



## Surface modification of polypropylene with poly(3-hexylthiophene) via oxidative polymerization



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### ABSTRACT

Poly(3-hexylthiophene)-graft-polypropylene (P3HT-g-PP) was successfully prepared through a two-step reaction by incorporating poly(3-hexylthiophene) (P3HT) onto the surface of polypropylene (PP). PP was first functionalized with styrene, yielding polystyrene-graft-polypropylene (PS-g-PP) and 3HT was subsequently polymerized on PS-g-PP via FeCl<sub>3</sub> oxidative polymerization. Crosslinking between the 3HT unit and aromatic ring of styrene attached to the surface of PP improved the thermal stability and conductivity of PP. The absorption and emission peaks of P3HT-g-PP in the range of 500–600 nm provided evidence of  $\pi$ - $\pi^*$  conjugation in the 3HT unit grafted to PP. The presence of the P3HT layer on the surface of PP also changed the crystal structure of PP. The presence of sulfur originating from P3HT was confirmed by elemental mapping using transmission electron microscopy energy dispersive X-ray (TEM-EDX) analysis.

### 1. Introduction

Recently, surface modification of polymers has become a field of growing interest for the development of macromolecules and as a means of improving the polymer properties and performance. The various methods of modifying polymers can be broadly classified as blending, grafting, and curing [1]. Polypropylene (PP), one of the most recognized polymers, finds application in a wide variety of fields such as packaging, textiles, and automotive materials [2–4]. However, due to its highly non-polar nature and low surface energy, PP must be modified in order to improve the surface properties, such as the wettability, adhesion, and dye-ability.

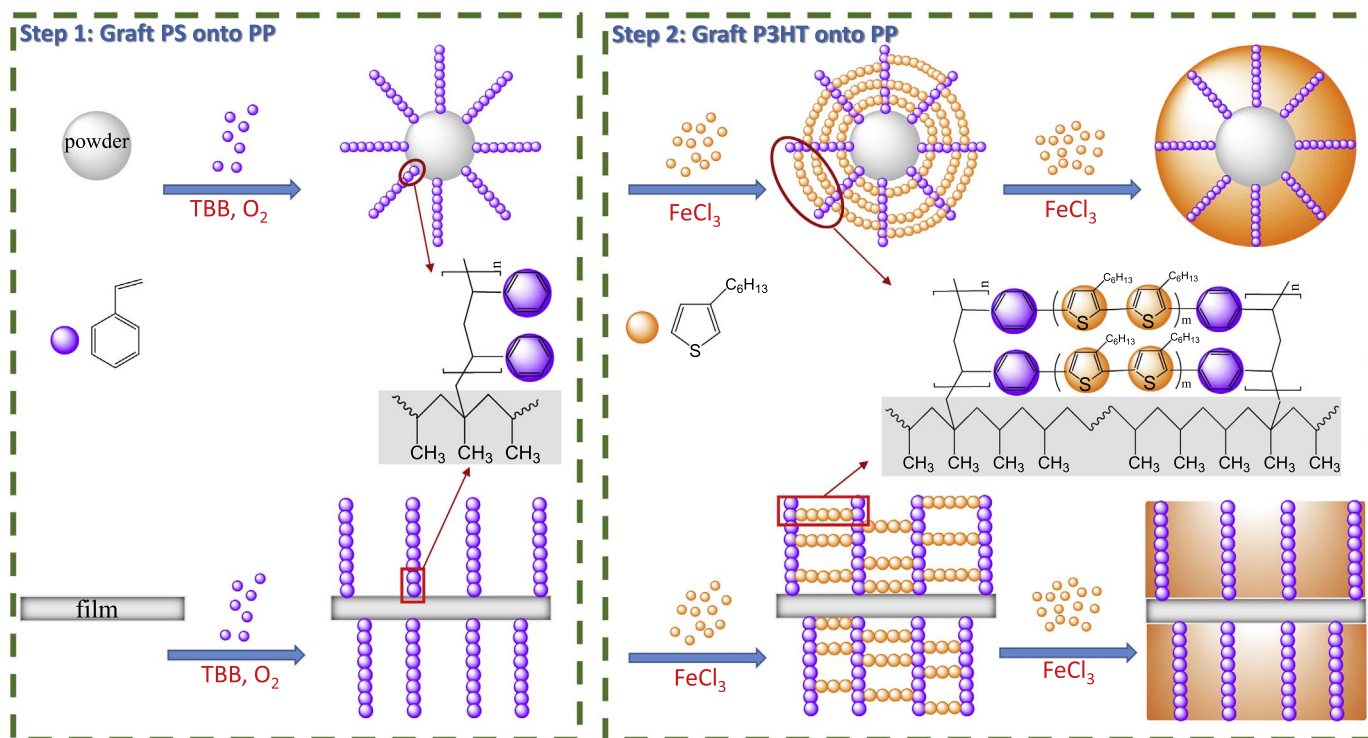
Several techniques have been reported for PP surface modification, including impulse corona discharge [5], surfactant immobilization [6], melt-grafting using a twin-screw extruder [7], plasma treatment [8,9], ultraviolet photo-grafting [10], air dielectric barrier discharge (DBD) [11], and diazonium chemistry [12].

