Conducting Copolymers of Polytetrahydrofuran and Their Electrochromic Properties

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ABSTRACT: Living polytetrahydrofuran (PTHF) was terminated with sodium thiophene methonate to yield a polymer with a thiophene group at one end. Copolymerizations of PTHF with pyrrole and thiophene were achieved in water-*p*-toluene sulfonic acid and acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couples via constant potential electrolyses. Characterizations of the samples were performed by NMR, cyclic voltammetry, FT-IR, thermal analyses, and scanning electron microscopy. Electrical conductivities were measured by the four-probe technique. PTHF/PTh film that was deposited on ITO-glass in a dichloromethane-TBAFB solvent-electrolyte couple was found to exhibit electrochromic behavior and it electrochemically switches between blue oxidized and red reduced states. Optical analyses were carried out to investigate the electronic structure of PTHF/PTh electrochromic copolymer. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1014–1023, 2005

Key words: conducting polymers; polypyrrole; living polymerization; polytetrahydrofuran; electrochromic copolymers

INTRODUCTION

Conducting polymers are materials that exhibit the electrical and optical properties of metals or semiconductors and retain some of the mechanical properties and processing advantages of polymers.[1] These materials with conjugated Π-electron backbones display unusual electronic properties such as low-energy optical transitions, low ionization potentials, and high electron affinities; thus they can be oxidized or reduced more easily and more reversibly than conventional polymers. They could be p- or n-doped either electrochemically or chemically to the metallic state. The electrochemical polymerization has been extensively studied because it allows the formation of homogeneous freestanding films with good environmental stability and conductivity.[2]

Conducting polymers have been extensively studied in the past 3 decades and used for technological applications due to their stability, processibility, and low cost. Present and potential future applications include membranes,[3] light-emitting diodes,[4] enzyme immobilization,[5] electromagnetic interference shielding,[6] rechargeable batteries,[7] sensors,[8] and electrochromic displays.[9,10]

Various methods such as introducing alkyl groups into the main chain, synthesis of soluble precursors, the preparation of conducting polymer composites, blends, and copolymers can be used to improve mechanical properties of conducting polymers. Electropolymerization of the conducting component on an electrode previously coated with insulating polymer is one of the most widely used methods for that purpose. Polystyrene,[11] poly(methyl methacrylate),[12] polysiloxanes,[13] and polytetrahydrofuran (PTHF)[14] were previously used as the host matrices.

Macromonomers, macroinitiators, functional polymers, and block and graft polymers with a well-defined structure could be synthesized using the living polymerization technique. Controlled polymerization proceeds by anionic or cationic group transfer or radical mechanism. Cationic living ends could be quenched with electrochemically polymerizable thiophene moieties, thus allowing the preparation of polymers with the desired functional groups.[15–18]

Conducting polymers exhibit a change in their optical spectra when they are exposed to a dopant. Electrochromism is the reversible and visible change in the absorbance of a material as a result of an electrochemical oxidation or reduction and it is closely related with the band gap of the polymer. The electronic band gap could be controlled structurally, which in turn controls the redox and optical properties of the material. The incorporation of electron-donating substituents onto a conjugated chain is a commonly employed strategy to decrease the polymer's oxidation potential by raising the energy of the valance band electrons, thus decreasing the energy of the electronic band gap.

Copolymerization by introducing new groups alters the existing structure and band gap, leading to absorbance at different wavelengths and colors. Among all conjugated polyheterocyclic polymers polythiophenes are of particular interest as electrochromic materials owing to their chemical stability, ease of synthesis, and derivatization.[19–22] Therefore, copolymers of polythiophene are promising as electrochromic materials.

Electrochemically grown conducting polyheterocycles are good candidates for electrochromic displays, since each polymer possesses two forms whose colors are different and there is high contrast between the two forms. During reduction and reoxidations thin films of polyheterocycles undergo a color change. Spectroelectroelectrochemical analysis and colorimetry are the methods employed to investigate electrochromic behaviors of polymers.

In this study the living ends of PTHF were terminated with sodium thiophene methonate to yield a polymer with a thiophene group at one end. Then, copolymers of PTHF with pyrrole and thiophene were synthesized electrochemically in two different solvent-electrolyte couples, water-p-toluene sulfonic acid (PTSA) and acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB). Characterization of the films was done by NMR, cyclic voltammetry, FT-IR, TGA, DSC, and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Pyrrole (Py) and thiophene (Th) were distilled before use and stored at 4°C. Dichloromethane and acetonitrile (AN) were used without further purification. TBAFB PTSA were used as received.

Synthesis of thiophene terminated PTHF

Synthesis of thiophene methonate.

