

# Synthesis and characterization of poly(3-hexylthiophene)-grafted polyvinyl alcohol

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## ABSTRACT

Poly(3-hexylthiophene) (P3HT) was grafted onto the surface of polyvinyl alcohol (PVA) through simple chemical oxidative polymerization with  $\text{FeCl}_3$  in three different solvents, namely acetonitrile, chloroform, and hexane. Among these solvents, hexane best stimulated the grafting of P3HT to PVA; the modified PVA was obtained with a high grafting ratio and molecular weight. The resultant modified PVA was characterized by Fourier-transform infrared (FT-IR), ultraviolet visible (UV-vis), fluorescence spectroscopies, X-ray diffraction (XRD), as well as thermo gravimetric analysis (TGA), contact angle and field emission scanning electron microscopy (FE SEM) coupled with energy dispersive X-ray (EDX) analysis. The presence of P3HT on the PVA surface imparted hydrophobic character, and the PVA modified with P3HT exhibited enhanced electrical conductivity compared to PVA. The peaks in the XRD spectrum of PVA were less intense following P3HT grafting to the PVA surface, and the build-up of P3HT on the PVA surface led to the appearance of absorption and emission peaks in the visible wavelength range. PVA was less stable following grafting by P3HT and the existence of elemental sulfur originating from P3HT was detected on the modified PVA by FE-SEM elemental mapping.

## 1. Introduction

Polyvinyl alcohol (PVA) is a semi-crystalline polymer commodity with interesting properties, including toughness, adhesiveness, biocompatibility, swelling behavior, and lack of toxicity. The excellent chemical and physical properties of PVA make it attractive for use in areas such as papermaking, textiles, coatings, adhesives, packaging, pharmaceuticals, and biomedicine [1]. Grafting is an interesting method for modifying the properties of fibers made from PVA, since it does not require modification of the bulk properties of the polymer, and is easily applied to mass production from an industrial perspective. The grafting reaction can be conducted simply and with a variety of monomers to obtain PVA fibers with the desired properties. The ability to modify the hydrophilic surface of PVA to a more hydrophobic one is crucial in order to minimize moisture sensitivity. Grafting of a poly (organophosphazene) to the surface of PVA resulted in a modified polymer with hydrophobic and improved oxygen-barrier properties at high humidity [2].

Conducting polymers have received considerable attention in recent years due to their relevance to a wide number of applications, including energy storage devices, sensors, diodes, and flexible transparent displays [3–8]. Among the conducting polymers, poly(3-hexylthiophene) (P3HT) became a leading candidate material for potential and

prospective applications in organic solar cell and other electronic devices due to its best characterizations such as high solubility, low glass transition temperatures, ease of processability, good electrical conductivity, high thermal stability and crystallinity [9,10].

Graft copolymers of PVA with thiophene side-groups and pyrroles were characterized many years ago. These copolymers were prepared in two-step; the thiophene-side-group-containing PVA was first synthesized by esterification at room temperature, after which it was oxidatively and chemically polymerized in order to graft polypyrrole onto the surface of the thiophene-side-group-containing PVA [11]. However, as reported, this method is unsuitable for grafting polythiophene onto the surface of PVA bearing thiophene side groups [11].

In our previous reports, oxidative polymerization was used to graft conducting polymers, such as fluorene (F) and 3-hexylthiophene (3HT), onto the surfaces of cellulose, chitin, and chitosan through one-step reactions [12–14]. Recently, the multicolor PVA was obtained through surface modification with conjugated polymers including 3HT and F by oxidative polymerization [15].

In this article, we report the effect of various solvents on the grafting of poly(3-hexylthiophene) on the surface of polyvinyl alcohol. The P3HT-modified PVA is a conducting product with the physical properties of a common polymer. In addition, the presence of P3HT on the PVA surface improves its hydrophobic properties, which is very useful

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for high-humidity packaging applications.

