Reactive & Functional Polymers 83 (2014) 33-41



Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Use of poly(3-methylthio)thiophene blends for direct laser tracing and bulk heterojunction solar cells



REACTIVE & FUNCTIONAL POLYMERS

霐

Massimiliano Lanzi^{a,*}, Luisa Paganin^a, Filippo Pierini^b, Francesco Errani^a, Francesco Paolo Di-Nicola^a

^a Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento, 4 I-40136 Bologna, Italy ^b Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi, 2 I-40126 Bologna, Italy

ARTICLE INFO

Article history: Received 5 August 2013 Received in revised form 6 June 2014 Accepted 5 July 2014 Available online 17 July 2014

Keywords: Electrical conductivity Laser tracing Bulk heterojunction polymeric solar cells Regioregular polyalkylthiophenes Polymer blends

ABSTRACT

In this article we demonstrate the use of a blend made of two regioregular polythiophenic derivatives, namely poly(3-methylthio)thiophene and poly(3-hexyl)thiophene, to obtain conductive traces by the simple laser exposure of their thin films to a suitable laser source. The polymeric blend was also tested as a photoactive layer for BHJ solar cells, showing an improved surface morphology and a wider absorption spectrum, thus resulting in an enhanced photovoltaic performance. In the standard condition normally used for the cell preparation, we obtained a 3.16% power conversion efficiency. The device showed good reproducibility and stability over time.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The need for flexible, lightweight, easily processable new materials for electronics has pushed research toward the synthesis of organic materials able to compete with the "classic" inorganic semiconductors in their own application fields. Organic semiconductors, such as conjugated polymers, are promising candidates for this replacement, as demonstrated both by the number of patent applications in 2013 (more than 100 on polythiophenes) and by the growing number of newly launched companies and existing manufacturers of materials or devices that have added organic photovoltaics to their portfolio.

In this context, polythiophenes are intriguing materials which have now been studied for a long time thanks to their electric and electronic properties. In fact, in the charged (doped) state they are very effective conductors of electricity, while in the neutral (undoped) state they are mainly employed in optoelectronic devices – for the construction of organic light emitting diodes (OLEDs), low-voltage field effect transistors and bulk heterojunction (BHJ) solar cells – and in devices such as optical filters, signal modulators and polarization rotators. Alkyl-substituted polythiophenes (PATs) are very soluble in common organic solvents and can be easily filmed and processed using a number of different techniques, e.g. spincoating [1], doctor blading [2], screen printing [3], inkjet printing [4] and roll-to-roll methods [5], making them very interesting materials from an industrial standpoint.

Structurally, PATs belong to the class of conjugated polymers the precursor of which is polyacetylene (PAc). PAc shows electronic characteristics similar to those of PATs; recently some researchers have reported that PAcs functionalized with a thioalkylic group (PAc-SR) are photosensitive polymers [6]. In fact, thin insulating films of PAc-SR can be traced by laser operating at suitable speed, power, and wavelength leading to electroconductive patterns on the film surface [7]. This approach is particularly intriguing since it makes it technically feasible to obtain high resolution patterns for electronic circuits while strongly limiting the number of processing steps and chemicals required. In fact, the line patterning of an insulating polymeric matrix by a laser-induced photopyrolysis process makes it possible to rapidly develop custom conductive circuits from a schematic drawing, by using simple CAD (computer aided design) systems to drive the laser source [8]. Various advantages are evident: over conventional inorganic conductors (metals, oxides, silicon), since no multiple etching and lithographic steps are required to obtain the final circuit, and over the most synthesized conjugated polymers, as no redox processes are necessary to make the polymer conductive, thus avoiding the well-known problems of time and environmental stability.

But conjugated polymers are also intensively studied for other technological applications. In fact, in recent years, conjugated polymers-fullerene mixtures have been widely investigated for use in organic solar cells. Bulk heterojunction (BHJ) polymer solar cells



^{*} Corresponding author. Tel.: +39 051 2093689; fax: +39 051 2093669. *E-mail address:* massimiliano.lanzi@unibo.it (M. Lanzi).

have been reported using either poly(p-phenylenevinylene) derivatives [9], poly(3-alkylthiophene)s [10,11], or low-bandgap polymers [12,13] as electron-donors combined with PCBM ([6,6]phenyl-C₆₁-buthyric acid methyl ester), a soluble fullerene derivative, as the electron acceptor thus creating the photoactive blend. In the standard architecture, the photoactive blend is sandwiched between a glass covered with indium tin oxide (ITO), acting as the anode, and a cathode made of a low-workfunction metal (usually Al). The light incident on the BHJ cell through the ITO electrode is mainly absorbed by the conjugated polymer, thus leading to the creation of bound excitons (holes/electrons couples). If the polymer and fullerene components are phase-segregated on a nanoscale length, the excitons can split into separated electrons and positive holes, which are transported along PCBM and conjugated polymer toward the metal and ITO electrode, respectively, thus generating the photocurrent and photovoltage.

One factor that strongly limits the efficiency of this kind of cell is the low exploitation of the sunlight due to the narrower absorption band of the absorption spectrum of the conjugated polymer in comparison to the solar spectrum; however some strategies have been adopted to overcome this limitation, in particular the synthesis of low band-gap polymers [14–16] and the preparation of polythiophenes containing chromophores in the side chain [17,18].

