*Polymer International*

*Polym Int* **52**:172–178 (2003)
DOI: 10.1002/pi.1016

# Grafting polythiophene on polyethylene surfaces

N Chanunpanich,[1,2] A Ulman,[1,2]* YM Strzhemechny,[2,3] SA Schwarz,[2,3] J Dormicik,[2,4] A Janke,[5] HG Braun[5] and T Kratzmüller[5]

[1] *Department of Chemical Engineering, Chemistry and Materials Science, Polytechnic University, Brooklyn, New York 11201, USA*
[2] *The NSF MRSEC for Polymers at Engineered Interfaces, State University of New York at Stony Brook, NY 11794-2275, USA*
[3] *Department of Physics, Queens College of CUNY, Flushing New York 11367, USA*
[4] *Department of Materials Sciences and Engineering, State University of New York at Stony Brook, NY 11794-2275, USA*
[5] *Institute for Polymer Research, Hohe Strasse 6, D-01069 Dresden, Germany*

**Abstract: Polythiophene (PT) was grafted on PE film using three reaction steps. First, PE films were brominated in the gas phase, yielding PE–Br; second, a substitution reaction of PE–Br with 2-thiophene thiolate anion gave the thiophene-functionalized PE; finally PT was grafted on the PE surface using chemical oxidative polymerization to give PE–PT. The polymerization was carried out in a suspension solution of anhydrous $FeCl_3$ in $CHCl_3$, yielding a reddish PE–PT film after dedoping with ethanol. ATR-FTIR shows that the PT was grafted on PE in the 2,5-position. SEM imaging revealed islands of PT on the PE film. AFM analysis found the thickness of islands to be in the range of 120–145 nm. The conductivity of these thin films was in the range of $10^{-6}$ S cm$^{-1}$, a significant increase from the value of $\sim 10^{-14}$ S cm$^{-1}$ measured for PE film.**

**Keywords:** surface modification; polyethylene; polythiophene; bromination; grafting

## INTRODUCTION

During the past 10 years, there has been growing interest in electrically conducting polymers due to their potential applications.[1] Among these polymers, polythiophene (PT) has attracted interest because of its high magnetic and optical properties, electrical conductivity and environmental stability (both to oxygen and to moisture).[2] PT films can be prepared both by an electrochemical reaction and by oxidative polymerization of thiophene. The electrochemical polymerization of PT is carried out in an organic solvent such as acetonitrile, nitromethane, nitrobenzene or propylene carbonate.[3]

Polyethylene (PE) is one of the most interesting commodity polymers. However, it exhibits low surface energy, and various different methods have been developed to increase surface energy. Reports on the modification of PE surfaces include chemical reactions with contacting solutions,[4] corona discharge treatment,[5] plasma or glow discharge treatment[6] and surface grafting of hydrophilic monomers after photo-irradiation.[3–5,7] Plasma treatments utilizing $N_2$,[8] $NH_3$,[9] $CCl_4$,[10] $CF_3Cl$,[11] or $CHBr_3$,[12] have been carried out in attempts to introduce different surface chemical functionalities.

Recently, we reported that bromination of PE films improves their wettability.[13] Amino-terminated PE films (PE—S—Ph—$NH_2$) were obtained using 4-aminothrophenolate as a nucleophile to substitute the surface bromide groups. Later we reported analogous surface substitution reactions using other aromatic thiols.[14] There, we demonstrated the grafting of thiophene thiol on PE films (PE–S–T), using the corresponding thiolate nucleophile. These films can be used, in principle, as substrates in oxidative polymerization with thiophene, to produce PE films grafted with polythiophene. Here we report on the oxidative polymerization at PE–S–T surfaces using a suspension of anhydrous iron(III) chloride ($FeCl_3$) in dry chloroform ($CHCl_3$) and thiophene. The resulting films were characterized using ATR-FTIR spectroscopy, XPS, SEM, AFM, UV–vis spectroscopy and conductivity measurements.

## EXPERIMENTAL

### Chemicals

Low-density polyethylene (LDPE) was purchased from Acros Organic. 2-mercaptothiophene was purchased from Maybridge Chemical Co. Bromine, thiophene, anhydrous iron(III) chloride and sodium

---

* Correspondence to: A Ulman, Department of Chemical Engineering, Chemistry and Materials Science, Polytechnic University, Brooklyn, New York 11201, USA
E-mail: aulman@duke.poly.edu

Contract/grant sponsor: NSF, MRSEC for Polymers at Engineered Interfaces
(*Received 15 July 2001; revised version received 1 February 2002; accepted 12 April 2002*)

metal were obtained from Fluka. All solvents were analytical grade and purchased from Fisher Scientific.

### PE film preparation

LDPE films were pressed from the pellet. The procedure and clean-up of the films were reported elsewhere.[13]

### Bromination

PE films were brominated by exposure to saturated bromine vapor and irradiation with short-wavelength UV light. The conditions and details of the procedure were reported elsewhere.[13]

### Substitution reactions with 2-thiophenethiolate

In a typical experiment, PE–Br samples were immersed in 10 ml of 0.025 M sodium 2-thiophenethiolate solution in *N,N*-dimethylformamide (DMF), at 33 °C for 20 h. The product films (PE–S–T) were washed several times with DMF, followed by absolute ethanol to remove the sorbed 2-thiophenethiolate and NaBr byproduct. The films were light red in color.