A solution of thiophene methanol (1.52 g, 13 mmol) in dry THF (30 mL) was added to a solution of NaH (0.50 g, 60% in oil, 12.3 mmol) in dry THF (20 mL) at room temperature under nitrogen atmosphere. The resulting solution was stirred at room temperature for 2 h. After removal of THF by rotary evaporation, the solution was dried in vacuum oven. An orange solid
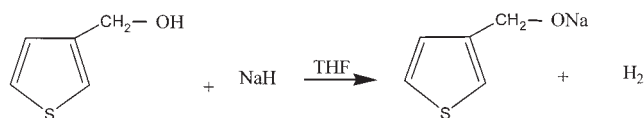
Scheme 1
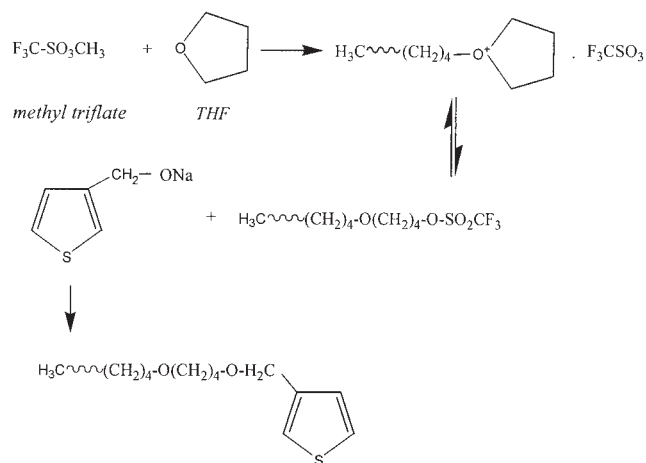
Scheme 2

product was obtained. The schematic representation of synthesis is demonstrated in Scheme 1.

Synthesis of PTHF having thiophene moiety at one end

A polymerization flask equipped with a nitrogen inlet and a magnetic stirrer was flushed with dry nitrogen. Then 10 mL of freshly distilled THF was introduced with a syringe. The polymerization was started at room temperature by injecting methyl triflate (0.097 mL, 8.9×10^{-4} mol) as the initiator. After 30 min, an aliquot was taken out from the reaction vessel and terminated by methanol. The rest was terminated with excess sodium thiophene methonate (8.9×10^{-3} mol), and the solution was stirred for additional night. The polymerization mixture was precipitated in methanol and cooled. The precipitated polymer was filtered off and dried in a vacuum. Scheme 2 shows the route for the synthesis of PTHF. The properties of synthesized PTHF are given in Table I.

Cyclic voltammetry (CV)

The oxidation/reduction behavior of PTHF was investigated in the presence of pyrrole and thiophene by CV. The system consists of of a HEKA potentiostat, an

TABLE I
Synthesis of Polytetrahydrofuran with Thiophene Moiety at One End

Code	M_n(GPC)[b]	M_w/M_n
PTHF[a]	9050	1.27

[a] THF, 10 ml; methyl triflate, 8.89×10^{-4} mol; sodium thiophene methonate, 8.89×10^{-3} mol; 25°C, 1 h.
[b] Determined by GPC with the calibration using polystyrene standards.

X-Y recorder, and a CV cell containing Pt-foil working and counterelectrodes and a Ag/Ag$^+$ reference electrode. Measurements were performed in an AN-TBAFB solvent-electrolyte couple under nitrogen atmosphere by coating the working electrode with PTHF-dichloromethane solution (1 w/v %).

Syntheses of conducting copolymers of PTHF with pyrrole and thiophene (PTHf/PPy1, PTHf/PPy2, PTHf/PTh)

Copolymer films of PTHF were synthesized electrochemically under nitrogen atmosphere in a conventional three-electrode cell using platinum (Pt) electrodes as the working and counterelectrodes. An Ag/Ag$^+$ was utilized as the reference electrode. Constant potential was supplied by a Wenking POS 73 potentiostat.

Before copolymerization processes, both sides of the working electrode were coated with PTHF-dichloromethane (1 w/v %) solution. The syntheses of PTHF/PPy1 and PTHF/PPy2 conducting copolymers were accomplished in water-PTSA and AN-TBAFB, respectively. Electrolyses in the presence of 0.02 M pyrrole were conducted at +1.1 V for water-PTSA (0.05 M) and AN-TBAFB (0.05 M) media. Electrolyses in the presence of 0.02 M thiophene were conducted at +2.0 V for AN-TBAFB (0.05 M) medium.

After electrolysis, black copolymer films on the working electrode were washed several times with dichloromethane to remove electrolytes as well as unreacted pyrrole and PTHF and then dried at room temperature to peel off from the electrode surface.

Characterization

^{1}H-NMR spectra of the pristine polymers were taken by a Bruker Instrument NMR Spectrometer (DPX-400) with tetramethylsilane as the internal standard. FT-IR spectra of the products and samples were recorded on a Nicolet 510 FT-IR spectrometer to detect the functional groups. Thermal behaviors of the films were analyzed by a Dupont 2000 thermal gravimetry analyzer and a Dupont 2000 differential scanning calorimeter at a heating rate of 10°C under N$_2$ atmosphere. Surface morphologies were inspected by a JSM-6400 scanning electron microscope. An HP 8453 diode-array UV-VIS spectrophotometer was employed in spectroelectrochemical studies. Conductivity measurements were performed by the four-probe technique.

Syntheses of films for spectroelectrochemical analyses

The copolymer film was potentiostatically (+2.3 V versus Ag/Ag$^+$, ITO working electrode, Pt counterelectrode) deposited from a solution of 10 mM PTHF

and 10 μL Th in dichloromethane-TBAFB (0.1 M) solvent electrolyte-couple on an indium tin oxide-coated glass slide. After electrochemical polymerization, anodically coloring film was switched between the fully oxidized and fully reduced states in acetonitrile-TBAFB. UV-VIS-NIR spectra of the film were recorded at various potentials in ACN/TBAFB (0.1 M).