Therefore, the aim of this work is to synthesize a regioregular polythiophenic derivative functionalized with thiomethylic groups – namely the poly(3-methylthio)thiophene (PTSMe) – and to study its electrical behavior before and after laser tracing. For this purpose, PTSMe was blended with regioregular poly(3-hexyl)thiophene (P3HT) to overcome its poor filmability caused by its incomplete solubility in organic solvents. The obtained blend showed a wider absorption spectrum than conventional P3HT and was employed for the preparation of BHJ solar cells. The assembled cells were fully characterized from the morphological and electronic standpoint and their performances was compared with a reference cell made of only P3HT.

2. Experimental

2.1. Synthesis and polymerization

Scheme 1 outlines the experimental route from monomer to polymer.

2.1.1. Synthesis of the monomer 2,5-dibromo-3-methylthiothiophene (2,5-BTSMe)

2.73 g (15.4 mmol) of N-bromosuccinimide (NBS) in 15.5 ml of N,N-dimethylformamide (DMF) were added dropwise - under



Scheme 1. Synthesis of the monomer 2,5-BTSMe and polymer PTSMe.

stirring and in an inert atmosphere – to a solution of 2.0 g (15.4 mmol) of 3-methylthiothiophene (TSMe, Atlantic Chemical Co., USA) in 15.5 ml of DMF. The mixture was reacted for 6 h at room temperature. 3.02 g (17.05 mmol) of NBS in 17.1 ml of DMF were added dropwise and the mixture was reacted for another 24 h at room temperature and under nitrogen. The reaction mixture was then poured into 500 ml of an aqueous solution of NaCl and the organic phase was extracted with 4×150 ml of n-pentane. The collected organic phases were washed with a 5% solution of NaHCO₃ (2 × 300 ml) and with water to neutrality. The organic phase was then dried and concentrated at reduced pressure thus giving the crude product, which was purified with column chromatography (SiO₂/n-heptane) leading to 3.19 g of pure 2,5-BTSMe (72% yield).

¹H NMR (CDCl₃, ppm) δ: 6.91 (s, 1H, H4); 2.55 (s, 3H, CH₃).

FT-IR (Ge disk, cm⁻¹): 3051 (ν C—H, thiophene β-hydrogen); 2960 (ν C—H, antisymmetric methyl); 2875 (ν C—H, symmetric methyl); 1503 (ν C=C, antisymmetric thiophene); 1468 (ν C=C, symmetric thiophene); 1368 (symmetric deformation CH₃); 991 (ν C—Br, thiophenic); 840 (γ C—H 2,3,5-trisubstituted thiophene); 690 (ν C—SMe).

2.1.2. Synthesis of the regioregular poly(3-methylthio)thiophene (PTSMe)

4.2 ml (4.2 mmol) of a 1 M solution of methylmagnesium bromide in di-n-buthyl ether were added to a solution of 1.20 g (4.16 mmol) of 2,5-BTSMe in 25 ml of anhydrous THF. The mixture was refluxed for 2 h under stirring and under Ar atmosphere and then 24.83 mg (0.0458 mmol) of Ni(dppp)Cl₂ were added and the reaction refluxed for 1 h more. The mixture was cooled down to room temperature, poured into 40 ml of methanol and filtered on a Teflon septum (0.45 μ m pore size). The recovered polymer was washed several times with methanol and dried, resulting in 0.320 g of PTSMe (60 % yield).

¹H NMR (CDCl₃, ppm) δ: 7.26 (s, 1H, H4); 2.49 (s, 3H, CH₃).

FT-IR (Ge disk, cm⁻¹): 3059 (v C—H, thiophene β-hydrogen); 2957 (v C—H, antisymmetric methyl); 2853 (v C—H, symmetric methyl); 1511 (v C=C, antisymmetric thiophene); 1462 (v C=C, symmetric thiophene); 1369 (symmetric deformation CH₃); 1014 (rocking CH₃); 823 (γ C—H 2,3,5-trisubstituted thiophene); 716 (v C–SMe).

2.1.3. Preparation of the PTSMe-P3HT blend (PB)

120 mg (0.94 mmol) of PTSMe and 60 mg (0.36 mmol) of regioregular poly(3-hexylthiophene) (P3HT, 92% HT, Mn = 32 kDa, PDI = 1.18), previously synthesized using the same procedure used for the preparation of PTSMe, were dissolved in 10 ml of CHCl₃ at room temperature and the obtained solution was sonicated for 10 min. The solution was then filtered over a Teflon septum (0.20 μ m pore size) and concentrated at reduced pressure producing the PB blend.

2.2. Measurements

¹H NMR were recorded on a Varian Mercury Plus spectrometer (400 MHz) using TMS as a reference. FT-IR spectra of the monomers (pure liquids) and polymers (films) were obtained on Ge disks using a Perkin Elmer Spectrum One spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards and THF as an eluent on a HPLC Lab Flow 2000 apparatus equipped with a PL Gel MXL column and a Linear Instrument UV–Vis detector model UVIS-200 working at 263 nm. UV–Vis spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer using polymer films on quartz slides cast from chloroform solutions (ca. 10⁻³ M). Cyclic voltammetry (CV) was performed on a Autolab PGSTAT 30 (EcoChemie, The Netherlands) with a three electrode system in a solution of 0.1 M Bu₄NPF₆ in CH₃CN, at a scan rate of 50 mV s⁻¹. Polymer films were coated on a Pt plate electrode (1 cm²) by dipping the electrode into the corresponding solution (5 × 10⁻³ M in CHCl₃) and then drying, obtaining films of the approximatively same thickness (0.4–0.5 µm). A Pt wire was used as the counter electrode and an aqueous saturated calomel electrode (SCE) as the reference electrode.

