# Synthesis of Poly(3-(2-benzotriazolovinyl)thiophene) (PBVT) Copolymers Containing the Alkyl, Electron-transporting, and Hole-transporting Groups

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(3-(2-Benzotriazolovinyl)thiophene (BVT) containing an electron-transporting moiety was polymerized through FeCl<sub>3</sub> oxidation. In addition, BVT was copolymerized with different functional groups: 3-octylthiophene (OT) containing alkyl groups for improving the solubility in common organic solvents; *N*-octylcarbazolylene (OcCz) containing hole-transporting groups for improving the optical property; and the alkyl groups for improving the solubility. Soluble  $\pi$ -conjugated poly(3-(2-benzotriazolovinyl)thiophene-*co*-3-(2-benzotriazoloethylthiophene)-*co*-*N*-octylcarbazolene) ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>)<sub>y</sub>) copolymer was synthesized. <sup>1</sup>H NMR analysis was used to verify the structure of the polyBVT copolymers. Especially, the emission of the ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymer (662 nm) was red-shifted by about 64 nm, compared to that of poly(3-(2-benzotriazolo-ethyl)thiophene) (polyBET, 598 nm).

Keywords: Poly(3-(2-benzotriazolovinyl)thiophene), OcCz, Hole-transporting, Electron-transporting

#### Introduction

Since polymer light-emitting diodes (PLEDs) based on poly (p-phenylenvinylene) (PPV) were reported by Burroughes et al. in 1990, a variety of  $\pi$ -conjugated polymers have been found to exhibit luminescence.<sup>1-3</sup> Especially, thiophenebased conjugated copolymers have been attracting much attention as light-emitting material for PLEDs because of their advantages of easy functionalization and controllable mechanical and thermal stability as well as electrical and optical properties.<sup>4–6</sup> However, their poor solubility in common organic solvents remains a serious problem for their application in commercial PLEDs.<sup>7–9</sup> Therefore, our laboratory previously reported on the characterization of soluble polythiophene (PT) derivatives containing an electrontransporting moiety.<sup>10,11</sup> The photoluminescence (PL) intensities of the prepared poly(3-(2-benzotriazolo-ethyl)thiophene) (polyBET) and poly(3-(2-(5-chlorobenzotriazolo) ethyl)thiophene) (polyCBET) were about 40 times higher than that of poly(3-octylthiophene) (polyOT).<sup>10</sup> However, their emission was blue-shifted by about 70 nm. This finding led us to develop a new kind of PT derivative for PLEDs.

We synthesized poly(3-(2-benzotriazolovinyl)thiophene) (polyBVT) as a  $\pi$ -conjugated polymer. Since the polyBVT has a vinylene chain as a spacer to connect the thiophene and benzotriazole with the electron-withdrawing groups, it will lead to a decreased bandgap, a red-shifted emission wavelength, and a stable planarization from the main chain by reducing the torsional strain among side chains and extending the effective conjugation chain. However, polyBVT was insoluble in organic solvents such as CHCl<sub>3</sub>, THF, and DMF because of the rigid structure caused by the double bond between the thiophene and benzotriazole segments.

To overcome this drawback, polyBVT was copolymerized by introducing alkyl groups on the side chain in the BVT monomer for improving the solubility. Furthermore, we synthesized the PBVT copolymers containing hole-transporting and electron-transporting groups for improving the optical properties. The ultimate purpose of this work was to explore the relation between the PT derivative with the vinylene spacer and the introduction of the functional groups.

# Experimental

**Materials.** 3-Thiophenecarboxaldehyde (96%) was purchased from Alfa Aesar Co., (Ward Hill, MA, USA). 1-Benzotriazole-1-methanol (97%) was purchased from TCI Co., (Tokyo, Japan). Prydine (99%), *n*-BuLi (1.6 M solution in hexane), phosphorus tribromide (98%), triphenyl phosphine (99%), 3-(2-thienyl)ethanol (99%), benzotriazole (99%), potassium carbonate (99%), sodium hydroxide (65%), carbazole (99%), *n*-bromooctane (98%), and 3-octylthiophene (97%) were purchased from Aldrich Chem. Co., (St. Louis, MO, USA) and used without any further purification. Iron(III)chloride, *n*-hexane (anhydrous), and toluene (anhydrous) were purchased from Duksan Co., (Seoul, Korea). Chloroform, acetone, tetrahydrofuran (THF), and dimethylformamide (DMF) were purchased from Tedia Co., (Fairfield, OH, USA).

