion

In summary, a combination of ‘living’ anionic polymerization and Grignard reaction has been successfully utilized to synthesis of a thiophene-functionalized PSt macromonomer (ThPStM) with well-defined architecture. The macromonomer obtained was subsequently used in chemical and electrochemical oxidation copolymerizations with thiophene monomers to afford a polystyrene-*graft*-polythiophene (PSt-*g*-PTh) copolymer using “grafting from” methodology. The growth of thiophene onto functionalized polystyrene enhanced its solubility, and processability compared with pure polythiophene. The conductivity and electroactivity measurements showed that the PSt-*g*-PTh graft copolymer has lower electrical conductivity and electroactivity than those of the pure PTh. However, the lower electrical conductivity and electroactivity levels in this material can be improved at the price of solubility, and processability. As a result, we envision that the synthesized PSt-*g*-PTh graft copolymer could find applications in optoelectronic devices, electronic packaging, and corrosion protection due to its good redox, conductivity, solubility, and processability properties.

Acknowledgements

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Chemical and electrochemical grafting of polythiophene onto polystyrene synthesized *via* ‘living’ anionic polymerization

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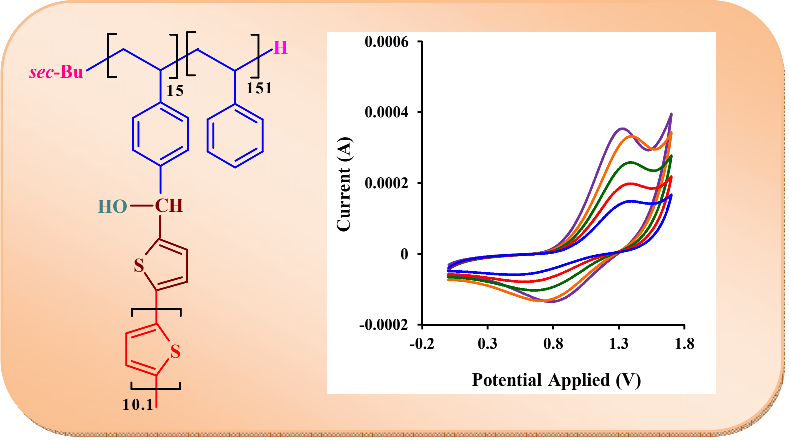

A novel strategy for chemical and electrochemical grafting of polythiophene onto a polystyrene backbone synthesized *via* ‘living’ anionic polymerization is reported. The number average molecular weights of PSt, and PSt-*g*-PTh graft copolymer were found to be 17300, and 29700 gmol^{-1}, respectively, from gel permeation chromatography (GPC).

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