Colorimetry analysis

Colorimetry analysis was run to transform the description of color from a subjective manner to an objective quantitative nature. To assign a quantitative scale to color measurements, the 1976 $L^*a^*b^*$ CIE Color Space System was chosen because of its common use in industry. The L value defines the brightness whereas the a and b values define hue and saturation, respectively. The films prepared for spectroelectrochemical studies were switched in ACN/TBAFB (0.1) and their colors at fully reduced and oxidized states were read by GretagMacbeth Color-eye XTH.

RESULTS AND DISCUSSION

^{1}H-NMR spectroscopy

^{1}H-NMR spectra were taken with CDCl$_3$ and DMSO-d$_6$ as the solvents. The ^{1}H-NMR spectrum of PTHF in CDCl$_3$ is shown in Figure 1. The signals at f (1.5 ppm) and e (3.5 ppm) arise due to the existence of two types of methylene protons in the structure, inner groups and OCH$_2$ groups, respectively. Peak d (4.5 ppm) implies the presence of protons of β methylene groups of thiophene. The ^{1}H-NMR spectrum of PTHF was also taken in DMSO-d$_6$ to detect the peaks that were obscured by CDCl$_3$. Peaks a, b, and c observed in DMSO-d$_6$ correspond to three protons on thiophene rings. ^{1}H-NMR results reveal that the preassumed structure was obtained.

Cyclic voltammetry

The absence of any redox peaks for PTHF (coated on Pt) indicates that the pristine polymer is not electroactive. After Py was introduced into the solution, an increasing redox peak revealing an increase in electroactivity with increasing scan number was observed (Figure 2b). A similar trend was observed upon addition of Th into the solution with the PTHF-coated electrode (Figure 2d). The voltammograms of the systems with PTHF resemble those of pure PPy and PTh due to the electroinert nature of the pristine polymer. However, the peaks of voltammogram b and d do not increase in height as do the ones in voltammograms a and c. This may be due to the fact that pyrrole reacts with the thiophene moiety of PTHF (Figure 2b) and similarly, thiophene reacts with the thiophene moiety
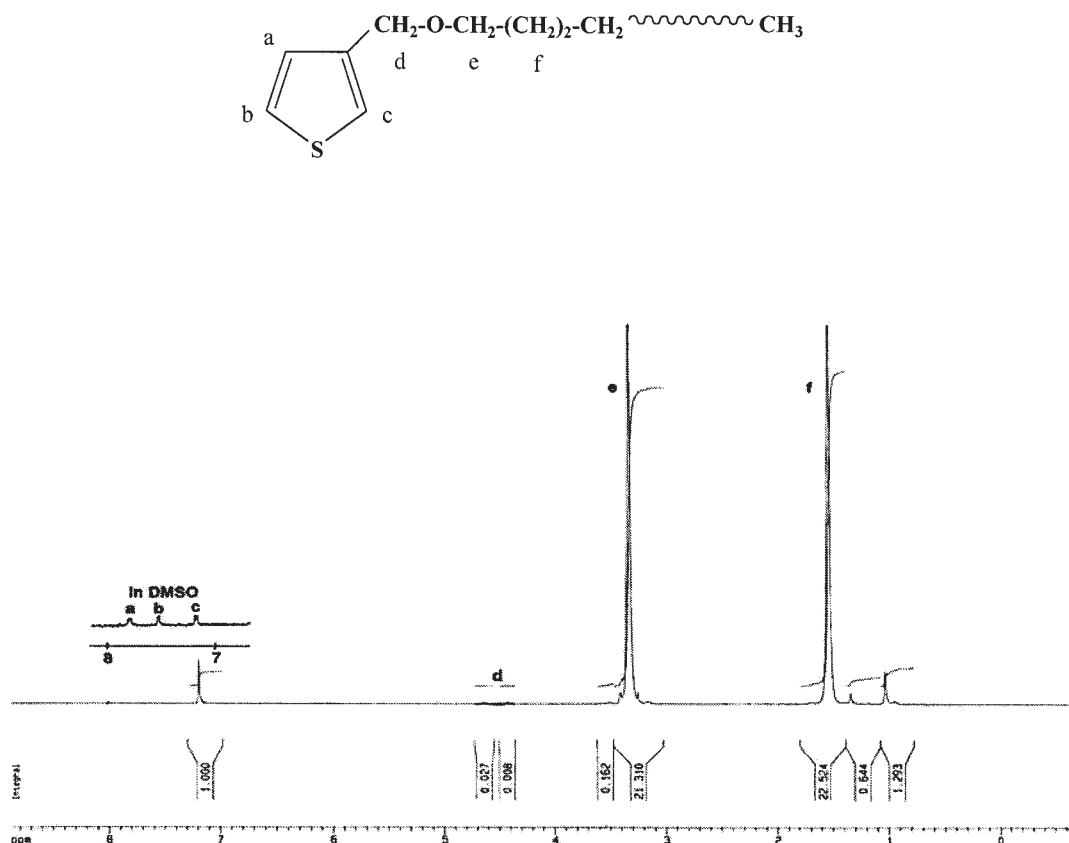
Figure 1 ^{1}H-NMR spectrum of PTHF.

of the PTHF (Figure 2d). To conclude on the process further, characterization methods were utilized.

