

# Synthesis and Characterization of Conductive Terpolymer for Solar Cell Application

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## How to cite

Santos BPS; Ribeiro AC; Furtado JG; Marques MFV (2019) Synthesis and Characterization of Conductive Terpolymer for Solar Cell Application. *J. Aerosp Technol Manag*, 11, Special Edition: 41-44. <https://doi.org/10.5028/jatm.etmq.07>

**ABSTRACT:** Polymeric solar cells (PSCs) are a promising alternative for harnessing solar energy and producing clean and renewable energy. In the present work, a new photovoltaic polymer was synthesized to be applied as an electron donor in PSCs. The conjugated polymer showed high solubility. The optical and electronic properties were investigated in which it was possible to observe wide absorption band and bandgap indicating that it is a promising material for application in solar cells.

**KEYWORDS:** Solar cell; Polymer; Photovoltaic.

## INTRODUCTION

Organic solar cells (OSCs) have considerably stood out in recent years due to their advantages compared to inorganic solar cells, such as low cost, environmentally friendly, flexibility and lightness. Polymeric solar cells are at an early stage of development and require further studies to improve stability for large-scale applications and increase power conversion efficiency (PCE). One of the strategies to achieve these goals is the synthesis of new conductive polymers using three monomer units known as photovoltaic terpolymers (Kang *et al.* 2014). This method allows the adjustment of energy levels and of absorption range. In the present work, a novel conjugated terpolymer made of 50% carbazole and 50% fluorene was synthesized and named as PCBF. The terpolymer was characterized using gel permeation chromatography, UV-visible, atomic force microscopy and cyclic voltammetry techniques.

## METHODOLOGY

### SYNTHESIS OF PCBF

In a Schlenk flask, 0.5 mmol of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 1 mmol of 4,7-dibromo-2,1,3-benzothiadiazole and 0.5 mmol of 9,9-dioctyl fluorene-2,7-bis(diboric acid pinacolester) were mixed in stoichiometric amounts. In this mixture, toluene was used as solvent after its degasification. Then Pd(PPh<sub>3</sub>)<sub>4</sub>, Aliquat 336 and aqueous K<sub>2</sub>CO<sub>3</sub> solution were added and the system was kept under N<sub>2</sub> atmosphere and reflux for 6 h. After that, phenylboronic acid was introduced, maintaining reflux for 2 h, and bromobenzene was added, maintaining the same conditions for more 1 h. The reaction mixture was cooled until room temperature, toluene was poured into it and deionized water was used for washing it.

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Received: 27 Nov 2019 | Accepted: 10 Dez 2019

Note: This paper was selected from the 10<sup>o</sup> Encontro Técnico de Materiais e Química (ETMQ) occurred in 27-29 november of 2019 and organized by Instituto de Pesquisas da Marinha (IPqM) in Rio de Janeiro/RJ, Brazil



Organic layer was separated, dried and concentrated in a rotary evaporator. Then methanol was added to precipitate the polymer and the purification was performed by extracting with hexane, acetone, and dichloromethane sequentially.

## CHARACTERIZATIONS

Molar mass and dispersity were determined by Prominence UFLC Shimadzu Permeation Chromatograph. Chloroform was employed as solvent and the calibration curve was obtained using polystyrene standards in an absolute method. For absorbance measurements, the Agilent 8453 UV-Vis Absorption Spectrophotometer was used. The wavelength was scanned from 300 to 700 nm in a polymer film deposited on glass substrate by spin coating. Cyclic voltammetry was obtained by Metron Autolab Enhancer/Galvanostat. The electrochemical system was composed of electrolyte (tetrabutylammonium hexafluorophosphate solution ( $\text{Bu}_4\text{NPF}_6$ ) in 0.1 mol/L of acetonitrile), reference electrode (ferri/ferrocyanide), counter electrode (Ag/AgCl) and work electrode (silver). The polymer solution with concentration of about 5 mg/mL was deposited on the working electrode. The experiments were performed on a high-power 30 V voltage and 1 MHz bandwidth with a potential scan rate of 50 mV/s. The atomic force microscopy technique was used to evaluate the surface mesostructure of the material. This characterization was performed by JPK Equipment using tapping mode.

