

Thiophene-Based Copolymers Synthesized by Electropolymerization for Application as Hole Transport Layer in Organic Solar Cells

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ABSTRACT: Electrically conducting thiophene-based copolymers were synthesized by electropolymerization. The potential range used has a strong influence on the film structure and properties. The extent of oxidation of the copolymers was determined from the ratio of the oxidation to reduction charge, Q_{ox}/Q_{red} . The use of wide potential range leads to reduced films, whereas the narrow range leads to partially oxidized films. The copolymers exhibit a characteristic band in UV-vis spectra at ~ 410 nm, which shifts to higher wavelengths for the more doped material. The electrical conductivity of the copolymers was correlated to their morphology and their structure. The copolymer with higher conductivity is partially reduced, has compact morphology and higher ratio of quinoid to benzenoid rings. The energy gap of the copolymers is reversely proportional to their electrical conductivity. The optical and electrical properties of the copolymers make them very well suited for use as hole transport layers (HTL) in organic opto-electronic devices. We prepared polymer : fullerene solar cells with copolymer HTLs. The solar cell performance was tested with very encouraging initial results. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Conducting polymers (CPs) are unique electronic elements for current applications, as they can be applied in many technological sections, such as thin film transistors, light-emitting diodes, solar cells, flexible displays, etc.^{1–7} The field of electrical conducting polymers is an important modern research field with scientific and technological importance.^{1–4} CPs can be synthesized by chemical polymerization or by electropolymerization, whereas the latter offers several advantageous features,^{1,8} such as absence of catalyst, direct formation of the doped polymer film on the electrode surface, easy control of the film thickness and the possibility of performing *in situ* characterization of the deposited film by electrochemical and other techniques.^{1,9}

Polyphenylenes (PP) have attracted much interest among various conducting polymers, because of their high stability in air even at high temperatures due to the aromatic nuclei.^{10–12} PPs can be prepared using biphenyl or other aromatic compounds leading to isomeric polyphenylenes containing both

ortho-, meta-, and para-couplings between the aromatic rings.^{10,11} Polythiophene and its derivatives have attracted considerable attention because they are stable in the oxidized and neutral state.^{12–15} Relative ease of substitution at the three-position of the thiophene ring has enabled the synthesis of a large number of derivatives, resulting in numerous polymers with different degrees of stabilities, conductivities, solubilities, and bandgaps. In particular, poly(3-methyl thiophene) has been the subject of extensive investigation due to its good environmental stability, relatively high electrical conductivity, and reliable adhesion to different electrodes.^{13,16}

Apart from the conducting homopolymers, copolymers based on different types of monomers have gained great scientific interest, because new electrically active materials could be produced combining properties of both of the homopolymers.^{11,12,17,18} By electrochemical copolymerization, a variety of conducting materials with different electrical and morphological properties can be produced.^{12,17,18} In the literature, the

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copolymerization of biphenyl with 3-octyl-thiophene has been reported for producing soluble copolymers.^{17,19,20} Compared to 3-octyl thiophene, 3-methyl-thiophene is quite an inexpensive reagent. Thus, it could be cost effective to study whether copolymers of 3-methyl thiophene with biphenyl could lead to materials with a combination of desirable properties (e.g., high conductivity, thermal stability, solubility). These tailored copolymer layers have great potential as functional layers in organic optoelectronic devices, such as solar cells.

Bulk-heterojunction organic photovoltaic (BHJ) cells are a potential competitor to amorphous silicon-based technologies and have experienced tremendous progress in performance during the last 3 years, with power conversion efficiency now routinely surpassing 8%.^{21–23} In addition to high efficiencies, device stability is a significant factor influencing the market viability of this technology. Several studies have demonstrated that the commonly used water-based PEDOT : PSS hole transport layer (HTL) influences the device stability and can be a major factor in device degradation.^{24–27} For this reason it is interesting to explore new materials for use as transport layers in organic devices. The requirements on such materials are a high transmittance in the spectral region in which the active layer absorbs as the incoming light transverses this layer, high conductivity, suitable energetics for charge collection, and long term stability. The deposition of the HTL onto the anode electrode of the cell by *in situ* electropolymerization is expected to lead to more control over the film properties compared to the solution deposition process (e.g., spin coating).

The aim of this work is to copolymerize biphenyl with 3-methyl thiophene by electropolymerization using cyclic voltammetry to produce soluble, electrically conducting and cost effective films. The influence of the applied potential and the number of sweeps on the structure, morphology, stability, and electrical conductivity of the films will be examined. Furthermore, the application of the copolymers as HTL in BHJ solar cells will be examined and the performance of the cells will be determined.