FT-IR

FT-IR experiments were first performed for insulating polymer PTHF and a characteristic C-O-C asymmetric stretching was detected at 1111 cm^{-1}. Three peaks between 2750 and 3000 cm^{-1} arose as a result of aliphatic CH$_2$ vibrations. A weak peak of aromatic C = C stretching at 780 cm^{-1} points to the presence of Th moieties at the ends. To investigate copolymers, tetrabutylammonium hexafluorate was also used as the electrolyte (PF$_6^-$ dopant anion), with a characteristic peak at 840 cm^{-1} to synthesize PTHF/PPy2 and PTHF/PTh films and low dopant concentration (10^{-3} M) was used to synthesize PTHF/PPy1 films since BF$_4^-$ and PTS$^-$ exhibit intense peaks at higher concentrations (0.05 M) that may obscure the characteristic bands around 1100 cm^{-1}. All copolymer spectra exhibited the characteristic peaks of pristine polymers. In PTSA doped copolymers the appearance was crowded between 1600 and 500 cm^{-1}. In all PPy copolymers a characteristic band of Py, N-H wagging at about 900 cm^{-1} was observed. The attenuated peaks at 780 cm^{-1} in PTh copolymer spectra prove the 2, 5

disubstitution on the Th ring by improving the idea of copolymerization.

Conductivities of the films

For both PTSA- and TBAFB-doped copolymer films, the conductivities of both solution and electrode sides were measured. Almost equal conductivities of the solution and electrode sides for both PTSA and TBAFB-doped copolymer films indicate the homogenity of the films, at least in terms of conductivity. In the view of conductivity data reported for PPy and PTh we may conclude that a new product, most probably a copolymer, was obtained at a small expense of electrical conductivity. The results of conductivity measurements are shown in Table II.

Thermal properties

The DSC thermogram of PTHF was obtained via heating from 0 to 100°C, revealing a sharp peak at 46°C as the melting point (Figure 3a). Pure PPy doped with PTSA yields two endotherms at 89 and 341°C. PTHF/PPy1 showed two endotherms at 82 and 330°C due to loss of solvent and dopant removal (Figure 3b). Pure PPy doped with TBAFB yields two endotherms at 107
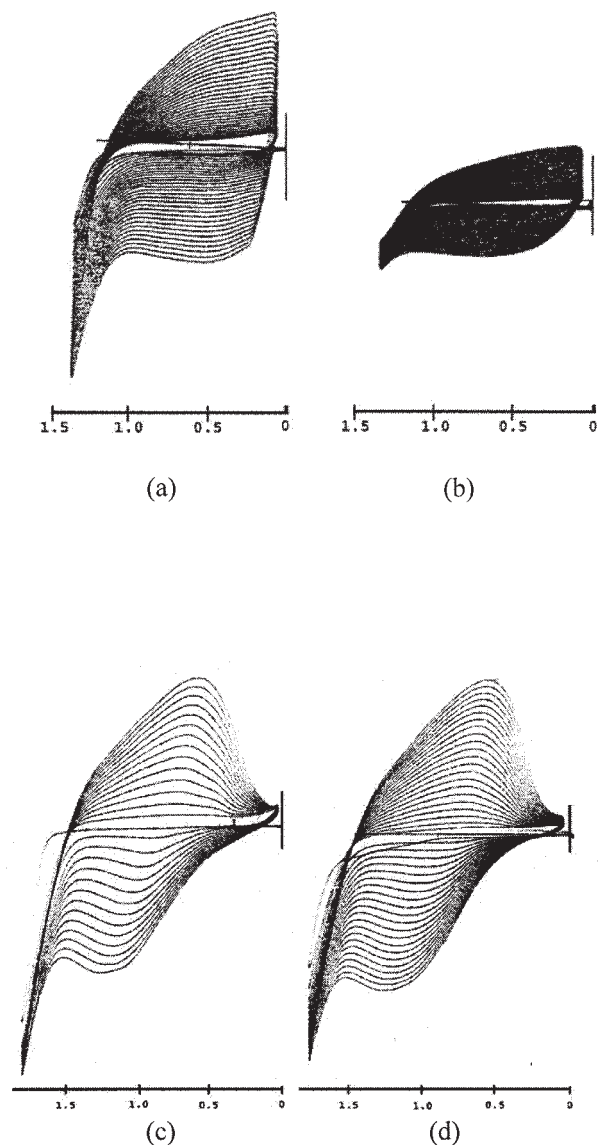
Figure 2 Cyclic voltammograms of (a) TBAFB-doped PPy (40 runs), (b) PTHF/PPy2 (30 runs), (c) TBAFB-doped PTh (15 runs), (d) PTHF/PTh (22 runs).

and 227°C and it is stable up to 480°C. Three endotherms observed for PTHF/PPy2 at 88, 183, and 296°C may be attributed to removal of the solvent, unreacted components, and dopant anion, respectively (Figure 3c). PTHF/PTh had two endotherms at 88 and 280°C, due to extraction of solvent and dopant anion removal (Figure 3d). Pure PTh is highly heat resistant and the main heat exchange is observed at at 296°C while solvent removal takes place at 91°C. The behavior of the new materials is quite different from that of either PPy (or PTh) or pristine polymer. All copolymers revealed very different curves than those of pure PPy, PTh, and pristine polymers. The melting transition around 46°C was not observed in DSC curves of the copolymers. All shifts from pure cases may reveal the fact that new structures are formed.