Electrical measurements were performed in air at room temperature using a Keithley 2101 electrometer (traced films) and an Alpha Lab teraohmeter (pristine films). The reported values were the mean of five measurements performed on different parts of the same sample as well as on five different samples prepared using the same experimental conditions. In all cases, differences did not exceed 5% of the final value. The laser source was a Wicked Lasers Spyder III Arctic class 4 diode laser, operating at 445 nm with a nominal power of 750 mW. The effective power of the laser beam on the polymer surface was measured with a Coherent FieldMax II laser power meter giving an effective power of 600 mW. Samples were mounted on a computer-controlled positioning system (Thorlabs L490MZ) and moved on a plane perpendicular to the focused laser beam by using two Thorlabs MTS TDC001 controllers thus making it possible to control both the tracing speed on the x-y plane and the laser-sample distance for the correct focus of the beam on the sample surface, while operating on the *z*-axis. Films thickness was measured using an AFM Burleigh Vista 100 as a profilometer. SEM analyses were performed on a Phenom-world ProX SEM apparatus, equipped with an EDS microanalysis probe. AFM of the blend was performed on a Burleigh Vista Atom Force Microscope equipped with a silicon-nitride tip and operating in a non-contact tapping mode. Optical 2D and 3D microscopy was performed using a Hirox KH-7700 Digital microscope.

2.2.1. ITO/PEDOT/PB: PCBM/Al solar cell assembly

ITO glass (Delta Technologies, Stillwater, Minnesota, USA; 2.5×2.5 cm; code CG-41IN-0107) was first cleaned in an ultrasonic bath using a non-foaming glass detergent in deionized water. ITO glass was then rinsed sequentially in double distilled water, isopropanol, and acetone reaching a final resistance of 6 Ω /sq. PEDOT:PSS (Aldrich Chemical Co.) was diluted 1:1 with isopropanol and deposited by doctor blading (DB) on top of the cleaned ITO glass using a Sheen Instruments Model No. S265674 (film thickness about 80 nm). Anhydrous chloroform was used to prepare solutions of P3HT or PB and PCBM (1:1 weight ratio), which were deposited by DB on the PEDOT:PSS layer. After baking films in a vacuum at 130 °C for 30 min, the active layer film thickness measured by AFM was about 100 nm. Lastly, to create the OPV devices, 50 nm of Al was thermally deposited under a vacuum of 6×10^{-7} mmHg by means of an Edwards E306A vacuum coating apparatus equipped with a dual-stage mechanical vacuum pump Edwards 2 E2H2 and with a selectable diffusion pump or turbo-molecular pump. The current-voltage characteristics were measured using a Keithley 2401 source meter under the illumination of a Abet Technologies LS 150 Xenon Arc Lamp Source AM1.5 Solar Simulator, calibrated with an ILT 1400-BL photometer.

3. Results and discussion

Polyacetylenes functionalized with thiomethylic (PAc-SMe) or thioethylic (PAc-SEt) groups were the first photosensitive polymers examined for laser patterning applications. In fact, they were able to increase their electrical conductivity by many orders of magnitude (up to 16) when exposed to a correctly focused laser radiation of a suitable wavelength (351 or 488 nm) without need for a chemical doping. The best conditions for the tracing of PAc derivatives were quite difficult to find but, when the system was correctly set-up, conducting traces became insoluble in common solvents and insensitive to humidity, chemical vapors and high temperature. When exposed to a coherent light source, these polymers undergo a photopyrolysis process, with the partial loss of the thioalkylic substituent, which leads to the formation of unsaturated backbones mainly made up of sp₂ hybridized carbon atoms which are only partly linked with sulfur substituents in side chains [19]. This process leads to an extended π -system delocalized over the polymeric chain with an enhanced main chain mean conjugation length (MCL), which explains the higher electrical conductivity.

In this work, we tried to substitute PAc-SMe [20] with an easier synthesizable polythiophenic derivative, i.e. poly(3-methylthio)thiophene (PTSMe), which possesses a photosensitive functional group and a polyconjugated backbone, similar to the acetylene-based polymer, but also shows an increased solubility, filmability and environmental resistance in the non-traced pristine state. Since regioregularity is a fundamental prerequisite for obtaining PATs with high electron mobility [21], PTSMe was prepared using the McCullough Grignard Metathesis (GRIM) polymerization procedure (Scheme 1), which generally leads to regioregular and soluble thiophenic polymers [22].

This procedure starts from a 2,5-dihalothiophene derivative and leads to the obtainment of functionalized polythiophenes with a good yield and a high degree of regioregularity through a simple and effective organometallic group exchange (Grignard Metathesis) reaction. With this aim, the monomer 2,5-dibromo-3-(methylthio)thiophene (2,5-BTSMe) was prepared through the dibromination of TSMe with N-bromosuccinimide (NBS) in anhydrous N,Ndimethylformamide (DMF). The halogenation conditions were accurately optimized, providing for the addition of NBS in two separate amounts while operating at room temperature, thus leading to a satisfying yield (72%) of 2,5-BTSMe. We tried also a faster way, which consisted of the one-step addition of the entire amount of NBS and a reaction time of only 4 h at 60 °C. This time, however, we observed a partial bromination of the $-CH_3$ in the side chain. The two bromine atoms in the α -positions of 2.5-BTSMe were exploited for the organometallic coupling involving the magnesium-halogen exchange (metathesis reaction) with a preformed Grignard derivative (1st reaction step), followed by a Ni(II) catalyzed cross-coupling reaction (2nd reaction step), thus leading directly to the regioregular polymer. These two steps are consecutive and the polymerization is a simple and fast one-pot process.