EXPERIMENTAL

Tetrabutylammonium tetrafluoroborate (TBABF₄, Merck) was dried at 110°C up to constant weight. Acetonitrile (ACN, Merck, water content ~ 0.05 %) was stored over molecular sieves (Fluka, 4 Å, 8–12 mesh) for about 1 month. Biphenyl (Biph, Fluka) and 3-methyl thiophene (3MTh, Fluka) were used as received. The copolymer films based on Biph and 3MTh were synthesized by cyclic voltammetry using different potential ranges. Specifically, a wide range (from 0 V up to +2 V and backward) and a narrow one (from +1 V up to +2 V and backward) were applied, for 80 sweeps, with scan rate of 100 mV s⁻¹. The electropolymerization solution consisted of the monomers (Biph and 3MTh), TBABF₄ as supporting electrolyte and ACN as solvent. The monomers were used in concentration: [Biph]/[3MTh] = 0.05 M/0.05 M and the electrolyte concentration was [TBABF₄] = 0.1 M. All electropolymerizations took place at room temperature, in an one-compartment electrochemical cell of 60 mL volume using a system of three electrodes. The latter includes the working and the counter electrodes,

both of Pt-plated Pt in the form of plates (with surface area of 4.8 and 9.0 cm², respectively) and the calomel electrode (SCE) as reference, placed into Luggin capillary.^{19,28} Before electropolymerization, the surface of the working electrode was cleaned by heating over a flame to remove residues. The solution was deoxygenated by bubbling nitrogen for 10 min before the beginning of the electropolymerization. The corresponding apparatus was a CV Potentiostat Wenking POSS88 (Bank Elektronik). The thickness of the films synthesized was estimated from the charge during the electropolymerization. After polymerization, the films synthesized were immersed in acetonitrile to remove TBABF₄ residues and the soluble oligomers and then were vacuum dried at 30°C up to constant weight. The solubility of the copolymers synthesized was tested in various common solvents (i.e., ethanol, methanol, acetone, *N*-methylpyrrolidone, tetrahydrofuran, *N,N'* dimethylformamide, chlorobenzene, 1,2-dichlorobenzene, *N,N'* dimethylsulfoxide etc.). The FTIR spectra of the polymers were recorded using a Perkin Elmer Spectrum GX spectrometer using KBr discs and the UV-vis spectra were recorded using a Varian Cary 300. The morphology of the films was examined using a FEI Quanta 200 Scanning Electron Microscope with simultaneous Energy Dispersive X-Ray Analysis (EDAX) and their electrical conductivity was determined with constant current at room temperature by the two-probe technique.²⁹ The energy levels of the highest occupied molecular orbital (E_{HOMO}) and that of lowest unoccupied molecular orbital (E_{LUMO}), as well as the energy gap (E_g), were determined by cyclic voltammetry in a 0.1 M TBABF₄ solution in ACN, using the previously described electrochemical cell. The film (as deposited on the electrode) was placed in the solution and underwent cyclic potential sweep, firstly from 0 to -2 V and then from 0 to +2 V (scan rate : 50 mV s⁻¹).^{12,30–32}

The hole transport layer (HTL) based on the copolymer (PP-3MPTh) was deposited by *in situ* electropolymerization onto prepatterned indium tin oxide (ITO, from PGO, Germany) substrates (dimensions 2.54 × 2.54 cm²) in the same electrochemical cell as already described, using ITO as working electrode. The HTLs were deposited by cyclic voltammetry using the narrow scan range (from +1 V up to +2 V and backward) for 10 and 20 sweeps, with scan rate of 100 mV s⁻¹. The electropolymerization solution consists of monomers, supporting electrolyte and solvent. The details of the experimental procedure are the same as those described above. After deposition, the HTLs were vacuum dried at 30°C up to constant weight. To prepare the active layer of the solar cell, regio-regular poly(3-hexylthiophene) (P3HT, supplied by Merck Chemicals Ltd, UK) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, purchased from Solenne BV) were dissolved in *o*-dichlorobenzene in a weight ratio of 1 : 1 and stirred at 70°C overnight. The blend solution was then spun on top of the electropolymerized layers. The cathode was deposited by thermal evaporation of a 20-nm thick Ca layer covered with 100 nm of Al. The active area of the devices was of 0.5 cm². Current-voltage characteristics of the solar cells were measured with a Keithley 4200 semiconductor characterization system using a four-point contact bridge. The standard reference spectrum AM 1.5G was provided by a P.E.T. class A solar simulator calibrated with a reference silicon solar

Table I. Raw Materials, Experimental Parameters, Total Charge, and Characteristics (Thickness, Color) of Synthesized Polymeric Films Using Pt as Working Electrode

Code of copolymers (1)	Synthesis of the films				Total charge (mC cm ⁻²) (6)	Characteristics of films synthesized	
	Raw materials Monomers		Experimental parameters			Thickness (μm) (7)	Color (8)
	Biphenyl (mol L ⁻¹) (2)	3-methyl-thiophene (mol L ⁻¹) (3)	Scan range (V vs SCE) (4)	Number of scans (5)			
(PP-3MPTh) ₁	0.05	0.05	0 → +2 → 0	80	2137.3	8.6	Pink
(PP-3MPTh) ₂			+1 → +2 → +1	80	2141.6	9.6	Dark red

Supporting electrolyte : Tetrabutyleammonium tetrafluoroborate (TBABF₄), 0.1 M Solvent: Acetonitrile (ACN).

cell from Fraunhofer ISE (Germany). Transmittance spectra of the HTL and active layers were measured with a double-beam Varian Cary 100 spectrometer.