## 2. Material and experiments

### 2.1. Chemicals

PVA was purchased from Tokyo Chemical Industry Ltd (TCI). Commercial PVA from TCI has degree of saponification of 97 to 100 mol %. PVA was kept and stored in the UNICO UN 650 F mode box under an atmosphere of argon, as it is hygroscopic. 3-Hexylthiophene (3HT) and anhydrous  $\text{FeCl}_3$  were obtained from TCI and used without any further purification. Solvents such as chloroform, acetonitrile, hexane and methanol were analytical grade, purchased from Wako Pure Chemical Industry Ltd and used as received.

### 2.2. Measurement

The UV–vis spectrophotometers were analyzed using the diffuse reflectance measurement in a Jasco V-650 UV–vis spectrometer. Fluorescence spectra were recorded at room temperature on a Jasco spectrofluorometer FP-8300. Thermogravimetric analyses (TG) were measured on a Hitachi Thermal Analysis System STA 7200 RV in air from 20 to 700 °C at a flow rate of 25 ml min<sup>-1</sup> and heating rate of 10 °C min<sup>-1</sup>. <sup>1</sup>H NMR spectra (400 MHz) and IR spectra were conducted on a Bruker Acsend 400 spectrometer and a Jasco FT/IR – 480 Plus, respectively. Samples were dissolved in  $\text{CDCl}_3$  for the <sup>1</sup>H NMR measurements. X-ray diffraction (XRD) patterns were recorded with  $\text{Cu-K}\alpha$  radiation (X-ray wavelength: 1.5418 Å) in steps of 0.02° over the 2 $\theta$  range of 5–70° from a Rigaku Smartlab diffractometer equipped with a D-tex detector. Gel permeation chromatography (GPC) was measured on a system equipped with a Jasco PU-2080 Plus pump and a Jasco RI-2031 plus intelligent RI detector. Chloroform served as the polymer solvent and eluent in an equilibrated system at 40 °C. Contact angle was analyzed on portable contact angle analyzer PGX. For contact angle measurement, the samples are prepared as followed step: the PVA and modified PVA are compressed to form flat and smooth samples. Electrical conductivity was carried out with an Agilent 34401 A 6<sup>1/2</sup> Digit Multimeter resistometer by a four-probe method. Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi system. Energy dispersive X-ray (EDX) mappings and line scan spectra were recorded on an Oxford INCA Energy 250.

### 2.3. Grafting and sample preparation

The procedure is reported in previous reports [14]. An amount of 0.33 g PVA and 0.37 g  $\text{FeCl}_3$  were dispersed in 7 ml chloroform with a magnetic stirrer. The chloroform (3 ml) solution of 3HT (100 mg, 0.6 mmol) was dropped into a magnetically mixture of PVA and  $\text{FeCl}_3$ . The reaction was conducted for 2 h at 0 °C under an argon atmosphere. The stoichiometric ratios of 3HT to  $\text{FeCl}_3$  is 1:4. The reaction was terminated by adding methanol. The obtained product was washed with methanol by Soxhlet extract apparatus to remove any residual  $\text{FeCl}_3$ , and then it was extracted with chloroform to eliminate free poly(3-hexylthiophene) (P3HT) homopolymer using a Soxhlet extractor. The final products were dried under vacuum for 12 h. The grafted PVA with P3HT are hereinafter referred as P3HT-g-PVA.