Recently, advances in the research on combining conjugated polymers with polyolefins have fueled new interest in enhancing the novel functionalities of materials and further opening the scope of applications. For example, polypyrrole (PPy) was applied as a coating on PP for application as a thermal desalination membrane using solar energy [13]. A composite of PPy and a fibrous PP film was fabricated for potential application as an electrochemical capacitor [14]. Novel conductive composite fibers made of PP and poly(3,4-ethylenedioxythiophene) (PEDOT) were prepared for gas sensing [15]. Polyaniline

(PANi) was coated onto PP to produce novel collecting electrodes for efficient particle removal [16]. Among the wide variety of conjugated polymers, poly(3-hexylthiophene) (P3HT) and its derivatives are recognized among the most promising conducting materials for organic solar cells [17–19], organic transistors [20,21], polymer light-emitting diodes [22], chemical sensors [23], non-linear optics, and energy storage [24]. In one report, polythiophene (PT) was grafted onto the surface of polyethylene (PE) via a three-step technique involving bromination, substitution, and oxidative polymerization [25]. In our previous report, a simple two-step reaction was used to graft P3HT onto the surface of PP [26]. However, in this method, 3-(4-ethenylphenyl)thiophene, used for surface-functionalization of PP in the first step, had to be synthesized via the Suzuki-Miyaura cross-coupling reaction. To simplify the procedure, in this study, the 3-(4-ethenylphenyl)thiophene monomer is replaced by the styrene monomer. The grafting of P3HT onto the surface of PP is illustrated in Scheme 1. In the first step, PP is functionalized with PS to form polystyrene-graft-PP (PS-g-PP) using radicals formed by mixing tri-*n*-butylborane (TBB) and diffuse oxygen molecules in air [27–30]. In the second step, the conductive P3HT layer is polymerized onto the surface of PP by oxidative polymerization of the 3HT monomers and PS-g-PP.

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Scheme 1. Grafting of PS and P3HT onto PP film and powder.

## 2. Experimental

### 2.1. Materials

Isotactic polypropylene (iPP) film and powder were purchased from Toyobo (Pylen Film-CT; Japan) and Mitsui Chemicals (Japan), respectively. 3-Hexylthiophene and anhydrous  $\text{FeCl}_3$  were procured from Tokyo Chemical Industry Ltd., Japan, and used without any further purification. Tri-*n*-butylborane and styrene monomer were obtained from Nippon Aluminum Alkyls Ltd., Japan and Wako Pure Chemical Industry Ltd., Japan, respectively. Solvents such as chloroform, methanol, and hexane were of analytical grade and were purchased from Wako Pure Chemical Industry, Ltd., Japan and used as received. Hexane was used as the reaction medium because of its low polarity, affinity for PP [28], and the insolubility of  $\text{FeCl}_3$  in hexane [31]. Hexane was dried by standing over 4A molecular sieves for 8 h and purged with argon gas for 20 min before use.