RESULTS AND DISCUSSION

Synthesis of Polymer Films and Analysis of Cyclic Voltammograms

Table I presents the raw materials, the experimental parameters, the total charge and the characteristics (thickness, color) of the synthesized copolymer films using Pt as working electrode. Figure 1(a,b) show the cyclic voltammograms during synthesis of copolymer (PP-3MPTh)₁ in the potential range from 0 to +2 V for different sweeps. For the 1st up to 10th sweep, the oxidation of the monomers (leading to the production of the copolymers) and the doping of the synthesized copolymer film with BF₄⁻ (which takes place simultaneously) begin at around 0.50 V, where the slope of the current increases abruptly, Figure 1(a). At the same time, no cathodic current is observed. Above 10th sweep and up to 40th, an oxidation peak (ranging from 0.85 V up to 1.00 V) and a reduction peak (ranging from 0.45 V up to 0.30 V) appear, due to the doping of the film with BF₄⁻ and the subsequent undoping, respectively.^{17,33} The oxidation peak shifts to higher potential with increasing the number of sweeps, whereas the reduction peak shifts to lower potential. Above 40th sweep and up to 80th, Figure 1(b), the oxidation and reduction peaks can not be distinguished, and the current during the successive sweeps remains almost the same. Based on the data of current versus time, which are obtained during a cyclic voltammetric experiment, the area under the corresponding curve is determined, which gives the oxidation charge, Q_{ox} , and the reduction charge, Q_{red} , from the positive and the negative current, respectively. To determine if the copolymers synthesized were fully oxidized, partially oxidized (or partially reduced) or fully reduced, the ratio Q_{ox}/Q_{red} was calculated for each sweep. Concerning the copolymer (PP-3MPTh)₁, up to 10th sweep only Q_{ox} is observed. Then, by increasing the number of sweeps the ratio of Q_{ox}/Q_{red} decreases gradually up to 50th sweep and then it remains almost constant having a value of 0.8 (Figure 2). This value is very low and it indicates that the film produced is in the reduced state. During every sweep, the color of the film (PP-3MPTh)₁ changes from blue (oxidized form) to pink (reduced form). These colors are similar to those

of homopolymer poly(3-methyl-thiophene) in its two different corresponding redox states.^{34,35} The final color of (PP-3MPTh)₁ was pink confirming that it was indeed reduced.

To avoid the reduction as much as possible, copolymer (PP-3MPTh)₂ was synthesized in the narrow potential range (from +1 V up to +2 V) and the corresponding cyclic

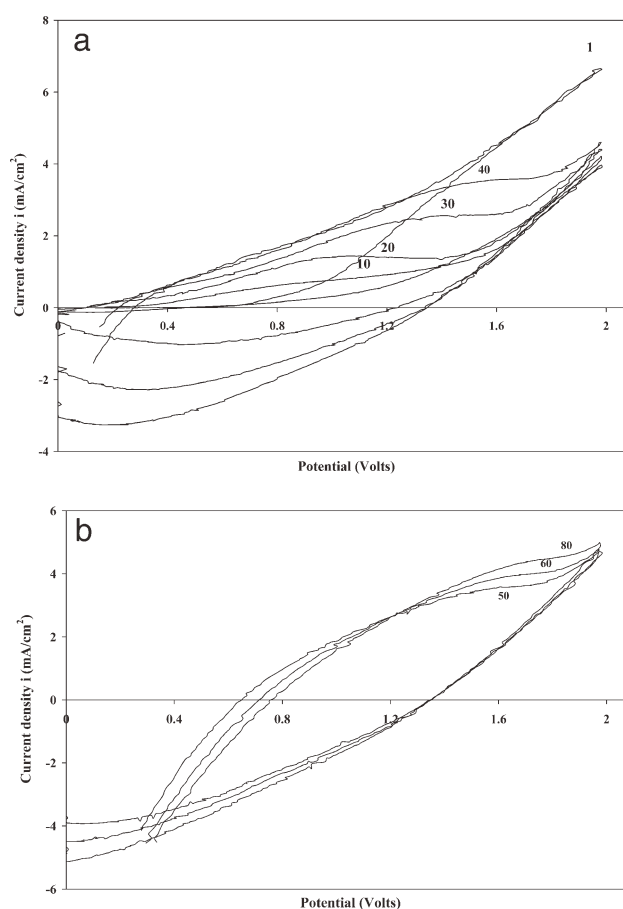


Figure 1. Cyclic voltammograms during synthesis of copolymer (PP-3MPTh) using Pt as working electrode, in the scan range 0 V up to +2 V vs SCE (scan rate 100 mV s⁻¹) (a) from 1st up to 40th sweep (b) from 50th up to 80th sweep.