### Oxidative polymerization

A suspension of 0.1 g of anhydrous $FeCl_3$ and 20 ml of dry $CHCl_3$ was vigorously stirred under a nitrogen atmosphere for 10 min at 20 °C. The dried PE–S–T films were introduced, followed by a thiophene solution (0.07 g in 5 ml dry $CHCl_3$). The mixture was stirred for 5 min and the films (PE–PT) were taken out and shaken with dry $CHCl_3$ several times to remove the sorbed PT oligomers and thiophene monomer. The films turned from green to red after dipping in ethanol.

### ATR-FTIR spectra

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra were recorded on Nicolet 760 spectrophotometer, equipped with an MCT detector. A zinc selenide Single Reflection setup was used with the incidence angle of 45°. The effective path length was 2.2 µm. Five hundred scans were collected on each sample and background, and PE film spectrum was subtracted in all cases. Transmission FTIR spectra were also recorded on the same apparatus.

### UV–vis spectra

UV–vis spectroscopy was performed on a computer-controlled Varian, DMS 100 spectrometer, using Origin software to evaluate the data

### X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained using a Kratos ES300 X-ray photoelectron spectrometer with a monochromatic Mg K$\alpha$ X-ray source (1253.6 eV photons). The hemispherical energy analyzer was operated in the fixed retardation ratio mode. The samples were mounted on standard sample studs by means of a double-sided adhesive tape. The pressure in the analysis chamber was at $\sim 10^{-8}$ torr during measurements. Core level S2p, O1s, and C1s spectra were monitored at an electron takeoff angle of 15°. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 285.0 eV. Deconvolution of complex peaks was performed using Origin non-linear curve fit software with the full width at half-maximum (fwhm) of Gaussian line shape of 1.3–1.4 eV. Quantitative measurements were made by correction of integrated peak intensities with the Scofield correction factors.[15] The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors, and may be subject to a maximum of ±20% error.

### Atomic force microscopy (AFM)

Topography images of PE-PT films were made using a Nano Scope III, Multimode-AFM from Digital Instruments, Santa Barbara, CA. The measurements were carried out in both tapping and friction modes.

### Scanning electron microscopy (SEM)

Scanning electron micrograph images of PE and PE-PT were obtained from a low voltage field emission SEM, Zeiss Gemini DSM 982, operated at an acceleration voltage of 1 kV.

## RESULTS AND DISCUSSION

Grafting of thiophene onto PE films is easily accomplished by a two-step reaction: bromination of PE films, followed by a substitution reaction with 2-mercaptothiophene in the presence of 50%, of 0.04 M sodium ethoxide in DMF. Bromination of PE films in the gas phase has been reported recently.[13] Since 2-mercaptothiophene and its anion do not dissolve well in ethanol, DMF was added to increase solubility. Sodium ethanolate was added at slightly sub-stoichiometric concentrations to produce the corresponding thiolate, and to avoid competition from dehydrobromination of PE–Br films (Fig 1).

The nucleophilic substitution reaction of PE–Br with 2-thiophenethiolate was carried out at 33 °C for 20 h, yielding a light-reddish PE–S–T film. The ATR-FTIR (Fig 2) spectrum of PE–S–T shows a characteristic peak at 1434 cm$^{-1}$ ($\nu$ C=C); a broad band at 1134 cm$^{-1}$ (stretching vibration of thiophene ring), a peak at 1018 cm$^{-1}$ ($\delta$ C—H in-plane vibration); and a peak at 806 cm$^{-1}$ ($\delta$ C—H$_\beta$ out-of-plane vibration).

The XPS high-resolution peak of S2p could be deconvoluted into four peaks (Fig 3), centered at 164.0 ± 0.1, 165.3 ± 0.2, 169.0 ± 0.2 and 170.1 ± 0.2 eV. The first two peaks were assigned to neutral

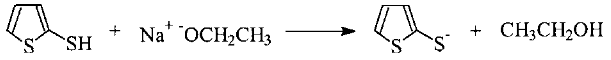

Figure 1. Preparation of 2-thiophenethiolate in sodium ethoxide solution.

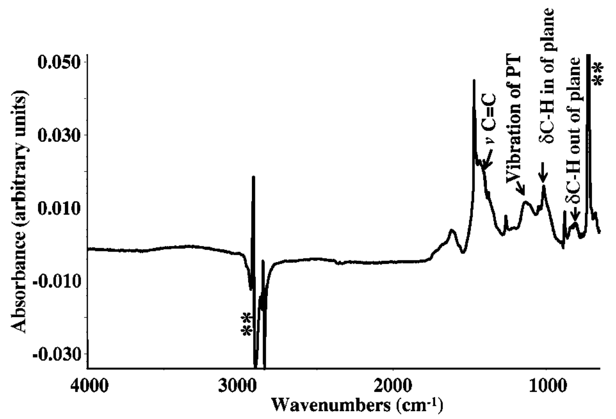

**Figure 2.** ATR-FTIR spectrum of PE–S–T after subtraction of the PE spectrum. Peaks marked with asterisks denote polyethylene peaks.

sulfur (S2p$_{3/2}$ and S2p$_{1/2}$),[16,17] while the peaks centered at 169.0 and 170.1 eV were assigned to S2p$_{3/2}$ and S2p$_{1/2}$ of the corresponding sulfone compound, which results from oxidation of the original PE–S–T films by air.[18,19] This is supported by the fact that if oxidative polymerization is carried immediately following PE–S–T film formation, only the 164–168 eV peaks appears in the XPS spectra.