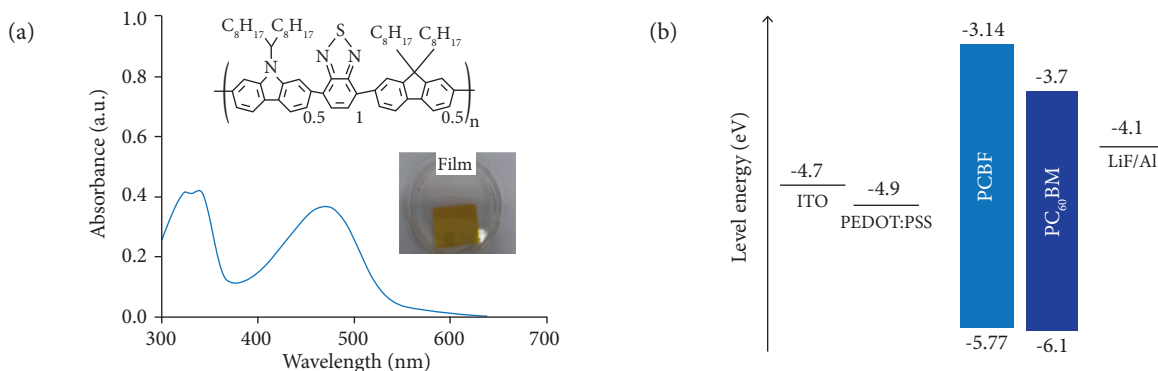
## RESULTS AND DISCUSSION

### GEL PERMEATION CHROMATOGRAPHY (GPC)

In the Suzuki-Miyaura coupling reaction, a carbon-carbon single bond is formed by coupling organoboro species with a halide using a palladium catalyst. This method of synthesis is advantageous because high yield can be obtained. In the present work, the reaction of PCBF synthesis yielded 90-93%. The average numerical molar mass ( $M_n$ ) of PCBF after dichloromethane extraction was 7489 g/mol and a narrow dispersion of approximately 1.4 was obtained, showing that Soxhlet extraction was efficient. The polymer was extracted mostly in dichloromethane and is also soluble in many organic solvents. Since factors such as molar mass can affect the energy conversion efficiency of a device, controlling the molar mass is one of the most important parameters. When a device is produced it is necessary to deposit the active layer (conductive polymer and fullerene derivative mixture) as a film by passing it through a filter. In this sense, a high molar mass can be a problem because the filter can be clogged by the polymer, resulting in a low efficiency of energy conversion.

### OPTICAL AND ELECTRONIC PROPERTIES

The absorption spectrum of the terpolymer film is shown in Fig. 1. PCBF showed two absorption peaks at  $\lambda_{\text{max}}$  of 338 and 470 nm. The first peak is due to  $\pi$ - $\pi^*$  transition while the other is related to the internal charge transfer interaction between donor and acceptor units. In addition, the optical bandgap was calculated through the correlation  $E_g = 1240/\lambda_{\text{onset}}$ , where  $\lambda_{\text{onset}}$  is determined by the tangent of the absorbance peak, and a result of 2.32 eV was obtained.

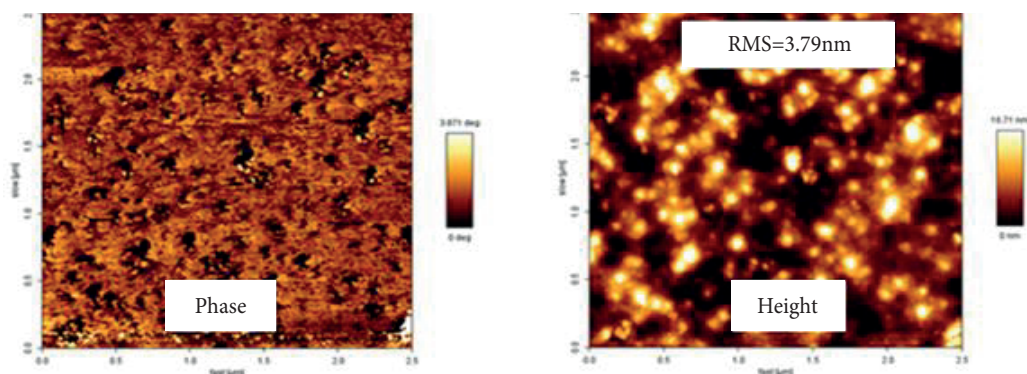


**Figure 1.** UV-Vis absorption and a scheme of energy levels of conventional OSC.

The electrochemical property of the PCBF was investigated using cyclic voltammetry. The terpolymer exhibited a chemical reversible oxidation. The onset of oxidation wave was located at 1.37 V and a HOMO energy level of  $-5.77$  eV was obtained by the equation  $\text{HOMO} = [\text{Eox} + 4.4]$ . The LUMO was estimated using the equation  $\text{LUMO} = [\text{Ered} + 4.4]$ , in which an  $\text{Ered}$  and a LUMO of  $-1.26$  V and  $-3.14$  eV, respectively, were obtained, resulting in an electronic band gap of 2.3 eV. A higher bandgap when is employed CV in comparison with UV-Vis was observed. According to literature, this is due to the shielding energy of exciton in conjugated organic materials (Wakim *et al.* 2009). Figure 1 shows the energy diagram of the system that could be used to produce the devices. The energetic levels of PC<sub>60</sub>BM and polymers are cascaded, which is required for efficient charge transport in solar cells, which indicates the possibility of using this terpolymer as donor in active photovoltaic layer.

## MORPHOLOGY

In order to investigate the effect of terpolymer on devices, the surface morphology and film coverage were studied (Fig. 2). The low film coverage induces increased interfacial loading recombination, which decreases hole extraction and interferes the device performance. It is believed that better morphology on a less rough surface can lead to higher power conversion efficiency (PCE) and charge transport. PCBF showed a homogenous surface when together with PC<sub>60</sub>BM acceptor and also low RMS, indicating promising aspects in order to be applied in solar cells.



**Figure 2.** Morphology phase and height of PCBF:PC<sub>60</sub>BM blend.

## CONCLUSION

The synthesis and characterization of a new electron donor were reported. PCBF showed good optical and electrical properties, as well as good solubility. This new terpolymer is believed to be a promising material for solar cell application.

## FUNDING

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior [<http://dx.doi.org/10.13039/501100002322>]  
Centro de Pesquisa de Energia Elétrica

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## AUTHORS' CONTRIBUTION

Conceptualization, Santos BPS and Ribeiro AC; Methodology, Santos BPS; Research, Santos BPS, Ribeiro AC, Furtado JGM and Marques MFV; Writing - First version, Santos BPS, Ribeiro AC, Furtado JGM and Marques MFV; Writing - Review & Editing, Furtado JGM and Marques MFV; Acquisition of Funding, Marques MFV; Resources, Marques MFV; Supervision, Furtado JGM and Marques MFV.

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