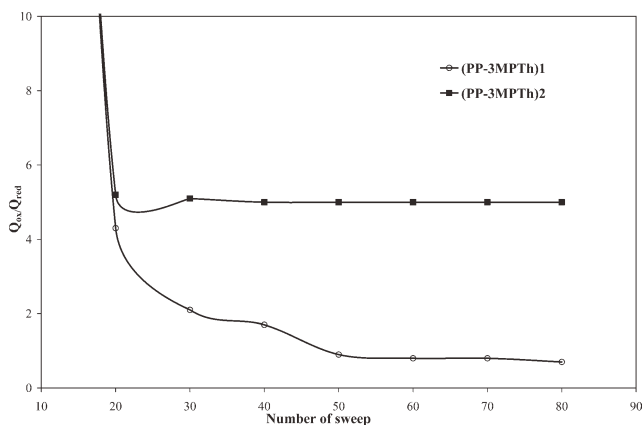


Figure 2. Ratio of oxidation Q_{ox} to reduction charge Q_{red} , versus number of sweep during the synthesis of copolymer, in the scan range 0 V up to +2 V (PP-3MPTh)₁ and +1 V up to +2 V (PP-3MPTh)₂ (scan rate 100 mV s⁻¹) using Pt as working electrode.

voltammograms are presented in Figure 3(a,b). The oxidation of the monomers and the doping of the synthesized films begin at around 1.4 V, where the slope of the current increases abruptly. No cathodic peak is observed up to the 9th sweep;

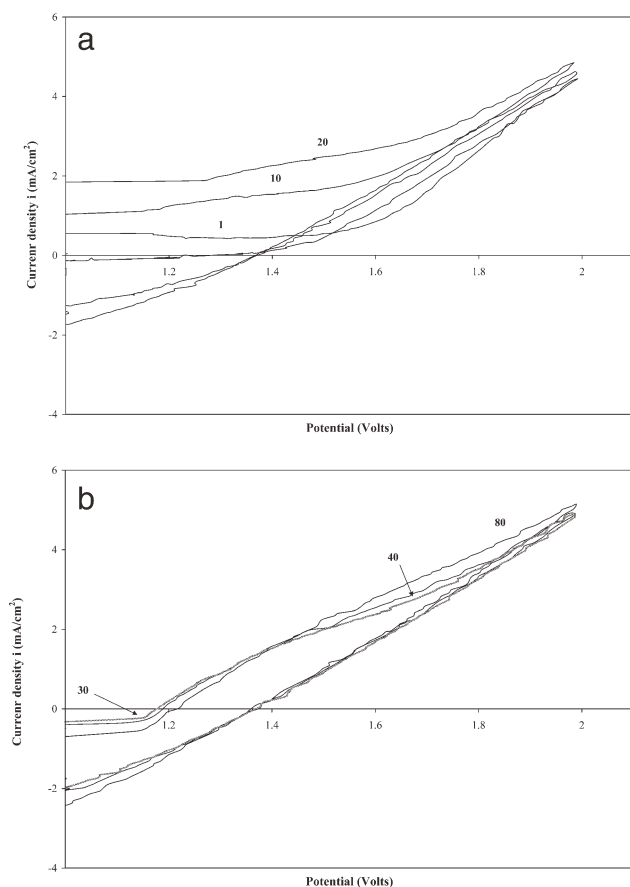


Figure 3. Cyclic voltammograms during synthesis of copolymer (PP-3MPTh) using Pt as working electrode, in the scan range +1 V up to +2 V vs. SCE (scan rate 100 mV s⁻¹) (a) for 1st up to 20th sweep (b) for 30th up to 80th sweep.

however, cathodic current starts appearing after the 10th sweep. By increasing the number of sweeps up to 20, the ratio Q_{ox}/Q_{red} decreases but afterward it remains constant up to the 80th sweep having a value of 5 (Figure 2). This value is relatively high, indicating that the film produced is still oxidized. The color of the (PP-3MPTh)₂ was dark red, confirming that it is only partially reduced.

Summarizing, the use of wide potential range leads to the synthesis of reduced films, whereas the narrow range leads to partially oxidized film.

The total charge ($Q = Q_{ox} - Q_{red}$) during the electropolymerization was determined (Table I, Column 6) and from that the thickness of the films was estimated according to literature.^{12,18,36–38} The synthesis of a polyphenylene film with thickness of 1 μm requires 143 mC cm⁻²^{12,18} and that of poly(3-methyl-thiophene) requires 1000 mC cm⁻².³⁸ From these values the corresponding charge of copolymer is calculated^{12,18} as ~ 250 mC cm⁻². The thickness of the copolymer (PP-3MPTh)₁ and (PP-3MPTh)₂ was calculated as 8.6 and 9.6 μm , respectively (Table I, Column 7).