Polythiophene and its derivatives can be synthesized by electrochemical[20,21] and by chemical polymerization. Since thiophene is not stable in protic acid media, Lewis acids are selected as oxidants. The strength of interactions between the solvent and the Lewis acid depends on the donor number of the solvent. This interaction increases with the increasing donor number; thus, the stronger the interaction, the weaker the acidity of the acceptor.[22] For example, $AlCl_3$ or $BF_3$ can initiate the additive polymerization of thiophene in nitromethane ($CH_3NO_2$, donor number 2.7)[23] resulting in non-conjugated chains. With a higher donor number solvent, such as acetonitrile ($CH_3CN$) or diethyl ether ($(C_2H_5)_2O$)—donor numbers 14.1 and 19.2, respectively—the solvation interactions increase and the acidity of the Lewis acid become too weak to initiate the additive polymerization of thiophene.

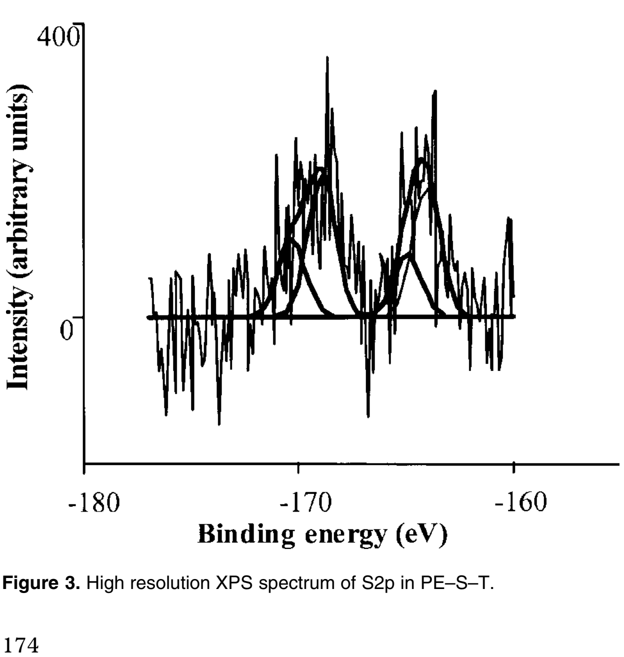

**Figure 3.** High resolution XPS spectrum of S2p in PE–S–T.

An inexpensive method of producing polythiophene is the oxidative polymerization of thiophene in a suspension solution of anhydrous $FeCl_3$ in dry chloroform ($CHCl_3$).[16,24] Niemi and coworkers[25] concluded that the polymerization starts from the solid $FeCl_3$. Hence, the active sites in the polymerization are the crystal $Fe^{3+}$ surface ions. These surface $Fe^{3+}$ ions have one unshared chloride and one empty orbital, which is the source of their Lewis acidity. The soluble part of $FeCl_3$ is inert because it exists in a dimeric form without empty orbitals.

Figure 4 shows the proposed mechanism for thiophene oxidative polymerization. The reaction starts by complexation between the thiophene sulfur and the $FeCl_3$ to form a cation radical, which upon deprotonation yields the initiating radical. The mechanism also proposes that the combination of thiophene radicals gives mainly the 2,5-disubstituted thiophene moieties in the PT chains.[21] The effective reaction needs a 4:1 mole ratio of $FeCl_3$: thiophene. This requirement is because the polymerization process requires solid $FeCl_3$, and 50% of the $FeCl_3$ dissolves in the $CHCl_3$. In addition, the HCl byproduct consumes $FeCl_3$ to form the $FeCl_4^-$ complex ion.

Homopolymerization also takes place in this reaction mixture, yielding a reddish PT powder after dedoping with ethanol. It has been established that chemical polymerization of thiophene can occurred via both the 2,5, and 2,4 positions. However, the FTIR spectrum of PT (Fig 5) clearly reveals that the reaction preferentially occurs at the 2,5-positions. The spectrum (transmission, KBr pellet) shows the appearance of 3064 cm$^{-1}$ ($\nu$ C—H$_\beta$) and 1634 cm$^{-1}$ bands (free carriers and metallic characteristics). Other characteristic peaks of 2,5-disubstituted PT are 1489 cm$^{-1}$, 1451 cm$^{-1}$ and 1432 cm$^{-1}$ ($\nu$ C=C); 1066 cm$^{-1}$ and 1037 cm$^{-1}$ ($\delta$ C—H in-plane); and 788 cm$^{-1}$ ($\delta$ C—H out-of-plane) which are in agreement with the literature.[26,27] However, a small amount of 2,4-coupling does exist, as is indicated by the appearance of a peak

