



# PVDF based flexible piezoelectric nanogenerators using conjugated polymer:PCBM blend systems



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## ABSTRACT

Piezoelectric energy harvesting technology has received much attention as a powerful source of energy for a self-powered system. In this study, three main conjugated polymers that have delocalized  $\pi$ -electrons and excellent charge transport properties were studied: poly(3-hexylthiophene) (P1), poly[(4,8-di-(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)-alt-(5,5'-yl-4,4'-bis(dodecyl)-2,2'-bithiophene)] (P2) and poly[(4,8-di-(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)-alt-(5,5'-yl-4,4'-bis(2-ethylhexyl)-2,2'-bithiophene)] (P3). Each of three polymers was blended with phenyl-C61-butyric acid methyl ester (PCBM<sub>61</sub>), and the blend systems were used to make PVDF based piezoelectric nanogenerators (PNG-0–3). Polymers showed bimodal structures that have a majority edge-on orientation, forming a minority face-on orientation. At a 2 Hz frequency and 0.2 mm displacement, the output voltages (peak-to-peak) of PNG-(0–3) were 35.0 V, 41.2 V, 42.2 V and 43.1 V, respectively, and the output currents (peak-to-peak) were 558.5 nA, 569.5 nA, 572 nA and 589 nA, respectively. The energy conversion efficiencies of PNGs (0–3) were 6.47%, 11.62%, 13.36%, and 14.33%, respectively; therefore, the efficiency was improved by up to about 2.2 times.

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## 1. Introduction

As the market for portable and wearable electronics, such as smartphones, smart watches, tablets, body sensors and medical devices, rapidly grows, electronics based on low-power technologies are playing an increasing role in our everyday lives [1–6]. Accordingly, there have been many studies on self-powered systems using various applications, such as piezoelectric, triboelectric, and electromagnetic energy conversions [7–12].

Some examples of mechanical energy in our daily lives are body motions, vibration, pressure, wind, sound-waves, waterfalls, and so on. This mechanical energy can be converted to electrical energy using a piezoelectric energy harvesting technology, which has been proven to be a powerful source of energy [13–19].

As piezoelectric energy conversion materials, lead zirconate titanate (PZT), barium titanate (BaTiO<sub>3</sub>), zinc oxide (ZnO) and poly(vinylidene fluoride) (PVDF), have been used in many studies [20–27]. Although piezoelectric properties are one of the most important features, these materials should also be robust against

environmental impact, vibration and pressure. In addition, they should meet biocompatibility and environmental considerations.

Organic piezoelectric materials have shown good flexibility and can be used in applications where large deformation is required. Particularly, PVDF is known to be a semicrystalline polymer that has excellent piezoelectric properties. PVDF can have four different crystalline phases: the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -phases. The  $\alpha$ -phase shows non-polar properties. The  $\beta$ -phase shows polar properties and can be created by mechanical and electrical polling. The excellent piezoelectric properties come from the TTTT (all trans) conformation, where the  $-\text{CH}_2$  and  $-\text{CF}_2$  groups of molecular structure are ordered in opposing directions along the polymer main chain [28].

However, since PVDF has relatively lower piezoelectric coefficients ( $d_{ij}$ ) than ceramic materials, there have been many attempts to increase their output performance [29,30]. Kim et al. proposed a micropatterning of trigonal line-shaped and pyramid-shaped surfaces on P(VDF-TrFE) film-based piezoelectric nanogenerators (PNG). These surfaces yielded higher sensitivity than a flat film [16]. Ou et al. fabricated textile-fiber-based PVDF nonwoven fiber fabric (NFF) harvesters using a hollow cylindrical near-field electrospinning (HCNFES) process to control the diameter, length and density of the fiber [31]. Kim et al. fabricated hybrid-type piezoelectric nanogenerators using both BaTi<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>3</sub> nanocubes and PVDF

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[32]. J H Yang et al. reported research on the interaction between  $-\text{CH}_2$  and  $-\text{CF}_2$  groups of PVDF and functional groups of graphene oxide (GO). Particularly, they presented composites in which PVDF created  $\beta$ -phase crystallites by using graphene oxide [33].