The thermogravitmetry scan of PTHF showed stability against heating up to 230°C, after which it lost weight to a 1% remaining (Figure 4a). PTHF/PPy1 showed two weight loss patterns at 71 and 348°C with 54% char residue (Figure 4b). A drastic weight loss is observed at 113 and 347°C to a remaining of 58% for pure PTSA-doped Ppy; thus the loss at 347°C might be attributed to the removal of dopant ion. The thermal resistivity of copolymer showed similiar behavior with pure PPy. Two weight loss patterns were observed for PTHF/PPy2 at 248 and 321°C and the weight loss observed at 743°C may be attributed to removal of nonvolatile dopant and char (Figure 4c). When compared to BF_4^- doped pure PPy, the trends were similiar except for some shifts in decomposition temperatures. The main loss observed in pure PPy at 276°C and the decomposition at 248°C in PTHF/PPy2 were most probably due to loss of dopant. BF_4^- doped pure PTh lost most of its weight at 210°C, indicating that a similar component exists in the structure of PTHF/PTh at 243°C, which is expected from the dopant decomposition (Figure 4d). Large differences in the values for char residues draw attention. While it is nearly 15% for pure PTh, it is 55% in the copolymer PTHF/PTh at the same temperature. We may conclude that the copolymer formed is more resistant to heat compared to PTh.

The consistency between weight loss patterns obtained from thermogravimetric analyses and heat flow behaviors detected by differential scanning calorimetry (DSC) analyses confirms the formation of copolymers with different thermal properties.

Morphologies of the films

It is known that PPy has a smooth appearence at the electrode side and a cauliflower-like structure at the solution side of the film. The type of the dopant only affects the sizes of the grains, and they are larger in the case of TBAFB. For PTHF/PPy1, the electrode surface is not as smooth as that of PPy (Figure 5a). At the solution side small globules of PPy come together with a chain-like structure forming voids in between (Figure 5b). For PTHF/PPy2, in addition to the interwoven appearance of the electrode side, a worm-like structure was observed at the solution side, which highly deviates from the cauliflower structure of PPy (Figures 5c) and d). SEM micrographs of PTHF/PTh
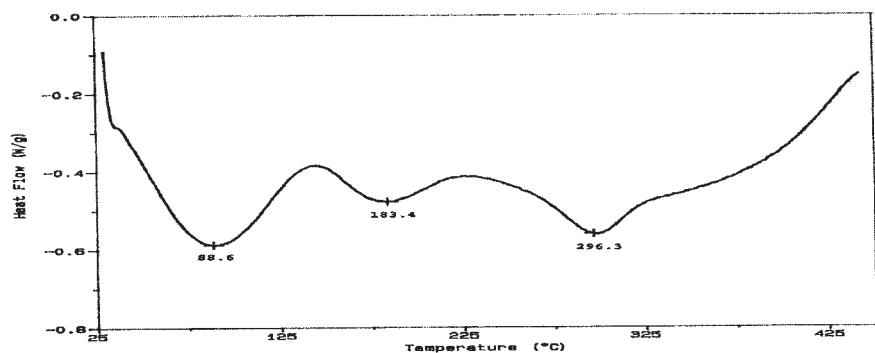
TABLE II
Conductivities of the Films