PSMe was then obtained as a red-brownish powder highly soluble in aromatic chlorinated solvents (chlorobenzene and odichlorobenzene) up to 30 mg/ml, but its solubility decreases to about 5–10 mg/ml in common organic solvents (CHCl₃, THF) at room temperature. This can be ascribed to PTSMe short side chains, which are not able to produce a strong plastifying effect, and not to the polymer main chain lengths, since its molecular weight was not particularly high (Mn = 18.000, PDI = 1.2).

Films of PTSMe cast on glass slides or PET foils show poor homogeneity, some dots, and brittleness and do not have good and permanent adhesion on different surfaces. In order to overcome this problem, we blended the prepared PTSMe with a previously synthesized P3HT sample prepared with the same polymerization technique (GRIM procedure), since P3HT is well soluble in common organic solvents, from which it produces thick, homogeneous free-standing films, while its optical and electrical properties have been well known for a long time now.

The polymeric blend (PB) was prepared starting from a 2:1 weight ratio (about 7:3 M ratio) between PTSMe and P3HT. The FT-IR analysis of PB was performed on a thin film cast on a Ge disk from CHCl₃ solution (Fig. 1).

The spectrum clearly shows the peaks ascribable to the presence of both polymers. Most of them are common to both



Fig. 1. FT-IR spectrum of PB in film cast on Ge disk from CHCl₃ solution. The C-SMe stretching band is evidenced by an asterisk.

the polymers but some peaks can be ascribed to each single structure. In detail, the signals (in cm⁻¹) at 3055 (v C–H, thiophene β -hydrogen), 2955 (v C–H, antisymmetric methyl), 2856 (v C–H, symmetric methyl), 1510 (v C=C, antisymmetric thiophene), 1455 (v C=C, symmetric thiophene), 1377 (symmetric deformation CH₃) and 820 (γ C–H 2,3,5-trisubstituted thiophene) are common to both the polymers while the signals at 2925 (v C–H, antisymmetric methylenes) and 757 (CH₂ rocking) are characteristics of P3HT and that at 716 (v C–SMe) is exclusive to PTSMe.

¹H NMR spectrum of PB in CDCl₃ is reported in Fig. 2.

Starting from the aromatic region, the peak at 7.26 ppm is ascribable to the thiophenic H-4 proton of the TSMe monomer and the fact that it is a singlet confirms that we obtained a regioregular PTSMe polymer. The signal at 6.99 ppm is ascribable to the aromatic H-4 protons of the T6H moieties; this time also, the spectrum confirms the high regioregularity of the P3HT sample, since the intensity of the peak attributable to the HT-HT dyads is strongly prevalent over those belonging to the other kinds of linkages, also visible at about 7.00 ppm. The singlet at 2.49 ppm is ascribable to the thiomethylic protons, while the triplet at 2.80 ppm ($-CH_2 \alpha$ to the thiophene ring), the multiplet at 1.73 ppm ($-CH_2 \beta$ to the thiophene ring), the broad multiplet in the 1.50–1.20 ppm range ($-CH_2$ of the central units) and, lastly, the triplet at 0.90 ppm ($-CH_3$) are due to the protons of the P3HT side chains. The composition of the blend can be determined by means of the normalized integral ratio of the signals at 2.49 and 0.90 ppm and, alternatively, by the normalized integral ratio of the two signals at 7.26 and 6.99 ppm. The real composition of PB was quite different from the starting ratio of the two polymers. In fact, the final molar ratio between PTSMe and P3HT was around 1:2 instead of the 7:3 feed ratio used. This can be ascribed to the low solubility of PTSMe in common organic solvents which caused a kind of fractionation when we filtered the PB solution on the Teflon septum.

However, PB was well soluble in CHCl₃, producing homogeneous and glossy dark-red films.

Fig. 3 shows the UV-Vis spectra of the polymers in film cast from CHCl₃ solutions. Regioregular P3HT shows a λ_{max} at 554 nm, corresponding to the first vibronic quantum, and an evident shoulder at 595 nm, corresponding to the pure electronic transition E_{0-0} [23] which derives from the vibronic absorption of ordered P3HT crystalline regions in films [24]. PTSMe shows only one peak at 415 nm, blue-shifted with respect to the λ_{max} of P3HT and does not show any evident vibronic transition, since short side chains are not able to interact with themselves, thus giving more ordered main chains conformations [25]. The spectrum of the blend shows a very large absorption region, starting at 350 nm and ending at about 650 nm. The blend spectrum clearly evidences the main absorptions of its two components: the PTSMe absorption maximum is now embedded in the spectrum and becomes visible as a shoulder at 410 nm, while the transitions ascribable to the P3HT component are found at 599 nm (E_{0-0}), 546 nm (first vibronic quantum), and 488 nm (λ_{max}). The broad absorption range of the blend can be very useful for polymeric solar cells, since a wider light absorption in the visible region of the solar spectrum can generate more excitons in the BHJ active layer, thus increasing the Jsc of the final device [26].

A few drops of PB solution (5 mg in 5 ml) in CHCl₃ were deposited on a quartz slide $(4.0 \times 4.0 \text{ cm})$ using the DB technique thus



Fig. 2. ¹H-NMR spectrum of PB in CDCl₃. CHCl₃ peak is indicated by an asterisk.



Fig. 3. UV-Vis spectra of polymers in film cast from CHCl₃ solutions.



Fig. 4. Optical microscope image of a traced PB sample (\times 50). The film was cast from the polymer solution in CHCl₃.

giving an homogeneous $1.5 \,\mu\text{m}$ thick film that was used for the laser tracing procedure. The best tracing conditions were found at a $1.0 \,\text{mm/s}$ tracing speed, by making three contiguous parallel lines with an inter-trace distance of 0.33 mm (Fig. 4).