Structural Characterization and Morphology of the Copolymers

Figure 4 shows the FTIR spectra of the copolymers (PP-3MPTh)₁ and (PP-3MPTh)₂. The various bands of the copolymers were attributed to chemical bonds according to the literature for the corresponding homopolymers, i.e., polyphenylenes^{10–12,18,28,39} and poly(3-methyl-thiophenes).^{14,15,17,20,40–42} The bands at 2960, 2920, and 2870 cm⁻¹ are attributed to aliphatic C–H stretching vibration.^{17,18,41} The bands at 1600, 1570, 1480, 1400, and 1375 cm⁻¹ are associated with the aromatic ring.^{12,14,15,41} Specifically, the band at 1600 cm⁻¹ is characteristic for C=C stretching vibration in the phenylene ring, due to the biphenyl unit of the copolymers.^{11,19,20,39,40} Moreover, the bands at 1570 and 1480 cm⁻¹ are attributed to quinoid and benzenoid structures, respectively.^{12,19} The bands at 1400 and 1375 cm⁻¹ are due to the C–C stretching vibrations in aromatic ring.^{12,18} The band at 1312 cm⁻¹ can be assigned to

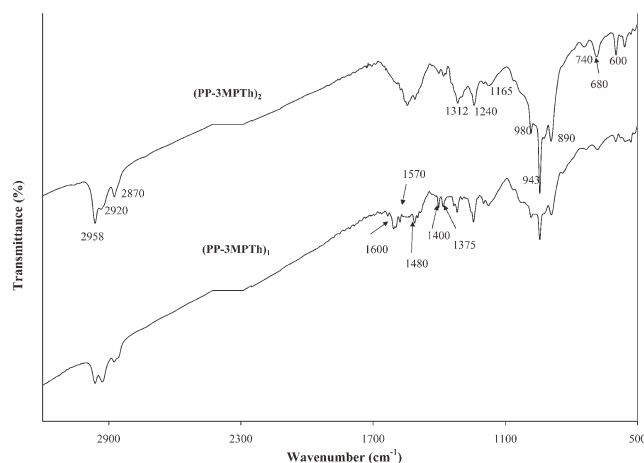


Figure 4. FTIR spectra of the copolymers synthesized using Pt as working electrode.

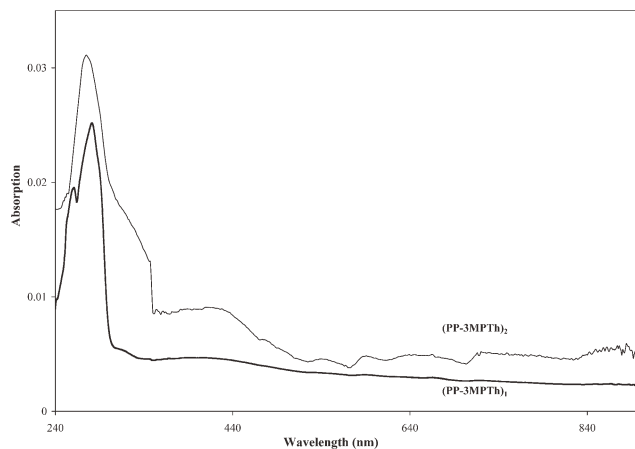


Figure 5. UV-vis spectra in dimethylformamide (DMF) of copolymers (PP-3MPTh) synthesized using Pt as working electrode.

the methyl deformation of 3-methyl-thiophene (3MTh) units⁴¹ and the bands at 1240, 1165, 980, and 943 cm^{-1} to the aromatic C—H in-plane deformations.^{14,41} The band at 890 cm^{-1} can be attributed to methyl groups of 3MTh.²⁰ Furthermore, the band at 740 cm^{-1} is attributed to short terminal phenylene rings of radical cations,²⁰ whereas the bands at 680 and 600 cm^{-1} are attributed to C—S—C ring deformations and C—S bending vibrations due to 3-methyl-thiophene units, respectively.^{14,15,20,42}

The solubility of the copolymers was tested in various common solvents and it was found that they were totally soluble in dimethylformamide (DMF) and totally insoluble in the corresponding solvents of polyphenylenes/PPs and poly(3-methyl-thiophenes)/3MPThs homopolymers. Namely, PP is totally soluble in *N*-methylpyrrolidone (NMP) and 3MPTh in chloroform, and both are totally insoluble in DMF. If the materials synthesized were blends of homopolymers and not copolymers, the part of PP should

have been dissolved in NMP and that of 3MPTh should have been dissolved in chloroform, something that was not observed.

Figure 5 presents the UV-vis spectra of copolymer (PP-3MPTh)₁ and (PP-3MPTh)₂ solutions in DMF (0.1 mg of copolymer in 1 mL DMF). From the literature,¹⁰ it is known that para-phenylene homologue oligomers have their main absorption at 251 nm (biphenyl), 280 nm (terphenyl), 298 nm (quaterphenyl), 310 nm (quinquephenyl), 318 nm (sexiphenyl), and 323 nm (septaphenyl). Poly(para-phenylene) has its main absorption at 340 nm and it also exhibits a “shoulder” in the region of 420 with 440 nm.¹⁰ On the other hand, the poly(3-methyl-thiophene) homologue oligomers have their main absorption at 248 nm (monomer), 320 nm (dimer), 368 nm (trimer), 396 nm (tetramer), whereas that of the polymer appears at 420 nm.^{14,43–45} The latter absorption band is attributed to the π – π^* transition of the thiophene backbone.^{14,45} It has been reported that the absorption band of PTh in the doped state appears at 770 and 440 nm in the undoped state.¹⁴

Copolymer (PP-3MPTh)₁ exhibits two bands at 262 and 282 nm, which can be attributed to low molecular weight copolymer, since in this region absorb the oligomers. Moreover, it exhibits a band at 407 nm, due to the copolymer. Likewise, copolymer (PP-3MPTh)₂ exhibits two absorption bands at 277 and at 424 nm. The main band due to the copolymer, \sim 410 nm, shifts to higher wavelength for more doped material.