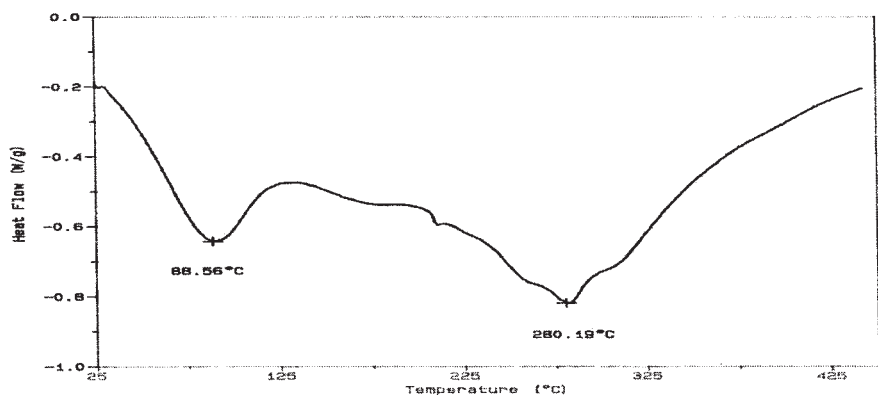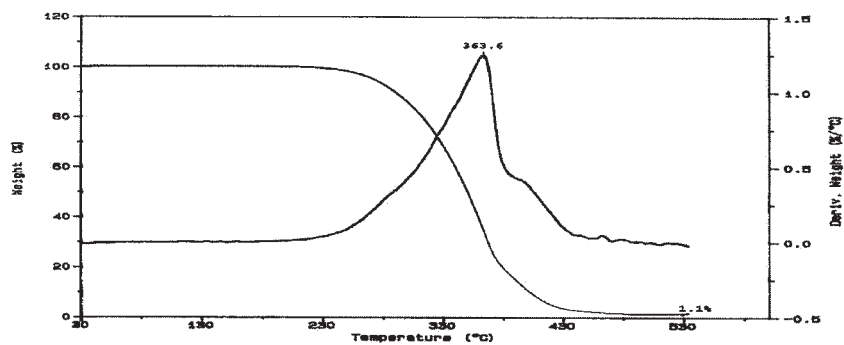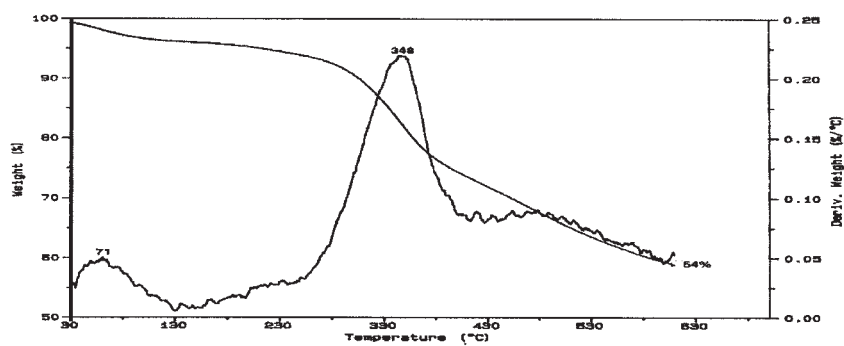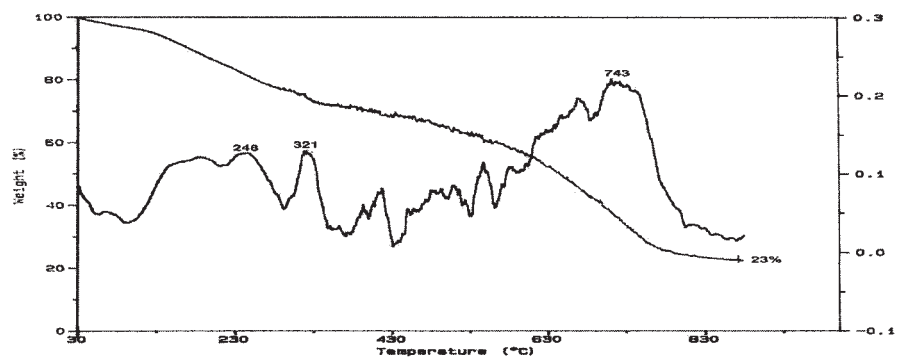| Polymers	Conductivities (S/cm)
PTHF/PPy1	2×10^{-2}
PTHF/PPy2	3×10^{-3}
PTHF/PTh	3×10^{-3}
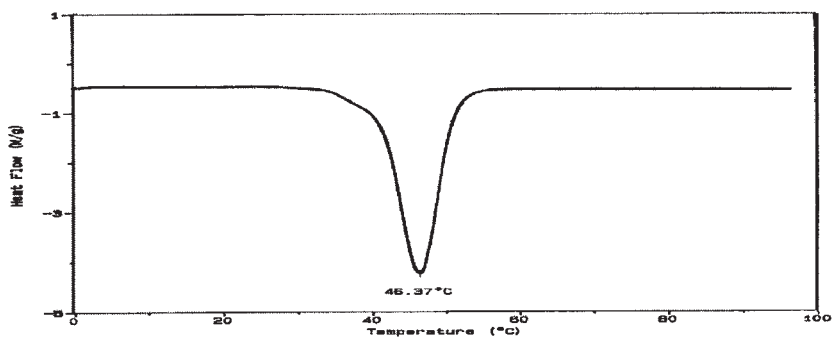
(a)
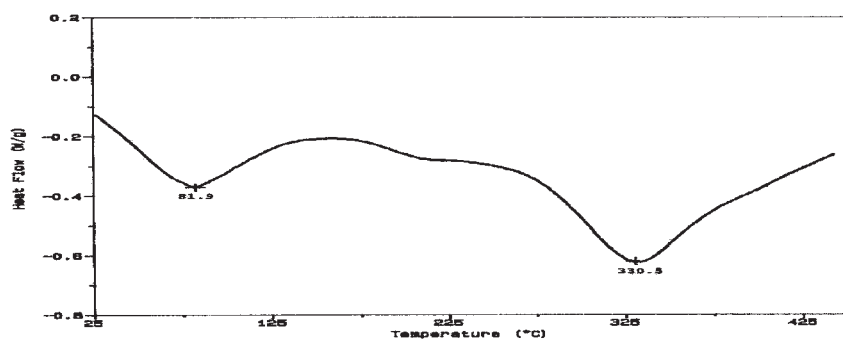
(b)

(c)

(d)

Figure 3 DSC thermograms of (a) PTHF, (b) PTHF/PPy1, (c) PTHF/PPy2, (d) PTHF/PTh.
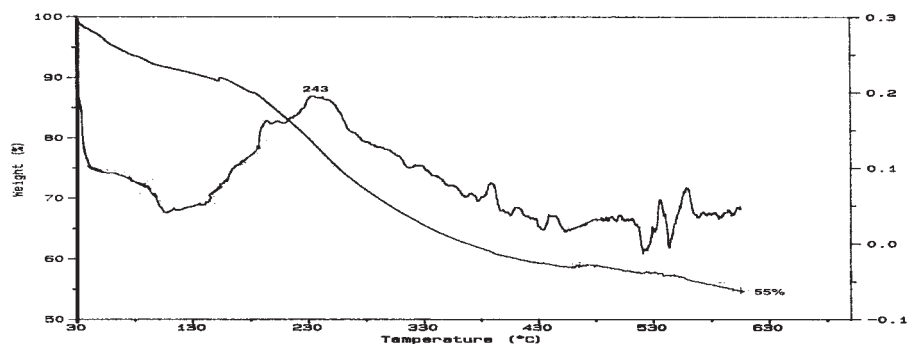
(a)

(b)

(c)

(d)