The obtained traces are clearly visible since the polymer surface changed notably after the laser exposure, going from a very smooth, homogeneous surface to a rough, porous surface. This is also evident in the 3D image and in the SEM micrograph of Figs. 5 and 6, respectively.

Film porosity is determined by the outflow of gaseous reaction products – mainly sulfides and mercaptanes [27] – which leaves the polymer surface during the laser patterning.

The band at 716 cm^{-1} in the IR spectrum of PB, ascribable to C—S stretching [28], decreases in intensity after the laser tracing, thus confirming the partial loss of the thiomethylic group after the photopyrolysis procedure (Fig. 7).

We observed that the resistance of the sample decreases as the number of contiguous traces increases, rapidly reaching an asymptotic value corresponding to about three lines. A droplet of an Ag conductive paint (Ted Pella Inc., USA) was then applied to the two ends of the 3-cm-long trace and the resistance was measured with a Keithley 2401 source meter. We prepared five samples of the traced PB blend and measured their surface resistance, which was 150 k Ω /sq with a very good reproducibility of this value among the samples, with a deviation from the reported value of 3%.



Fig. 5. 3D image of PB traces on the polymer film cast from CHCl₃ solution.



Fig. 6. SEM micrograph of a PB film after laser tracing. The polymer film was cast from PB solution in CHCl₃.



Fig. 7. FT-IR spectrum (expansion) of a PB film on Ge disk from CHCl₃ solution before and after the laser tracing procedure. The C-SMe stretching band is evidenced by an asterisk.

The surface resistance of the samples before tracing was 210 G Ω /sq (±5%) and was measured with a teraohmeter (Alpha Lab Inc., USA) using a two probe measuring system. Samples and probes were carefully shielded from surrounding EMF with a Faraday-cage homemade device.

We then prepared another series of samples under the same experimental conditions, i.e. by depositing the $CHCl_3$ solution of PB on a quartz slide using DB technique. This time, samples were annealed for 2 h at 130 °C under a vacuum (0.5 mmHg) by using



Fig. 8. SEM micrograph of a pre-annealed PB film, cast from \mbox{CHCl}_3 solution, after laser tracing.

a Büchi B-585 glass oven before the laser tracing. Even if their initial resistance was essentially unchanged (about 200 G Ω /sq (±4%)), the final resistance of the traced samples was $27 \pm 2\%$ k Ω /sq. This time, the laser treatment of samples enabled a resistance decrease of six orders of magnitude. It must be stressed that the annealing procedure was also performed on the previously traced samples but - this time - it was ineffective, since no evident changes in the final resistance values were found. In fact, the exposure to the laser light makes the traced polymer apparently harder, more scratch-resistant, and insoluble in organic solvents, thus suggesting that the exposed polymer no longer has the characteristics of a substituted polythiophene but rather those of a system of π -conjugated C atoms. Fig. 8 shows the SEM micrograph of an annealed PB sample, prepared by DB technique using PB chloroform solution, after laser tracing. Its appearance is nearly identical to the unannealed film sample, because the laser exposure converted the polymer into worm-like dull traces, devoid of a fine texture, which are always apparently identical one to another.

Fig. 9 shows the topographic microanalysis of the sample shown in Fig. 8 in relation to the C and S elements recorded using an energy-dispersive spectrometer (EDS) probe.

In Fig. 9 it is evident that the laser-exposed polymer has a higher amount of C and a lower amount of S in the traces, since the concentration of the examined element is proportional to the intensity of white. More deeply, C and S concentration passed from 65% and 28% of the unexposed area to 68% and 25% of the laser-treated portions, respectively, thus confirming the partial loss of

thiomethylic side chains. It is worth noting that this slight changes in the PB composition due to the laser exposure is capable of determining such a high surface resistivity change.

Lastly, we prepared a new set of samples made of P3HT alone, in order to evaluate whether the laser treatment was capable of decreasing their electrical resistance. P3HT films were deposited by DB using a polymer solution in CHCl₃. In this case, the surface resistance of these samples was the same before and after the exposure to laser radiation i.e. $220 G\Omega/sq$ (±6%). This test confirms that the electrical conductivity enhancement is ascribable to the presence of the photo-sensitive thiomethylic groups, which are involved in a laser-induced photocleavage which leaves the polythiophenic backbone able to partially crosslink and, then, to rearrange in a more planar and more conjugated conformation, thus aiding the electroconductivity of the final material [29].

Fig. 10 shows the *J*–*V* characteristic curves of solar cells which have the structure of ITO/PEDOT:PSS/composite (photoactive polymer:PCBM)/Al. PEDOT:PSS acts as a hole-transporting layer, the photoactive polymer (P3HT or PB) as an electron donor, and PCBM as an electron acceptor, while the Al electrode is the cathode of the solar cell and the ITO layer the anode [30]. The operational procedures followed for the preparation of cells are described in the experimental section. We used a polymer/PCBM 1:1 weight ratio since some studies have shown that devices with this ratio achieve the highest power conversion efficiency [31,32] and the film thicknesses of the blend absorber layers were each about 100 nm, in order to make the measurement of the photocurrent independent of the thickness of the samples.

The device parameters: short circuit current (J_{sc}), open circuit voltage (V_{oc}), Fill Factor (FF), and power conversion efficiency (PCE) are summarized in Table 1.