### 2.2. Measurement

The UV–vis spectra were obtained via diffuse reflectance measurement at room temperature using a Jasco V-650 UV–vis spectrometer in the absorbance photometric mode with a UV/vis bandwidth of 2.0 nm, a data interval of 1.0 nm, and scan speed of  $400 \text{ nm min}^{-1}$ . The photoluminescence spectra were acquired by excitation at 360 nm at room temperature by using a Jasco FP-8300 spectrofluorometer. Thermogravimetric analysis (TGA) was carried out in air from 20 to  $900 \text{ }^\circ\text{C}$  at a flow rate of  $25 \text{ mL min}^{-1}$  and a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  using a Hitachi thermal analysis system (STA 7200 RV) (Tokyo, Japan). X-ray diffraction (XRD) patterns were obtained using grazing incidence X-ray diffraction (GIXRD) on a Rigaku Smartlab diffractometer (Tokyo, Japan) with graphite-monochromatized  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in steps of  $0.02^\circ$  over the  $2\theta$  range of  $2\text{--}90^\circ$ . Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F microscope. Energy dispersive X-ray (EDX) maps and line-scan spectra were acquired on an Oxford INCA Energy TEM250

instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FT/IR–480 Plus instrument. Raman spectra were obtained by using an HR800 Horiba Raman spectrometer. Gel permeation chromatography (GPC) was carried out using a system equipped with a Jasco PU-2080 Plus pump and a Jasco RI-2031 Plus intelligent refractive index (RI) detector (Tokyo, Japan). The electrical conductivity was measured with an Agilent 34,401 A  $6^{1/2}$  Digital Multimeter resistometer using a four-probe method. Proton nuclear magnetic resonance ( $^1\text{H NMR}$ ) spectra (400 MHz) were recorded on a Bruker Ascend 400 spectrometer (Bruker, Kanagawa, Japan).

### 2.3. Grafting of PS onto the surface of PP (PS-g-PP)

The grafting method applied herein is similar to that used for grafting the vinyl monomer onto the surface of PP by employing TBB and diffuse molecular oxygen in air [28–30]. The PP film (25 mg,  $1 \times 1 \text{ cm}$ , 0.3 mm thickness), styrene monomer (2 mL), and TBB (0.3 mL) were gently stirred for 1 h under argon. The molar ratio of TBB to the styrene monomer was 1/30. After stirring for 1 h, TBB was reacted with diffuse oxygen to form radicals by exposure of the reaction mixture to air. The reaction mixture was stirred gently for another 24 h. The reaction mixture was transferred to a Soxhlet extractor to extract the free PS homopolymer by using chloroform for 24 h. The PS-g-PP was dried under vacuum for 12 h. Grafting of PS onto the PP powder was carried out using a similar procedure to that described above.

### 2.4. Grafting of P3HT onto PP (P3HT-g-PP)

Chemical oxidative polymerization was conducted in an oven-dried Schlenk flask fitted with a stopcock under an atmosphere of argon [31,32].  $\text{FeCl}_3$  (0.37 g), PS-g-PP (25 mg) and hexane (7 mL) were placed in a Schlenk flask, and the mixture was subjected to ultrasonic treatment for 20 min. A hexane solution (3 mL) of 3-hexylthiophene (95 mg) was dropped into a magnetically stirred suspension of the mixture, and the reaction was stirred for 24 h under argon atmosphere at room temperature ( $23 \text{ }^\circ\text{C}$ ). The obtained product was washed with

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