Figure 4 TGA thermograms of (a) PTHF, (b) PTHF/PPy1, (c) PTHF/PPy2, (d) PTHF/PTh.
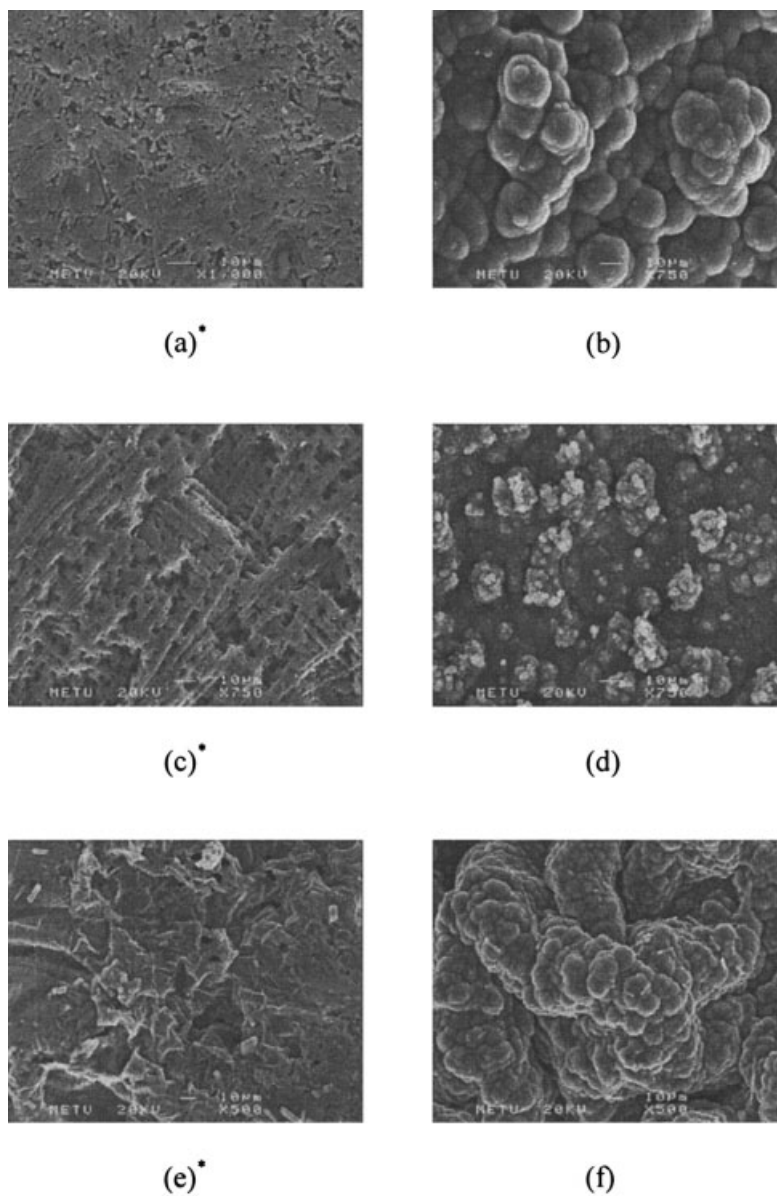
Figure 5 SEM micrographs (a)* PTHF/PPy1, (b) PTHF/PPy1, (c)* PTHF/PPy2, (d) PTHF/PPy2, (e)* PTHF/PTh, (f) PTHF/PTh.* electrode sides.
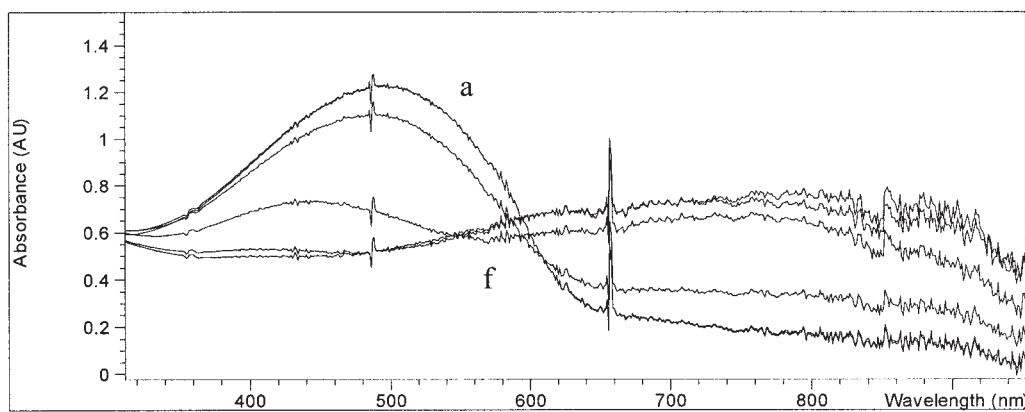

Figure 6 Spectroelectrochemistry of PTHF/PTh, potentials applied (V): a, 0.2; b, 0.6; c, 1.0; d, 1.6; e, 1.8; f, 2.0

TABLE III
Electrochemical, Electronic, and Electrochromic Properties of PTh and PTHF/PTh

	E_{pa}[a]	E_{pc}[a]	$\lambda_{max(nm)}$	L	a	b	E_g (eV)
PTh	0.63	0.58	495	(ox) 57	(ox) −7	(ox) −2	1.92
				(red) 51	(red) 52	(red) 46	
PTHF/PTh	1.4	0.6	495	(ox) 54	(ox) −10	(ox) −7	1.88
				(red) 57	(red) 36	(red) 19	

Note. ox, oxidized state; red, reduced state.
[a] Volts vs Ag/Ag$^+$.

showed that PTh grows uniformly in the host polymer and the crests are hilly rather than for clear cauliflower, which reveals that there is a certain chemical interaction other than a simple physical adhesion in between the two polymers (Figures 5e and f). Holes in those washed films are related to the loss of ungrafted precursor polymers, which are popped out to let the dissolved and ungrafted component leave the film. The presence of PTHF changes the film morphology of resultant polymers.