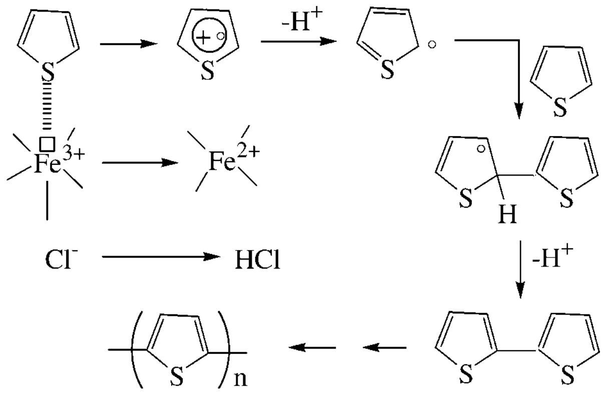

**Figure 4.** Proposed mechanism of thiophene oxidative polymerization with $FeCl_3$ in $CHCl_3$.

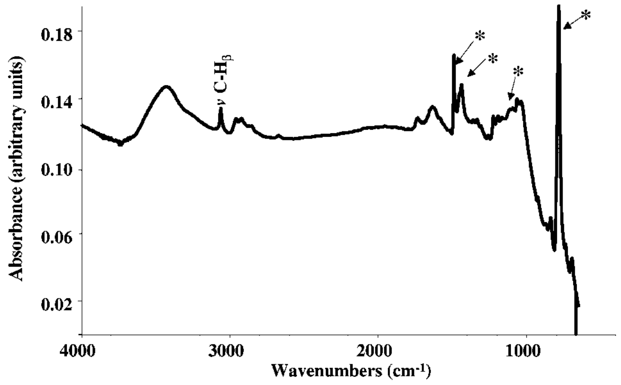

**Figure 5.** Transmission FTIR spectrum of PT powder in KBr. The asterisks denote characteristic bands for 2,5-disubstituted PT.

at 834 cm$^{-1}$. The small carbonyl peak at 1730 cm$^{-1}$ suggests that the PT chains may be terminated by carbonyl moieties, as has been observed by Hyodo and coworkers[28] in the electrochemical polymerization of pyrrole.

The oxidative polymerization of PE–S–T with $FeCl_3$ in $CHCl_3$ was carried out at 20 °C for 5 min, yielding a reddish film (PE–PT). The suspension solution of anhydrous $FeCl_3$ in $CHCl_3$ is green, indicating that part of the $FeCl_3$ was consumed by $CHCl_3$ and trace water to yield $FeCl_2$. Nitrogen gas was therefore bubbled through the solution to remove HCl before adding thiophene and PE–S–T. After adding PE–S–T and thiophene, the solution turned immediately dark green, indicating that the polymerization took place, yielding the dark green doped PT. However, after washing with $CHCl_3$ to remove thiophene monomer and soluble oligomers, following by dedoping with ethanol, the film turned from dark green to red. The ATR-FTIR spectrum (Fig 6) shows the appearance of a peak at 3064 cm$^{-1}$ (C—H$_\beta$ stretching); 1490 cm$^{-1}$ (C=C stretching); 1340 and 1200 cm$^{-1}$ (stretching vibration of PT ring); 1106–1020 cm$^{-1}$ (C—H in-plane bending); and 789 cm$^{-1}$ (C—H out-of-plane bending of 2,5-disubstituted PT). No evidence for 2,4-substitution could be detected, suggesting that the surface-initiated polymerization proceeds exclusively by 2,5 coupling.

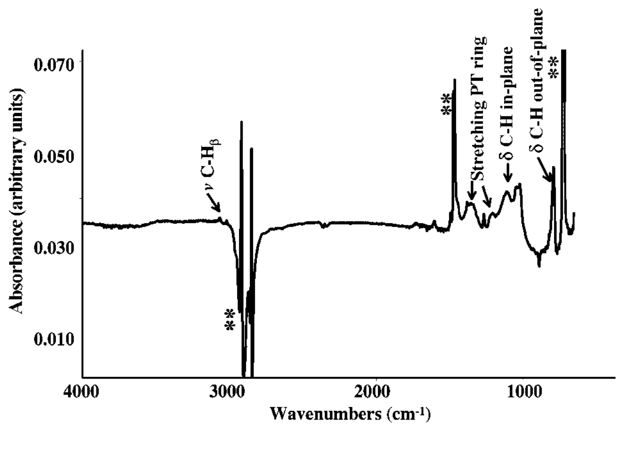

**Figure 6.** ATR-FTIR spectrum of PE–PT film. Peaks marked with asterisks are from polyethylene.

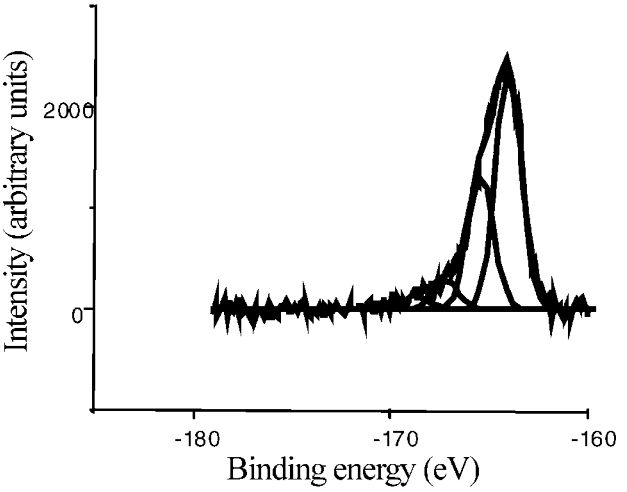

**Figure 7.** The S2p band in the high resolution XPS spectrum of PE–PT films.

The S2p band in the high resolution XPS of PE–PT could be deconvoluted into four peaks (Fig 7) centered at 164.1, 165.4, 166.5 and 167.5 eV. The first two peaks are assigned to neutral $S2p_{3/2}$, and $S2p_{1/2}$, while the other two are associated with the formation of positively charged, oxidized sulfur ($S^{\delta+}$).[16,17] This positive charge is consistent with the formation and transport of polarons and bipolarons in the conductive grafted polythiophene chains.