The electrochemical behavior of the three examined polymers has been evaluated performing cyclic voltammetry (CV) on their thin films cast on a Pt electrode from CHCl₃ solutions (Fig. 11). We decided to characterize also a film of PSMe even if, as already mentioned, this polymer was not employed as active layer for solar cells since its adhesion to the ITO-glass coated with PEDOT-PSS was very poor and prevented the homogeneous deposition of the Al cathode.

All voltammograms exhibited reversible oxidation and a quite good symmetry for the p-doping/undoping process, and this can be useful for practical applications based on the charge/discharge process since the required potential range needed for passing between neutral and doped states is limited. The HOMO levels of the polymers were measured by CV, while the LUMO energies were calculated indirectly, taking into account that they correspond to the HOMO energies plus the optical energy gaps (E_{opt}) evaluated from the onsets of the UV–Vis spectra of the polymers in film



Fig. 9. EDS topographic microanalysis of PB film reported in Fig. 8. Left: Carbon; Right: Sulfur.



Fig. 10. J-V characteristic curves for the prepared solar cells under AM 1.5 irradiation with an intensity of 1 sun (100 mW/cm^2) from a calibrated solar simulator.

 Table 1

 Photovoltaic parameters for the devices obtained using the two different photoactive blends.

Polymer	$J_{\rm sc}$ (mA/cm ²)	$V_{\rm oc} ({\rm V})$	FF (%)	PCE (%)
РЗНТ	7.73	0.61	52.8	2.48
PB	8.58	0.65	56.7	3.16

[33]. The obtained values are reported in Table 2. PSMe showed the lower oxidation potential, according to the electron-donor character of its thiomethylic side chain directly linked to the thiophene ring [34], and the higher bandgap, probably determined by disorder phenomenon like steric effects, cross linking or chain terminations [35].

In Fig. 12 is reported the band diagram with HOMO/LUMO levels of the ED polymers used for the solar cells in relation with the levels of PCBM and the work function of ITO and Al, according to Ref. [36].

PB sample showed an energy difference between its LUMO level and the LUMO of the EA molecule (ΔE_{LUMO}) higher than P3HT (0.69 vs 0.48 eV) and this can be favorable for the photoinduced charge separation. In fact, it has been reported that a $\Delta E_{LUMO} = 0.3$ eV is the minimum value required to overcome the binding energy of the excitons generated in organic semiconductor polymeric films [37,38]. The total photovoltage of the organic solar cells is ideally equal to the band gap value of the conjugated polymer employed in the light-absorbing (active) layer. In the examined case, the theorical values should be the same for P3HT and PB since they have the same bandgap (1.89 eV). However, there exists a loss factor related to the high exciton binding energy in organic materials which determines the need for a LUMO-LUMO Donor/Acceptor offset in D/A cells to polarize the exciton [39,40]. Practically, the LUMO offset should be large enough to obtain an effective and fast charge transfer and the loss factor is inversely proportional to the ΔE_{LUMO} value. This could explain the V_{oc} value of PB slightly higher than that of the reference cell.

The factors limiting the PCE of polymeric solar cells include the low exploitation of the sunlight mainly due to the narrower absorption band of the absorption spectra in the polyconjugated materials used in the photoactive layer, in comparison with the solar spectrum and the mismatch of the two spectra [13]. The increased efficiency of PB:PCBM solar cells compared to the reference cell made of the normally used regioregular P3HT could be ascribed to the stronger absorbance of PB blend in the 350–500 nm range. Our results are very much in line with those reported in literature. In



Fig. 11. Cyclic voltammograms of the polymer films on Pt recorded in 0.1 M Bu_4NPF_6 acetonitrile solution at a scan rate of 50 mV s⁻¹.

able 2	
Optical and electrochemical properties of the films cast from $CHCl_3$ solutions.	

Polymer	λ_{edge}^{abs} (nm)	$E_{\rm g,opt}~({\rm eV})$	$E_{\rm ox}^{\rm onset}$ (V)	HOMO (eV)	LUMO (eV)
PSMe	520	2.38	0.18	-4.58	-2.20
P3HT	655	1.89	0.76	-5.16	-3.27
PB	655	1.89	0.55	-4.95	-3.06

fact, Li et al. [41] reported that a series of solar cells prepared with polythiophene derivatives functionalized with bi(thienylenevinylene) side chains (biTV-PTs), reached a maximum PCE of 3.18% under AM 1.5, 100 mW/cm², with a 38% efficiency increase compared to that of the cells based on P3HT under the same operative



Fig. 12. Band diagram with HOMO/LUMO levels of the ED polymers and EA PCBM in relation to the work functions of ITO and Al electrodes.

conditions. The enhanced performance was attributed to the increased absorption of (biTV-PTs) in the region between 350 and 450 nm [42]. In fact, the J_{SC} represents the maximum photocurrent density produced by a solar cell under solar illumination at short circuit condition. This current is directly related to the external quantum efficiency (EQE) which depends on the absorption effi-

ciency of the photoactive layer [43]. When the organic cells are made of a conjugated polymer and PCBM, a wider and more intense absorption spectrum of the photoactive blend can raise the PCE of the device acting on its photocurrent density. In our case, since the integrated intensity of the UV–Vis spectra of P3HT, PSMe and PB in film are in a 1:0.95:1.57 ratio respectively, and the thicknesses of the active layers in the cells are almost the same (about 100 nm), the higher value of J_{SC} observed for PB (if compared with the reference cell) can be ascribed to its more extended absorption range.