Figure 6 presents the SEM micrographs of copolymers. In Figure 6(a), (PP-3MPTh)₁ has a fibrillar structure with many round shaped pores. The copolymer (PP-3MPTh)₂, Figure 6(b) has a sponge-like structure with aggregates of size from 2 up to 7 μm . This morphology is more compact than that of (PP-3MPTh)₁. The different morphology of the copolymers confirms that the potential range have a strong influence on the film structure. For the copolymers, the ratio of structural unit derived from biphenyl per that derived from 3-methyl thiophene was calculated according to the literature.^{12,18} In (PP-3MPTh)₁ the ratio of structural

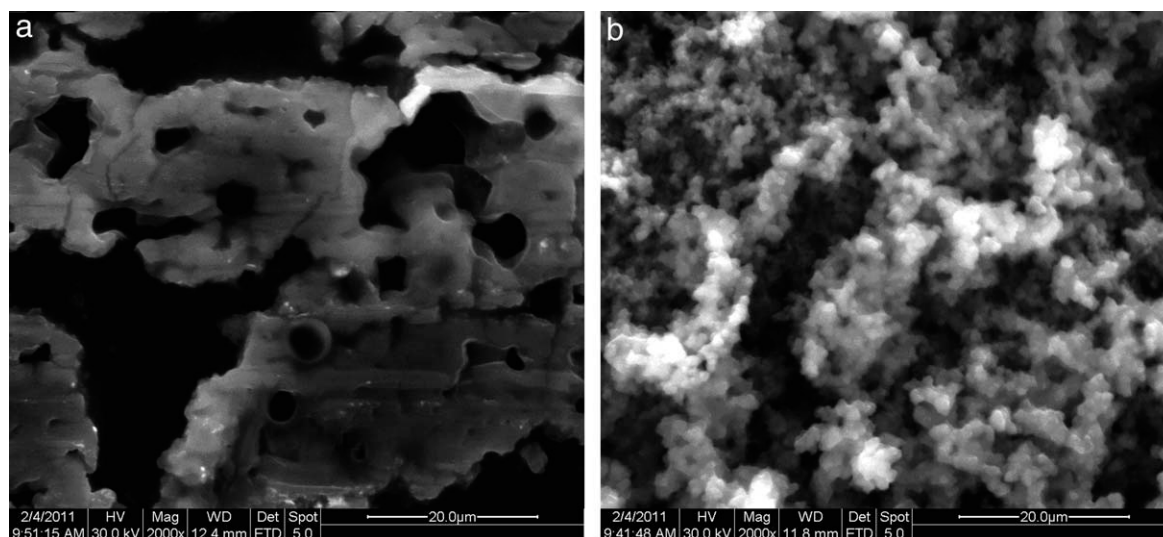


Figure 6. SEM photographs ($\times 2000$) of copolymer films (a) (PP-3MPTh)₁ and (b) (PP-3MPTh)₂.

Table II. Values of $E_{\text{onset}}^{\text{ox}}$, $E_{\text{onset}}^{\text{red}}$, E_{HOMO} , E_{LUMO} , E_g and the Electrical Conductivity of the Copolymer Films Synthesized Using Pt as Working Electrode

Code of copolymers	$E_{\text{onset}}^{\text{ox}}$ (V)	E_{HOMO} (eV)	$E_{\text{onset}}^{\text{red}}$ (V)	E_{LUMO} (eV)	E_g (eV)	Electrical conductivity, σ , (S cm ⁻¹)
(PP-3MPTh) ₁	+0.50	-4.90	-1.02	-3.38	1.52	2.5×10^{-3}
(PP-3MPTh) ₂	+0.48	-4.88	-1.00	-3.40	1.48	6.0×10^{-3}

$E_{\text{onset}}^{\text{ox}}$: onset potential for p-doping, vs. SCE, $E_{\text{onset}}^{\text{red}}$: onset potential for n-doping, vs. SCE, E_{HOMO} : energy level of highest occupied molecular orbital (HOMO), i.e., of valence band, E_{LUMO} : energy level of lowest unoccupied molecular orbital (LUMO), i.e., of conduction band E_g : energy gap.

units Biph/3MTh was 1/2.6 and in (PP-3MPTh)₂ was 1/1.6, i.e., the copolymers contain more structural units of 3MTh than Biph. This is a result of the faster electropolymerization of 3MTh compared to that of biphenyl.