A key issue when dealing with grafting polymers at surfaces is the distinction between grafted and adsorbed chains. Therefore, a control experiment was carried out in which a PE film was added to the suspension of $FeCl_3$ in $CHCl_3$ and thiophene for 5 min at 20 °C. The reaction yielded PE–PT (blank). Table I shows the surface composition of PE–S–T, PE–PT, PE–PT (blank) and PT powder, calculated from XPS data. As expected, the composition of C and S in the PT powder is close to theory ($C_{100}S_{20}$). The oxygen moiety confirmed that carbonyl groups are attached to the polythiophene chains.

The sulfur intensity on PE–PT (blank) is very small, with a mole ratio of $C_{100}S_{1.2}$. This is the evident that the large intensity of sulfur in PE–PT indeed comes from grafted polythiophene chains formed by the oxidative polymerization reaction. Therefore, PT adsorption on PE films can be ignored.

**Table I.** Surface stoichiometric composition of PE–S–T, PE–PT, PE–PT (blank) and PT powder

| *Samples* | *Surface stoichiometry*[a] |
|---|---|
| PE–S–T | $C_{100}S_{1.0}O_{4.8}$ |
| PE–PT | $C_{100}S_{8.0}O_{5.9}$ |
| PE–PT (blank) | $C_{100}S_{1.2}O_{4.8}$ |
| PT powder | $C_{100}S_{20.8}O_{16.9}$ |

[a] Carbon concentration normalized to 100.

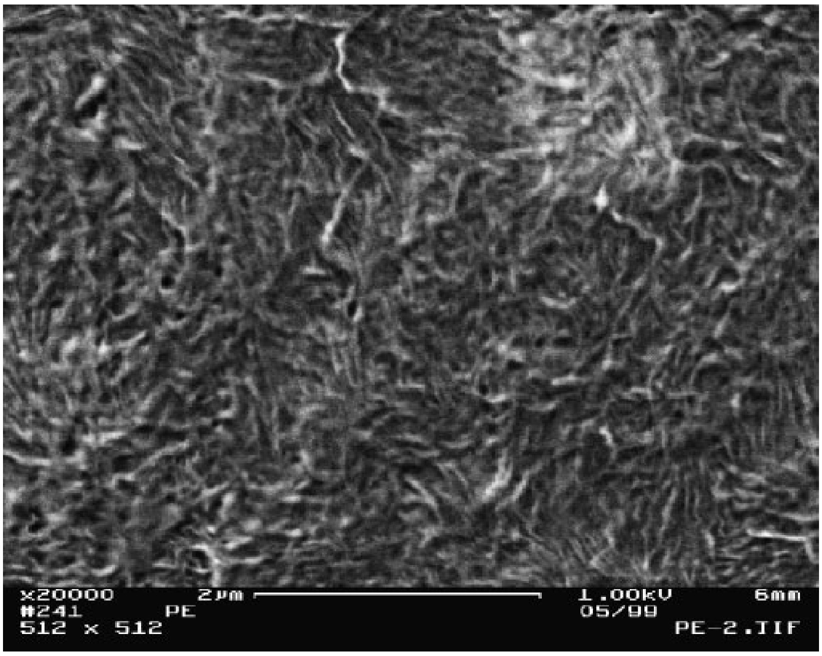

**Figure 8.** Scanning electron micrograph of a PE film. The picture shows lamella structure of the PE.

Fichou and cowokers[29] reported that PT oligomers (up to 7-mers) dissolve in organic solvents such as THF and $CHCl_3$. In our case both bulk PT and grafted PT did not dissolve in any solvent, indicating that high molecular weight polythiophene has been obtained. The PE–PT film was further investigated by SEM, recorded at 20 000× magnification. The SEM image of the PE film (Fig 8) shows contrast between the soft part (amorphous) and hard part (crystalline) in the PE film. Figure 9 reveals islands of PT on the PE film, showing that some parts of the film were not modified. This observation is supported by AFM analysis, which we discuss below. Unfortunately, we could not determine the thickness of the PT islands using the SEM method, due to detection limits. Therefore, a more sensitive method, AFM, was used.

The AFM topography images of PE–PT films in friction mode (a) and in tapping mode (b) are shown in Figure 10. As in the SEM image, the AFM topography image shows the same islands. The analysis curve for Fig 10(b) is shown in Fig 10(c). That the curve line goes down to zero is in agreement with the both SEM and AFM observations, ie that some parts of the PE film were not modified. The thickness of PT grafted on PE film is in the range 120–150 nm, indicating that the surface has been grafted with polymers and not with oligomers. For 120–150 nm-long polythiophene chains the degree of polymerization should be $\geqslant 300$, assuming a brush of rigid chains. This conjugation length should be evident in the absorption spectrum.

Although UV–vis spectroscopy is not very sensitive to surface modifications, a shoulder at 410 nm was observed for the PE–S–T sample (Figure 11). This shoulder is a characteristic $\pi$–$\pi^*$ transition of thiophene. The red shift of this band to 517 nm for PE–PT indicates extensive $\pi$-electron delocalization as is expected from a long conjugated polymer chain. After doping with $FeCl_3$ in acetonitrile, two shoulders appeared, one at 487 nm and the other at 360 nm. The $\pi$–$\pi^*$ band shifted from 517 nm to 487 nm indicating a shorter conjugation length as a result of the formed polarons and bipolarons.[30] The shoulder at 360 nm can be assigned to uncharged thiophene units.