To analyze the morphology of solar cells, we chose to use atomic force microscopy (AFM). Fig. 13 shows the surface morphology of P3HT or PB and PCBM (1:1 weight ratio) photoactive blends. Films were prepared by casting the chloroform solutions of the polymers on ITO glasses using the DB technique. The support had been cleaned beforehand using the same procedure used for the preparation of solar cells. After the blend deposition, samples were subjected to the annealing procedure (30 min at 130 °C under vacuum) and the surface images were recorded using an AFM in a non-contact (tapping) mode in height-modulated (HMM) and phase-modulated (PMM) modes.

The AFM images of the surfaces of the two prepared films (100 nm thick) are quite different; in fact the surface rms (root-mean-square) roughness is 5.4 nm for the P3HT:PCBM film (with



Fig. 13. AFM images of the examined blends (tapping mode, scale in nm; left: height modulated images; right: phase modulated images). The blends were obtained by casting the polymer/PCBM solutions in CHCl₃ on ITO glasses.

an average 18 nm diameter of grains) and 2.2 nm for PB:PCBM (average 11 nm diameter grains). The large black features in PMM, which correspond to bumps in topography (HMM), are ascribable to PCBM-rich domains. The rough surface indicates a P3HT self-organization in the blend, enhancing the ordered structure formation in the film [44]. However, an excessively rough surface morphology can cause poorer contact between the photoactive layer and the metallic cathode [45], leading to a decrease in the $V_{\rm oc}$ values as the shunt resistance of the cell increases [46]. Surface roughness was found to be a critical parameter also in polymer solar cells based on inkjet-printed PEDOT:PSS layers, where irregular surface morphologies of the layers led to very poor device performance in terms of J_{sc}, FF and PCE [47].

All devices showed good reproducibility and stability in time in terms of final PCE: the cells stored in vacuo, at room temperature. showed an average approximate 5% PCE decrease in the initial value after 30 days. The best solar cell performance was obtained using the PB/PCBM system as the active blend. This can be ascribed not only to the enhanced absorption spectrum of this blend, which acts positively on its generated photocurrent, but also to its very smooth surface and to the nanoscale homogeneous separation of its components, leading to a high interfacial area of the electron donor-acceptor domains, which acts positively on the final $V_{\rm oc}$ and FF, as confirmed by the data reported in Table 1. The obtained results are very promising since they demonstrate that it is possible to produce highly efficient active layers of polymer solar cells with good sunlight absorption by using a simple mixture of easily synthesizable polymers, thus avoiding the long and complex synthesis usually required to obtain low-bandgap conjugated polymers [48].

4. Conclusions

This work demonstrated the possibility to enhance the electroconductivity of some films made of thioalkylic-substituted polythiophene derivatives through laser light exposure. In particular, a blend made of regioregular poly(3-methylthio)thiophene (PTSMe) and poly(3-hexyl)thiophene (P3HT) proved to be an optimal solution for overcoming the incomplete solubility and poor filmability of the thioalkyl-substitued polythiophenic derivative alone. The blend used strategically combines the plastifying properties of the alkylthiophene polymer with the ability of the photosensitive polythiophene to increase its electrical conductivity by means of a fast, simple laser treatment. This way, we obtained very homogeneous polymeric films which were easily cast from common organic solvents and which proved to be capable of increasing their electrical conductivity by about 7×10^6 times after tracing. The final electrical conductivity of the conductive traces can be easily modulated by working on the blend composition, laser power, and tracing speed, thus making the preparation of integrated circuits faster and simpler. We also demonstrated that the performance of the BHJ solar cell prepared using the blend as the photoactive layer is higher than in the reference cell made of P3HT alone, thanks to the wider absorption spectrum and the more homogeneous morphology of the films obtained from P3HT/PTSMe mixtures. These results indicate that PTSMe and, in particular, its blends with P3HT, are promising multifunctional polymeric materials for application in electronics and in plastic solar cells.

Acknowledgement

Italian PRIN 2010-2011 is gratefully acknowledged.