Spectroelectrochemistry

The electrochemical spectra PTHF/PTh are shown in Figure 6. The graft copolymer PTHF/PTh shows distinct $\Pi \rightarrow \Pi^*$ transitions with band gap onset of 1.88 eV (660 nm) and peak at 2.51 eV (495 nm). Stepwise oxidation from (0.0 to 2.0 V) of the polymers shows a reduction in absorbance in the visible region as the color changes from red (fully reduced state) to blue (highly oxidized state). PTHF/PTh exhibits two distinct reversible colored states. This redox switching of polymer was reversible over multiple cycles (300).

Colorimetry analyses

L*a*b values of the films were measured at the fully reduced and fully oxidized states and the data are presented in Table III. The PTHF/PTh copolymer was pale blue at its fully oxidized state while pure PTh was blue. This difference may be attributed to the depletion of π-π^* transitions and the increase in the absorbance of the lower energy charge carrier transitions. This relatively small variation in color supports optical data that suggest a small difference in the polymer band gap, which is close to 2 eV for most of the conducting polymers. Copolymerization, by introducing new component into the structure, decreases the value of the band gap to a certain extent in the case of PTHF/PTh. Films are seen to exhibit disitinctive color changes upon doping and dedoping and this fact was confirmed by the differences in L*a*b values of pure PTh and PTHF/PTh.

CONCLUSION

In this work living polytetrahydrofuran was terminated with thiophene, which can be electropolymerized through 2 and 5 positions of the thiophene moiety. Conducting graft copolymers of PTHF in the presence of either pyrrole or thiophene were synthesized electrochemically in two different solvent-electrolyte couples. CV analyses showed that pure PPy (or PTh) and copolymers were not different from each other in regard to their electroactivities. FT-IR spectra of the copolymer films showed the characteristic bands of insulating polymer and PPy (or PTh), even after washing, revealing the chemical interaction between the polymers. Use of different electrolytes resulted in different thermal behavior, surface morphology, and electrical conductivity. Properties of the films were considerably different from that of pure PPy and PTh synthesized under the same conditions. Optical analyses of PTHF/PTh films support the idea that electrochromic copolymers that could be used in electrochromic devices were obtained. In the frame of characterization results we believe that PPy and PTh grow through the thiophene moieties of the insulating polymers.

References

1. Heeger, A. J. J. Phys Chem 2001, 105, 8475.
2. MacDiarmid, A. G., Angew Chem Int Ed 2001, 40, 2581–2590.
3. Gül°en, D.; P. Hacarlıoğlu, P.; Toppare, L.; Yılmaz, L. J Membr Sci 2001, 182, 29.
4. Wang, J.; Sun, R. G.; Yu, G.; Heeger, A. J., Synth Met 2003, 137, 1009.
5. Reyhan Erginer, R.; Toppare, L.; Alkan, S.; Bakir, U. React Funct Polym 200, 45, 227–233.
6. Dhawan, S. K.; Singh, N.; Venkatachalam, S. Synth Met 2002, 129, 261.
7. Gurunathan, K.; Murugan, A. V.; Marimuthu, R.; Mulik, U. P.; Amalnerkar, D. P. Mater Chem Phys 1999, 61, 173.
8. Gerard, M.; Chaubey, A.; Malhotra, B. D. Biosens Bioelectron 2002, 17, 345.

9. Sapp, S. A., Sotzing, G. A.; Reynolds, J. R. Chem Mater 1998, 10, 2101.
10. Rosseinsky, D. R.; Mortimer, R. J. Adv Mater 2001, 13, 11.
11. Alkan, S.; Toppare, L.; Hepuzer, Y.; Yağcı, Y. Synth Met 2001, 119, 133.
12. Alkan, S; Toppare, L.; Bakır, U.; Yağcı, Y. Synth Met 2001, 123, 95.
13. Kalaycıoğlu, E.; Toppare, L.; Yağcı, Y.; Harabagiu, V.; Pintela, M.; Ardelean, R.; Simionescu, B. C. Synth Met 1998, 97, 7.
14. Öztemiz, S.; Toppare, L.; Önen, A.; Yağcı, Y. Pure Appl Chem 2000 37, 277–291.
15. Kızılyar, N.; Toppare, L.; Önen, A.; Yağcı, Y. J Appl Polym Sci 1999, 71, 713.
16. Özdilek, C.; Toppare, L.; Yağcı, Y.; Hacaloğlu, J. J Anal Appl Pyrol 2002, 64, 363.
17. Kızılyar, N.; Toppare, L.; Önen, A.; Yağcı, Y. Polym Bull 1998, 40, 639.
18. Çırpan, A.; Alkan, S.; Toppare, L.; Hepuzer, Y.; Yağcı, Y. J Polym Sci A Polym Chem 2002, 40, 4131.
19. Kumar, A.; Reynolds, J. R. Macromolecules 1996, 29, 7629.
20. Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. Chem Mater 2000, 12, 1563.
21. Bois, C. J. D; Larmat, F.; Irvin, D. J.; Reynolds, J. R. Synth Met 2001, 119, 321.
22. Sankaran, B.; Reynolds, J. R. Macromolecules 1997, 30, 2582.