Because of the insulating nature of the polyethylene, it is impossible to measure conductivity along the grafted polythiophene chains. Moreover, as evidenced from the ample experimental data, the grafted PT film is not continuous. Therefore, we expected that these films will not exhibit high conductivity values, and it will only be possible to use them for conducting applications if improvements in grafting protocols are made.

Since the high electrical conductivity in the oxidized

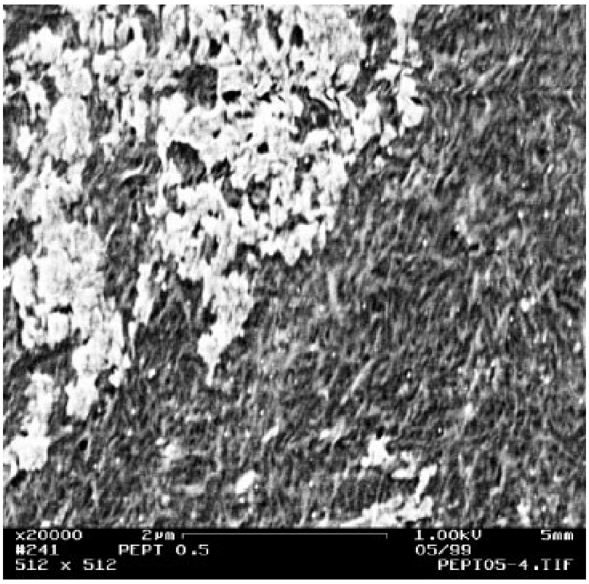

**Figure 9.** Scanning electron micrographs of a PE–PT film.

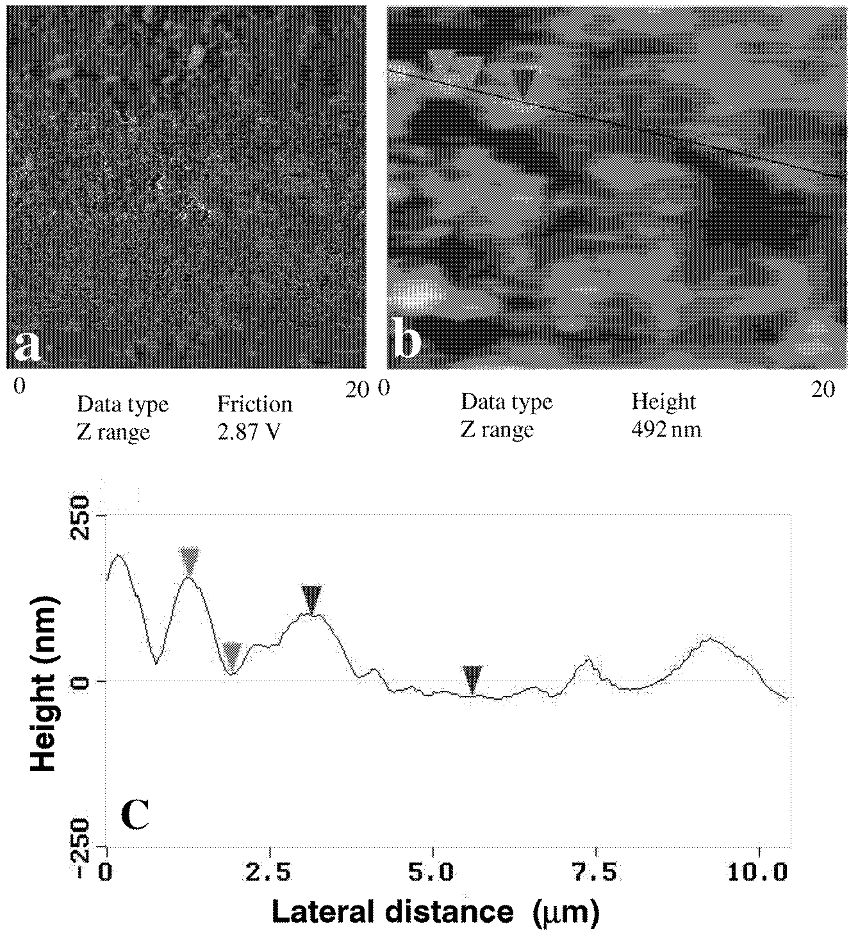

Figure 10. AFM friction (a) and topography (b) images of a PE–PT film. The analysis curve for the PE–PT AFM image in fig (b) is shown in fig (c). The imaging area was 20 × 20 μm.

PT results from the formation of mid-gap bipolaron bands, the bandgap of the neutral polymer directly determines the electrical conductivity in these materials. It is currently accepted that the mechanism for conductivity in PT, which is called the bipolaron mechanism, proceeds both through a charge movement along the polymer chain, and through polymer-to-polymer and grain-to-grain charge-hopping mechanisms, where charge carriers are bound dications. The energetic cost of moving charges along a conjugated chain is directly related to the degree of molecular orbital overlap. Hence, it is critical to have structurally homogeneous conducting polymers in order to allow for maximum intermolecular orbital overlap as well as interchain stacking and overlap to reduce highly resistive charge transport pathways.