In recent years, there have been many efforts to use conjugated polymers in piezoelectric devices. S W Kim et al. blended poly(3-hexylthiophene) (P3HT) with fullerene derivatives and successfully formed a  $p$ - $n$  junction with ZnO. In their study, P3HT removed free carriers in ZnO to increase the piezoelectric potential and thus increased the output power [34–36].

Conjugated polymers containing abundant delocalized  $\pi$ -electrons have been used in Organic electronics due to their proper charge transfer property [37]. Benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) is a good candidate for this type of polymer, which has planar and rigid structure having good  $\pi$ - $\pi$  stacking property. This is beneficial for charge transport. For this reason, polythiophene containing BDT showed high charge mobility [38], and it would help high output power due to more drift charges through external circuit in piezoelectric nanogenerators (PNGs).

In the present study, P3HT (P1) and two types of BDT containing polymers, poly[(4,8-di-(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)-alt-(5,5'-yl-4,4'-bis(dodecyl)-2,2'-bithiophene)] (P2) and poly[(4,8-di-(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)-alt-(5,5'-yl-4,4'-bis(2-ethylhexyl)-2,2'-bithiophene)] (P3), were used as electron-rich units. Also, phenyl-C61-butyric acid methyl ester (PCBM<sub>61</sub>), a fullerene derivative, was used as an electron deficient unit. They were mixed together to make blend systems, and introduced to PVDF-based PNGs for increasing output performance.

A control system with no blend was used in PNG-0. The output voltage (OV) (peak-to-peak) and output current (OC) (peak-to-peak) of PNG-0 were 35.0 V and 558.5 nA, respectively. On the other hand, when blend systems of polymers and PCBM<sub>61</sub> were used in the PNGs-(1–3), their OVs were increased to 41.2 V, 42.2 V, and 43.1 V and their OCs to 569.5 nA, 572 nA, and 589 nA, respectively. The energy conversion efficiencies were 6.47%, 11.62%, 13.36%, and 14.33% for PNG-0, 1, 2, and 3, respectively. As a result, the output power of PNG-(1–3) were increased by up to about 2.2 times compared to PNG-0 by using conjugated polymer blend systems.

## 2. Experiments

### 2.1. Materials

All starting materials were purchased from Sigma Aldrich, Alfa Aesar and Tokyo Chemical Industry Co., LTD. and used without an extra purification step. 3-dodecylthiophene was purchased from Sigma Aldrich, 80- $\mu\text{m}$  thick PVDF film from Fils Co. LTD., and P3HT (P1) and PCBM<sub>61</sub> from One material, Inc. Two types of bithiophene with dodecyl group (2) and 2-ethylhexyl group (5) in scheme S1 and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (a) and the polymers (P2 and P3) in scheme S2 were synthesized according to the Ref. [39].

### 2.2. Device fabrication and characterization

The fabrication process of the flexible PNG is shown in Fig. S1. PVDF film ( $35 \times 35 \text{ mm}^2$ ) was first sonicated with a detergent solution and DI water for cleaning. Then, the film was dried in an oven at  $60^\circ\text{C}$  for 10 min and cleaned with ultraviolet ozone (UVO) cleaner (AH 1700, Ahtech LTS).

P1 and PCBM<sub>61</sub> were mixed at a ratio of 1:0.6(w/w). This mixture was then blended at a concentration of 42 mg/ml with 1,2-dichlorobenzene (ODCB) to make the solution. The same amounts of

P2 and P3 were mixed and blended at a concentration of 21 mg/ml with ODCB to make the solution. These solutions were then spin-coated on the top surface of the pretreated PVDF film at 1000 rpm for 30 s and annealed at  $80^\circ\text{C}$  for 10 min.