## 3. Results and discussions

### 3.1. Grafting ratio and the characterization of the extracted P3HT

The process of grafting P3HT onto the surface of PVA employs two concurrent reactions, namely the self-polymerization of 3-hexylthiophene to form P3HT, and the graft polymerization of 3HT onto PVA. The ungrafted 3-hexylthiophene homopolymer was separated from the grafted PVA by Soxhlet extraction. The ratio of  $\text{FeCl}_3$  to the

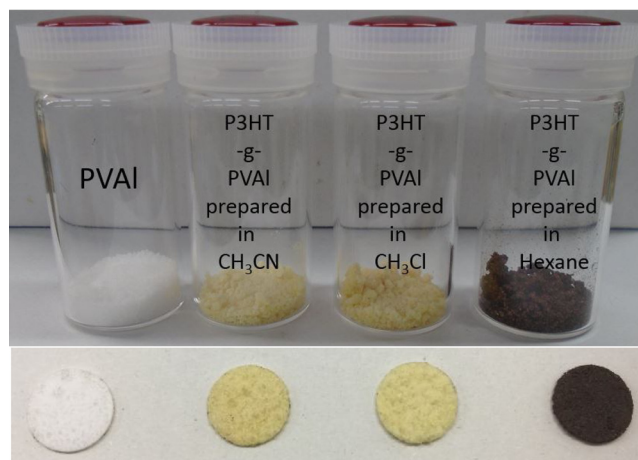


Fig. 1. Photographic images of PVA and P3HT-g-PVA synthesized in different solvents.

grafting material that provided the best grafting ratio for the conducting polymers prepared on the surfaces of cellulose and polysaccharides was found to be 1.33 [12–14]. Based on the results from our previous reports, we chose a  $\text{FeCl}_3$ /PVA ratio of 1.33 in this study. The effects of three different solvents, namely acetonitrile, chloroform, and hexane, on the grafting behavior of P3HT toward the surface of PVA was studied. Due to the different solubilities of  $\text{FeCl}_3$  in the three above-mentioned solvents, P3HT-g-PVA products were obtained that were clearly different, as shown in Fig. 1, which displays images of neat PVA and the P3HT-g-PVA samples in powder and compressed forms.

The grafting ratio (Gr) was calculated using the formula:  $(A - B - C) / B \times 100$ , where A is the total weight of the crude grafted PVA product, B is the weight of the original PVA, and C is the weight of the extracted 3-hexylthiophene homopolymer [16–18]. Although PVA ordinarily dissolves in hot water, the P3HT-g-PVA samples were absolutely insoluble in hot water and chloroform. As a result, the molecular weights of the P3HT-g-PVA samples were impossible to determine. Therefore, we assume that the molecular weight of the extracted P3HT is the same as the molecular weight of the P3HT grafted onto the PVA. Table 1 summarizes the grafting ratios and average molecular weights of the P3HT-g-PVA samples. As shown in Table 1, hexane stimulated the production of the polymer with the highest molecular weight ( $M_w = 90$  kDa), while the polymers produced in chloroform and acetonitrile had lower values ( $M_w \sim 48$  kDa). The insolubility of  $\text{FeCl}_3$  in hexane led to a heterogeneous grafting reaction in which the active sites on the surfaces of the  $\text{FeCl}_3$  crystals were efficient and highly effective [19,20]. In contrast, the homogeneous grafting reaction that was carried out in acetonitrile resulted in a lower value of polymer yield and molecular weight when compared to the heterogeneous system [21]. In summary, hexane is the best solvent in which to graft P3HT onto PVA due to the insolubility of  $\text{FeCl}_3$ , which remains in the solid state and is highly active and reactive.

The FT-IR and <sup>1</sup>H NMR spectra of the extracted P3HT are displayed in Fig. 2. Fig. 2a reveals peaks in the 3000–3050 cm<sup>-1</sup> range that correspond to the stretching mode of the C–H bond at position 4 ( $\text{C}_\beta\text{-H}$ ) of

Table 1  
Properties of the grafted and extracted polymers.

Used Solvent	Grafting ratio %	Molecular weight of graft copolymer (*)	
		$M_w$ , Da	PDI
Acetonitrile	4.1	45000	2.4
Chloroform	4.2	50000	2.2
Hexane	6.5	90000	2.3

Abbreviations: PDIpolydispersity index; (\*) Determined by GPC.

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