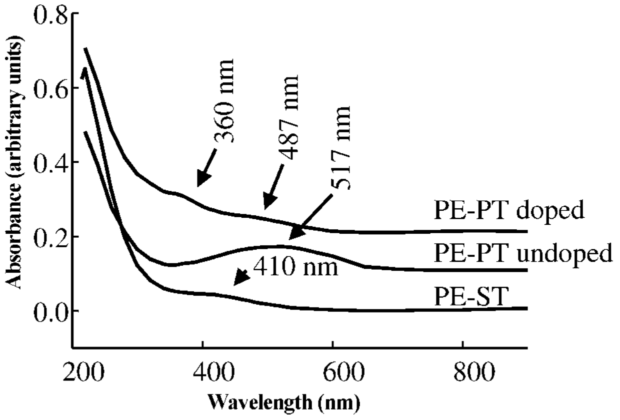

Figure 11. UV–vis absorption spectra of PE–S–T, and PE undoped and doped PE–PT films.

PT and its derivatives can be doped with $FeCl_3$ in acetonitrile or in nitromethane,[17] iodine gas, and $AsF_6^-$ in acetonitrile, $HClO_4$, $HBF_4$[31,32] and $CF_3SO_3H$.[32] In the present case, we have doped PE–PT with 0.1% $FeCl_3$ in acetonitrile. As a result, the color turned from red to dark green. The film could be easily dedoped by exposure to air or to ethanol. The color of the doped PE–PT film turned to purple after exposure to air. The conductivity of the PE–PT film was calculated from the equation

$$\sigma = 1/\rho = \frac{\ln 2}{\pi t}\left(\frac{I}{V}\right),$$

where $\sigma$ is the conductivity ($S\,cm^{-1}$), $\rho$ is the resistivity (ohm cm), $t$ is the thickness of the PT film, $I$ is the current ($1 \times 10^{-9}$ A), and $V$ is voltage drop (volt). The conductivity of doped PE–PT films was found to be very low ($\sigma = 1.4 \times 10^{-6}\,S\,cm^{-1}$),[33] confirming the expectation based on SEM and AFM images. However, it was ten orders of magnitude larger than that of an untreated PE film ($\sigma = 10^{-14}\,S\,cm^{-1}$).[34] Other factors that contribute to the low conductivity of the PE–PT film are the small thickness of the film that may have resulted in mechanical breakdown upon connection to electrodes, dedoping during measurement by air, and the full oxidation of the film to the bipolaron level, which does not conduct.

## CONCLUSIONS

We have grafted polythiophene on PE film using a three-step route: gas phase bromination of PE that yields PE–Br; substitution reaction of the PE–Br using 2-thiophene thiolate anion to provide the corresponding PE–S–T films, followed by chemical oxidative polymerization to give the polythiophene grafted films (PE–PT). SEM and AFM results revealed that the grafted PT forms island on the PE surface, with thickness of 120–150 nm, which indicated a polymerization degree of >300 assuming a polymer brush with rigid chains. The conductivity of these films was in the range of $10^{-6}\,\mathrm{S\,cm^{-1}}$, ten orders of magnitude higher than for PE films.

## ACKNOWLEDGEMENTS

Support for this project by the NSF through the MRSEC for Polymers at Engineered Interfaces is appreciated. We thank Prof Kalle Levon and Dr Lyubov Chigirinskaya for assisting in the conductivity measurements.

## REFERENCES

1 (a) Nalwa HS (Ed), *Handbook of Advanced Electronic and Photonic Materials and Devices*, Volume 8: Conducting Polymers, Academic Press, Boston (2001); (b) Yang SC and Chandrasekhar P, *Optical and Photonic Applications of Electroactive and Conducting Polymers* (1995); (c) Aldissi M (Ed), Intrinsically Conducting Polymers: An Emerging Technology, Proceedings of the NATO Advanced Research Workshop on Applications of Intrinsically Conducting Polymers, Burlington, Vermont, October 12–15, 1992, in NATO ASI Ser, Ser E, 1993, 246. (d) Gurunathan K, Murugan AV, Marimuthu R, Mulik UP and Amalnerkar DP, *Mater Chem Phys* **61**:173 (1999); (e) Sadik OA, *Electroanalysis* **11**:839 (1999); (f) Kumar D and Sharma RC, *Eur Polym J* **34**:1053 (1998).

2 (a) Fichou D (Ed), *Handbook of Oligo- and Polythiophenes* (1999); (b) Schopf G and Kossmehl G (Eds), Polythiophenes – Electrically Conductive Polymers, In *Adv Polym Sci* vol **129**, (1997); (c) Wurthner F, *Angew Chem Internat Ed Eng* **40**:1037 (2001).

3 (a) Diaz AF and Logan JA, *J Electroanal Chem* **111**:111 (1980); (b) Sata M, Tanaka S and Kaerigama K, *J Chem Soc Chem Commun*, pp 713 (1985); (c) Imanishi K, Sotoh M, Yasuda Y, Tsushima R and Aoki S, *J Electroanal Chem* **242**:203 (1988).

4 (a) Olafsen K, Stori A and Tellefsen DA, *J Appl Polym Sci* **46**:1673 (1992); (b) Zhang J, Kato K, Uyama Y and Ikada Y, *J Polym Sci: Part A* **33**:2629 (1995); (c) Foerch R, McIntyre NS and Hunter DH, *J Polym Sci: Part A* **28**:193 (1990); (d) Chtouru H, Riedl B and Kokta BV, *Polym Degrad Stability*, pp 149 (1994); (e) Mercx FPM, *Polymer* **35**:2098 (1994); (f) Kang ET, Tan KL, Kato K, Uyama Y and Ikada Y, *Macromolecules* **29**:6872 (1996); (g) Tsuchida M and Osawa Z, *Colloid Polym Sci* **272**:770 (1994).