Electrical Conductivity and Energy Gap of the Copolymers

In Table II, the electrical conductivity of the films is presented. (PP-3MPTh)₂ (which is synthesized in the narrow potential range) has higher conductivity than (PP-3MPTh)₁ (synthesized in the wide range). Namely, highest conductivity appears for the film synthesized in the narrow potential range, where reduction is limited. According to the literature,⁴⁶ materials with values of electrical conductivity of 10^{-3} S cm⁻¹ and higher can be used in many electrooptical applications, such as solar cells.

The electrical conductivity of the copolymers can be correlated to their morphology and their structure. The (PP-3MPTh)₂ film which exhibits the highest conductivity is also the most compact. This can be explained considering that the more compact films have a more extensive and continuous network of active paths, which facilitate the charge transfer. Additionally, from the FTIR spectra of other conducting polymers, such as polyanilines⁴⁷ and biphenyl copolymers,^{12,18} the ratio of the peak area of quinoid to benzenoid rings can be used as a measure of their oxidation level, and it has been connected to their electrical conductivity. Thus, the ratios R of the peak area of the quinoid (A_{1570}) to benzenoid (A_{1480}) absorption bands of the synthesized copolymers were calculated and it was found that for (PP-3MPTh)₁ $R = 1.1$ and for (PP-3MPTh)₂ $R = 1.4$, i.e., the electrical conductivity increases by increasing R . This comparison confirms the direct correlation between electrical conductivity and R , i.e., the electrical conductivity increases by increasing the quinoid structures in the macromolecules.

Figure 7 shows the cyclic voltammogram of copolymer film (PP-3MPTh)₂. The onset potentials of oxidation and reduction for the p-doping ($E_{\text{onset}}^{\text{ox}}$) and n-doping ($E_{\text{onset}}^{\text{red}}$), respectively, were determined graphically.^{12,18} Then, from the equations de Leeuw et al.,^{12,18,48} E_{HOMO} , E_{LUMO} , and E_g were calculated.

$$E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{ox}} + 4.4) \quad (1)$$

$$E_{\text{LUMO}} = -e(E_{\text{onset}}^{\text{red}} + 4.4) \quad (2)$$

$$E_g = e(E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \quad (3)$$

where

$E_{\text{onset}}^{\text{ox}}$: onset potential for p-doping, vs. SCE

$E_{\text{onset}}^{\text{red}}$: onset potential for n-doping, vs. SCE

E_{HOMO} : energy level of highest occupied molecular orbital (HOMO), i.e., of valence band

E_{LUMO} : energy level of lowest unoccupied molecular orbital (LUMO), i.e., of conduction band

E_g : energy gap

The values of $E_{\text{onset}}^{\text{ox}}$, $E_{\text{onset}}^{\text{red}}$, E_{HOMO} , E_{LUMO} , and E_g of the copolymers are presented in Table II. The values of E_g is 1.52 and 1.48 eV for (PP-3MPTh)₁ and (PP-3MPTh)₂, respectively, i.e., both are in the range of semiconductors. E_g is reversely proportional to the electrical conductivity, thus the copolymer with the highest conductivity had also the lower E_g .

Application of the Copolymers as HTL in BHJ Solar Cells

Because the highest possible conductivity is required for applying a material as a hole transport layer (HTL), the narrow scan range of +1 up to +2 V was chosen. Two different HTLs were deposited using 10 and 20 sweeps, and are denoted as (PP-3MPTh)_{2a} and (PP-3MPTh)_{2b}, respectively, with corresponding thickness 1.2 and 2.5 μm . Both of the copolymer films had pale blue color. It is noticed that the copolymers were insoluble in 1,2-dichlorobenzene, which is the solvent of the active layer.

In Figure 8 the transmittance spectra of copolymer (PP-3MPTh)_{2a} and (PP-3MPTh)_{2b} on ITO coated glass electrode are shown. For comparison reasons the absorption spectrum of the P3HT:PCBM blend in 1,2-dichlorobenzene (oDCB) is plotted. It can be seen that the copolymers have a broad transmittance

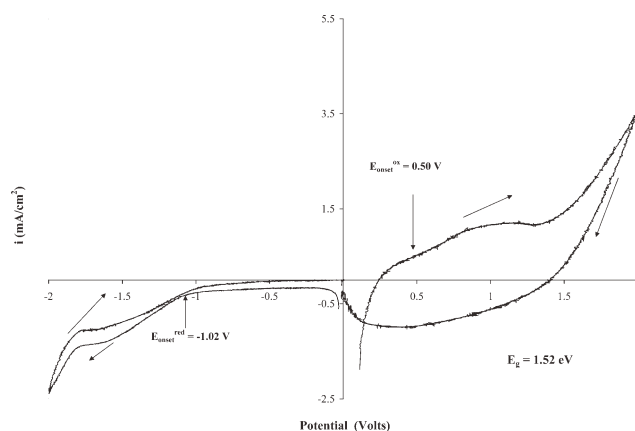


Figure 7. Cyclic voltammogram of the copolymer film (PP-3MPTh)₁ (synthesized using Pt as working electrode) with solution of 0.1 M TBABF₄ in ACN, scan rate = 50 mV s⁻¹, for the determination of the onset potential for p and n-doping.