On this spin-coated layer, MoO<sub>3</sub> (10 nm) and Ag (100 nm) were thermally evaporated in a high vacuum chamber ( $<10^{-7}$  Torr) in sequence. On the bottom side of the PVDF film, Al (100 nm) was thermally evaporated. Finally, the entire film was cut to  $25 \times 15 \text{ mm}^2$ .

### 2.3. Measurements

The <sup>1</sup>H NMR (400 MHz) spectra of P2 and P3 were measured using a NMR measurement (Bruker AMX400 spectrometer). The thickness of each blend layer (P1–P3:PCBM<sub>61</sub>) was measured using a focused ion beam (Helios nanolab 600, FEI company). A homemade test apparatus was designed and implemented to measure the outputs by repeatedly stretching and releasing the devices at different frequencies (Hz) and displacements (mm). The OVs and OCs were measured using MDO4104C Oscilloscope (Tektronix) with 100M $\Omega$  impedance probe (P6015A) and DMM7510 (7.5 digit graphical sampling multimeter, Keithley), respectively.

One side of the fabricated devices was fixed on the test apparatus. The displacement and frequency were set to 0.2 mm and 2 Hz, respectively, and the devices were repeatedly stretched and released.

To examine the crystalline phase of P1–P3 as pristine polymers and the blend systems with PCBM<sub>61</sub>, the solutions, with the same concentration of materials as used in the fabricated devices, were drop-casted on a Si wafer and annealed at  $80^\circ\text{C}$  to make a thin film. The X-ray diffraction (new D8-Advance, Bruker-AXS) patterns of this thin film were measured.

To determine the change of the work function of Ag and Ag with MoO<sub>3</sub> electrodes, ultraviolet photoelectron spectroscopy (UPS) spectra of them were measured using a UPS analysis chamber at  $2 \times 10^{-8}$  Torr with an AXIS Ultra DLD hemispherical electron energy analyzer (KRATOS, Inc.) with He I ( $h\nu = 21.2 \text{ eV}$ ) source.

Furthermore, to examine the charge-carrier mobility properties of the P1–P3 blend systems, the hole mobility was measured using the space-charge limited current (SCLC) method and calculated using the following equation:  $J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3} \exp \left[ 0.89 \gamma \sqrt{\frac{V}{L}} \right]$ , where  $\varepsilon$  is a dielectric constant,  $\varepsilon_0$  is the permittivity of the free space,  $\mu$  is the mobility,  $V$  is a bias voltage, and  $L$  is the film thickness [40].

## 3. Results and discussion

Fig. 1(a–c) shows the structures of the polymers (P1–P3) that were used in the PNG. In addition, Fig. 1(d) shows the structure of the  $\beta$ -phase PVDF, which has all of the dipoles lined up in the same direction. The yields of P2 and P3 were 80.9% and 87.8%, respectively. This synthesis process is shown in Scheme S2. P2 and P3 are black and red powders, respectively, and they dissolved well in organic solvents, such as chloroform, chlorobenzene, ODCB, THF and toluene. These structures were confirmed using <sup>1</sup>H NMR, as shown in Fig. S2 (a & b). The molecular weights for P1 were 35.4 kDa (Mn) and 78.0 kDa (Mw). Those of P2 were 24.1 kDa (Mn) and 53.2 kDa (Mw). Those of P3 were 28.3 kDa (Mn) and 52.8 kDa (Mw). Furthermore, the polydispersity index (PDI) for P1–P3 were 2.20, 2.21 and 1.87, respectively, indicating a relatively narrow distribution. These values are summarized in Table S1.

Fig. 2 shows the PNG structure (a and b,  $25 \times 15 \text{ mm}^2$ ) and the cross-sectional SEM images of the top side of PNGs (c–e). All of the Ag electrodes of samples were deposited by Pt layer to protect the damage of Ag surface from Ga ion source during milling

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