5 (a) Bentjen SB, Nelson DA, Tarasevich BJ and Rieke PC, *J Appl Polym Sci* **4**:965 (1992); (b) Ferguson GS, Chaudhury MK, Biebuyck HA and Whitesides GM, *Macromolecules* **26**:5870 (1993); (c) Blais P, Carlesson DJ, Csullog GW and Wiles DW, *J Colloid Interf Sci* **47**:367 (1974); (d) Holmes-Farley SR, Reamey RH, McCarthy TJ, Deutch J and Whitesides GM, *Langmuir* **1**:725 (1985); (e) Holmes-Farley SR, Bain CD and Whitesides GM, *Langmuir* **4**:921 (1988); (f) Rasmussen LR, Stedronsky ER and Whitesides GM, *J Am Chem Soc* **99**:4736 (1977).

6 (a) Tan KL, Woon LL, Wong HK, Kang ET and Neoh KG, *Macromolecules* **26**:2832 (1993); (b) Curto D, Valenza A and La Mantia FP, *J Appl Polym Sci* **39**:865 (1990); (c) Edge S, Walker S, Feast WJ and Pacynko WF, *J Appl Polym Sci* **47**:1075 (1993).

7 (a) Bai G, Hu X and Yan Q, *Polym Bull* **36**:503 (1996); (b) Lee N and Russell KE, *Eur Polym J* **25**:709 (1989); (c) Gugumus F, *Angew Makro Chem* **182**:111 (1990); (d) Kildal K, Olafsen K and Stori A, *J Appl Polym Sci* **44**:1893 (1992).

8 Foerch R and Hunter DH, *J Polym Sci: Part A* **30**:279 (1992).

9 (a) Brown JR, Chappell PJC and Mathys Z, *J Mater Sci* **27**:3167 (1992); (b) Chappell PJC, Brown JR, George GA and Willis HA, *Surf Interf Anal* **17**:143 (1991).

10 Inagak N, Tasaka S and Imai M, *J Appl Polym Sci* **48**:1963 (1993).

11 (a) Strolbel M, Vara KP, Corn S, Lyons CS and Morgen M, *J Appl Polym Symp* **4**:61 (1990); (b) Corn S, Vara KP, Strolbel M and Lyons CS, *J Adhes Sci Technol* **40**:1903 (1991).

12 Kiss É, Samu J, Tóth A and Bertóti I, *Langmuir* **12**:1651 (1996).

13 Chanunpnainch N, Ulman A, Strzhemechny YM, Schwarz SA, Janke A, Braun HG and Kratzmüller T, *Langmuir* **15**:2089 (1999).

14 Chanunpanich N, Ulman A, Malagon A, Strzhemechny YM, Schwarz SA, Janke A, Kratzmueller T and Braun HG, *Langmuir* **16**:3557 (2000).

15 Sensitivity factors for C, S and O are 1.0, 2.63 and 1.18 respectively.

16 Ng SC, Fu P, Yu W-L, Chan HSO and Tan DL, *Synth Metals* **87**:119 (1997).

17 Ng SC, Chan HSO, Miao P and Tan KL, *Synth Metals* **90**:25 (1997).

18 Lukkari J, Kleemola K, Meretoja M, Ollonqvist T and Kankare J, *Langmuir* **14**:1705 (1998).

19 Bandyopadhyay K, Sastry M, Paul V and Vijayamohanan K, *Langmuir* **13**:866 (1997).

20 Hotta S, Rughooputh SDDV, Heeger AJ and Wudl F, *Macromolecules* **20**:212 (1987).

21 Funt BL and Lower SV, *Synth Metals* **11**:129 (1985).

22 Jin S, Xue G, *Macromolecules* **30**:5753 (1997).

23 Gutmann V and Schmied R, *Coord Chem Rev* **12**:263 (1974).

24 (a) Kock TJJM and de Ruiter B, *Synth Metals* **79**:215 (1997); (b) Lowe J and Holdcroft S, *Macromolecules* **28**:4608 (1995); (c) Buvat P and Hourquebie P, *Macromolecules* **30**:2685 (1997); (d) Lanzi M, Bizzarri PC and Casa CD, *Synth Metals* **89**:181 (1997).

25 Niemi VM, Knuuttila P, Österholm J-E and Korvola J, *Polymer* **33**:1559 (1992).

26 Inganäs O, Liedberg B, Chang-ru W and Wynberg H, *Synth Metals* **11**:239 (1985).

27 Otta S, Shimotsuma W and Taketani M, *Synth Metals* **10**:85 (1984/85).

28 Hyodo K and Macdiarmid AG, *Synth Metals* **11**:167 (1985).

29 Fichou D, Xu B, Horowitz G and Gamier F, *Synth Metals* **41–43**:463 (1991).

30 Hill MG, Mann KR, Miller LL and Penneau J-F, *J Am Chem Soc* **114**:2728 (1992).

31 Hotta S, Shimotsuma W, Taketani M and Kohiki S, *Synth Metals* **11**:139 (1985).

32 Aleshin A, Kiebooms R, Menon R and Heeger AJ, *Synth Metals* **90**:61 (1997).

33 Conductivity was measured using the four-probe technique. See: (a) Lowe J and Holdcroft S, *Marcromolecules* **28**:4608 (1995). (b) Cao A, Andreatta A, Heeger J and Smith P, *Polymer* **30**:2305 (1989).

34 Skotheim TA, Handbook of Conductivity polymers, Vol 1, Marcel Dekker, New York and Basel (1986).