over the visible region of the spectrum. The transmittance decreases slightly for thicker film, but as will be shown later, the thicker films led to better solar cell performance. The copolymers show improved transmittance at higher wavelengths, making them potentially interesting candidates for use with low bandgap polymers.⁴⁹

The hole transport layer adjusts the workfunction of the anode and prevents short circuits in the solar cell. There are competing factors which influence the optimum thickness of the layer, namely the optical losses for thicker layers and holes for thinner layers. We examined copolymer films produced using 10 and 20 sweeps for the solar cells with different thicknesses. The blend was applied onto the electropolymerized layers via spin coating, according to the details described in the experimental section. In Figure 9 the JV curves of the solar cells are shown. The thinner copolymer (PP-3MPTh)_{2a} resulted in partially short circuited performance, as can be seen by the poor fill factor and high leakage current. Increasing the thickness of the copolymer layer improved the device performance considerably, copolymer (PP-3MPTh)_{2b}.

For application in solar cells the copolymer deposition should be further optimized with respect to the thickness, conductivity and transmittance. Because of the good stability of the copolymers, a positive impact on the device stability is expected.

CONCLUSIONS

Electrically conducting copolymer films were synthesized by electropolymerization of biphenyl with 3-methyl-thiophene using cyclic voltammetry. It was found that the potential range used, has a strong influence on the films structure and properties. The extent of oxidation of the copolymers was determined from the ratio of the oxidation to reduction charge, Q_{ox}/Q_{red} . For the copolymer (PP-3MPTh)₁ synthesized in the wide potential range (0 up to +2 V) the ratio decreases gradually up to 50th sweep and then it remains constant having a very low value of 0.8, indicating that the film is reduced. For the copolymer (PP-3MPTh)₂ synthesized in the narrow potential range (+1 up to +2 V), the ratio decreases by increasing the number of sweeps up to 20, but afterwards it remains constant with a

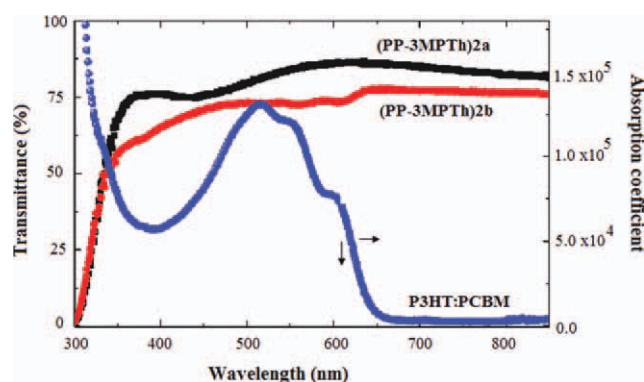


Figure 8. Transmittance spectra of copolymers (PP-3MPTh)_{2a} and (PP-3MPTh)_{2b} on ITO electrode and the absorption coefficient of the P3HT : PCBM blend for comparison. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

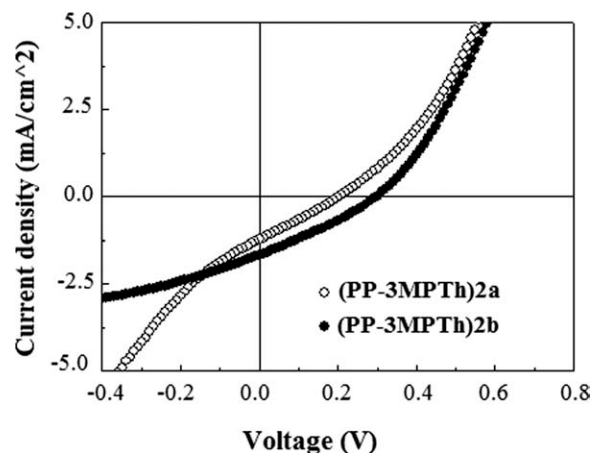


Figure 9. J-V characteristics of the solar cells containing PP-3MPTh as the HTL and P3HT : PCBM as the active layer under AM 1.5G illumination.

value of 5, up to the 80th sweep. This value is relatively high, indicating that the film produced is still oxidized. The use of wide potential range leads to reduced films, whereas the narrow range leads to partially oxidized films. The UV-vis spectra of the copolymers in dimethylformamide exhibit characteristic band at ~ 410 nm, which shifts at ~ 420 for the more doped material. The electrical conductivity of the copolymers was correlated to their morphology and their structure. Copolymer (PP-3MPTh)₂ which is partially reduced, which is compact and has higher ratio of quinoid to benzenoid rings, has higher conductivity ($6 \times 10^{-3} \text{ S cm}^{-1}$) than this synthesized in the wide potential range, which is fully reduced. The energy gap of the copolymers was determined by cyclic voltammetry and is reversely proportional to their electrical conductivity. The more doped copolymers were used as hole transport layer (HTL) in polymer : fullerene solar cells and their performance was tested. Given that the first results from these materials are very encouraging, further research about the influence of the HTL formation conditions on the performance and stability of solar cells will be very promising and useful for the possible commercial application of these copolymers.

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