References

- [1] K. Norrman, A. Ghanbari Siahkali, N.B. Larsen, Annu. Rep. Prog. Chem. Sect. C. 101 (2005) 174-201.
- P. Schilinsky, C. Waldauf, C.J. Brabec, Adv. Funct. Mater. 16 (2006) 1669–1672. [3] F.C. Krebs, M. Jorgensen, K. Norman, O. Hagemann, J. Alstrup, T.D. Nielsen, J.
- Fyenbo, K. Larsen, J. Kristensen, Sol. Energy Mater. Sol. Cells 93 (2009) 422-441 [4] A. Lange, M. Wegener, C. Boeffel, B. Fischer, A. Wedel, D. Neher, Sol. Energy
- Mater. Sol. Cells 94 (2010) 1816-1821.
- [5] F.C. Krebs, Sol. Energy Mater. Sol. Cells 93 (2009) 465-475.
- [6] H.K. Roth, K. Fidner, H. Roth, Circ, World 22 (2) (1996) 31-32.
- [7] R. Baumann, U. Kulish, M. Schroedner, H.K. Roth, D. Sebastian, J. Bargon, Synth. Met. 55-56 (1993) 3643-3648.
- [8] M. Lanzi, F.P. Di Nicola, M. Livi, L. Paganin, F. Cappelli, F. Pierini, I. Mater, Sci. 48 (2013) 3877-3893.
- [9] H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N.S. Sariciftci, Adv. Funct, Mater, 14 (2004) 1005–1011.
- [10] R. Hegde, N. Henry, B. Whittle, H. Zang, B. Hu, J. Chen, K. Xiao, M. Dadmun, Sol. Energy Mater. Sol. Cells 107 (2012) 112–124.
- [11] A.J. Moulé, S. Allard, N.M. Kronenberg, A. Tsumi, U. Scherf, K. Meerholz, J. Phys. Chem. C 112 (2008) 12583-12589
- [12] J. Hou, H.Y. Chen, S. Zhang, G. Li, Y. Yang, J. Am. Chem. Soc. 130 (2008) 16144-16145
- [13] Y. Li, Y. Zou, Adv. Mater. 20 (2008) 2952–2958.
 [14] E. Bundgaard, F.C. Krebs, Sol. Energy Mater. Sol. Cells 91 (2007) 954–985.
- [15] D. Muehlbaher, M. Scharber, M. Morana, Z.G. Zhu, D. Waller, R. Gaudiana, C. Brabec, Adv. Mater, 18 (2006) 2884-2889.
- [16] N. Blouin, A. Michaud, M. Leclerc, Adv. Mater. 19 (2007) 2295-2300.
- [17] K. Takahashi, Y. Takano, T. Yamaguchi, J. Nakamura, C. Yokoe, K. Murata, Synth. Met. 155 (2005) 51-55.
- [18] L. Angiolini, T. Benelli, V. Cocchi, M. Lanzi, E. Salatelli, React. Funct. Polym. 73 (2013) 1198-1206.
- [19] H.K. Roth, H. Gruber, E. Fanghaenel, A.M. Richter, W. Hoerig, Synth. Met. 37 (1990) 151–164
- [20] B.M. Novak, E. Hegen, A. Visnanathan, L. Magde, Polym. Prepr. 31 (1990) 482-483.
- [21] I. Zergioti, M. Makrygianni, P. Dimitrakis, P. Normand, S. Chatzandroulis, Appl. Surf. Sci. 257 (2011) 5148-5151.
- [22] R.S. Lowe, P.C. Ewbank, J. Lin, L. Zhai, R.D. McCullough, Macromolecules 34 (2001) 4324-4333.
- [23] M. Lanzi, L. Paganin, Eur. Polym. J. 44 (2008) 3987-3996.
- [24] S.P. Singh, C. Pavan Kumar, G.D. Sharma, R. Kurchania, M.S. Roy, Adv. Funct. Mater. 22 (2012) 4087-4095.
- [25] F. Bertinelli, P. Costa Bizzarri, C. Della Casa, M. Lanzi, Spectrochim. Acta A 58 (2002) 583 - 592
- [26] A. Mikroyannidis, P. Suresh, G.D. Sharma, Org. Electron. 11 (2010) 311-321.
- [27] H.K. Roth, R. Baumann, J. Bargon, M. Schroedner, Prog. Colloid Polym. Sci. 85 1991) 157-162.
- [28] J.B. Lambert, D.A. Lightner, H.F. Shurvell, R.G. Cooks, Introduction to Organic Spectroscopy, Macmillan Ed., New York, 1987.
- [29] M. Lanzi, L. Paganin, Eur. Polym. J. 45 (2009) 1118-1126.
- [30] M. Lanzi, L. Paganin, React. Funct. Polym. 70 (2010) 346-360.
- [31] D. Chirvase, J. Parisi, J.C. Hummelen, V. Dyakonov, Nanotechnology 15 (2004) 1317-1323
- [32] G. Li, V. Shrotriya, Y. Yao, Y. Yang, J. Appl. Phys. 98 (2005) 043704.
- [33] M. Lanzi, F.P. Di Nicola, F. Errani, L. Paganin, A. Mucci, Synth. Met. 195 (2014) 61-68.
- [34] J. Roncali, Chem. Rev. 92 (1992) 711-738.
- [35] A.J. Nelson, S. Glenis, A.J. Frank, J. Chem. Phys. 87 (8) (1987) 5002-5006.
- [36] M. Al-Ibrahim, H. Klaus Roth, U. Zhokhavets, G. Gobsch, S. Senfuss, Sol. Energy Mater. Sol. Cells 85 (2005) 13-20.
- [37] T.M. Clarke, J.R. Durrant, Chem. Rev. 110 (2010) 6736–6767.
- [38] M.C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldhauf, A.J. Heeger, C.L. Brabec, Adv. Mater. 18 (2006) 789-794.
- [39] M. Zhang, H. Wang, C.W. Tang, Appl. Phys. Lett. 97 (2010) 143503-143506. [40] A. Gadisa, M. Svensson, M.R. Andersson, O. Ingänas, Appl. Phys. Lett. 84 (2004)
- 1609-1611. [41] J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang, Y. Li, J. Am. Chem. Soc. 128 (2006) 4911-
- 4916.
- [42] B. Carsten, F. He, H.J. Son, T. Xu, L. Yu, Chem. Rev. 111 (2011) 1493-1528.
- [43] X. Yang, A. Uddin, Renew. Sustain. Energy Rev. 30 (2014) 324–336.
- [44] G. Li, V. Shrotriya, J.S. Huang, Y. Yao, T. Moriatry, K. Emery, Y. Yang, Nat. Mater. 4 (2005) 864-868.
- [45] G. Zhao, Y. He, Y. Li, Adv. Mater. 22 (2010) 4355-4358.
- [46] A. Moliton, J.M. Nunzi, Polym. Int. 55 (2006) 583-600. [47] S.H. Eom, S. Senthilarasu, P. Uthirakumar, S.C. Yoon, J. Lim, C. Lee, H.S. Lim, J.
- Lee, S.H. Lee, Org. Electron. 10 (2009) 536-542. [48] N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M.
- Belletete, G. Durocher, Y. Tao, M. Leclerc, J. Am. Chem. Soc. 130 (2008) 732-742.