**Instruments.** <sup>1</sup>H-NMR spectra were obtained on an Advance 500 spectrometer. Infrared spectra were obtained on a Perkin-Elmer instrument (GX1) (stamford, CT, USA). The molecular

weights were determined by gel permeation chromatography (GPC; YL Instrument Co.) (Anyang, Korea) with polystyrene standard calibration. The UV–visible spectra were recorded with a Mechasys spectrometer (Optizen 2120UV) (Daegue, Korea). Cyclic voltammetry was carried out on a CH Instrument Co., Instrument (CHI608D) (Austin, TX, USA). The PL spectra were recorded on a fluorescent spectrometer (FS 2; Scinco Co.) (Anyang, Korea). The thermal properties were obtained on a thermal analyzer (Q600; TA Instrument Co.) (Dallas, TX, USA) at a heating rate of 1 °C/min.

**Synthesis of the BVT Monomer and PolyBVT.** The detailed synthetic procedure was given in our previous papers.<sup>10–12</sup> The synthetic procedure of the BVT monomer is shown in Scheme 1.

**Synthesis of the BET and OcCz Monomers.** The detailed synthetic procedure was given in our previous papers.<sup>10–12</sup>

Copolymerization of ([(BVT)<sub>*n*</sub>-(OT)<sub>*m*</sub>]<sub>*y*</sub>) Copolymer with Molar Ratio of BVT/OT (1:1). The BVT (0.30 g, 1.32 mmol)/OT (0.26 g, 1.32 mmol)/CHCl<sub>3</sub> (10.0 mL) mixture was added dropwise to the FeCl<sub>3</sub> (1.72 g, 10.56 mmol)/CHCl<sub>3</sub> (20 mL) solution at room temperature. The mixture was stirred for 24 h. Then, the reaction mixture was placed in a rotary evaporator and CHCl<sub>3</sub> was removed. The residual monomer and FeCl<sub>3</sub> were Soxhlet-extracted using methanol/acetone solvent. The copolymer was Soxhlet-extracted again in chloroform. The red ([(BVT)<sub>*n*</sub>-(OT)<sub>*m*</sub>]<sub>*y*</sub>) copolymer was thus obtained (yield 0.51 g, 89.9%/chloroform soluble fraction 0.24 g, 40.3%). The resultant molar ratio of BVT/OT was 1:1.8. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, ppm):  $\delta$  8.16–7.42 (b, 11.39H),  $\delta$  7.26–7.00 (b, 6.29H),  $\delta$  2.8–2.56 (b, 8.95H), 1.70–0.85 (b, 128.43H).

Copolymerization of  $([(BVT)_n-OcCz_2]_y)$  Copolymer with Molar Ratio of BVT/OcCz (1:1). The BVT (0.1 g, 0.44 mmol)/OcCz (0.13 g, 0.44 mmol)/CHCl<sub>3</sub>(10 mL) mixture was added dropwise to the FeCl<sub>3</sub> (0.572 g, 3.53 mmol)/CHCl<sub>3</sub> (20 mL) solution at room temperature. The mixture was stirred for 24 h. CHCl<sub>3</sub> was removed from the reaction mixture using an evaporator. The residual monomer and FeCl<sub>3</sub> were Soxhlet-extracted using a methanol/acetone solvent for 12 h. The red ( $[(BVT)_n$ -OcCz<sub>2</sub>]<sub>y</sub>) copolymer was thus obtained (yield 0.085 g, 36.96%). The polymer was insoluble in organic solvents such as CHCl<sub>3</sub>, THF, and DMF.

Copolymerization of  $([(BVT)_n-(BET)_m-OcCz_2]_y)$  Copolymer with Molar Ratio of BVT/BET/OcCz (1:1:1). The BVT (0.20 g, 0.88 mmol)/BET (0.201 g, 0.88 mmol)/OcCz (0.25 g, 0.88 mmol)/CHCl<sub>3</sub>(10 mL) mixture was added dropwise to the FeCl<sub>3</sub> (1.64 g, 10.02 mmol)/CHCl<sub>3</sub> (20 mL) solution at room temperature. The mixture was stirred for 24 h. CHCl<sub>3</sub> was removed from the reaction mixture using an evaporator. The residual monomer and FeCl<sub>3</sub> were Soxhletextracted using methanol/acetone solvent for 12 h. The red ( $[(BVT)_n-(BET)_m-OcCz_2]_y$ ) copolymer was thus obtained (yield 0.59 g, 92.32%). The resultant molar ratio of BVT/BET/OcCz was 1.5:1.4:1. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, ppm):  $\delta$  8.16–7.42 (b, 11.39H),  $\delta$  7.26–7.00 (b, 6.29H),  $\delta$  2.8–2.56 (b, 8.95H), 1.70–0.85 (b, 128.43H). The synthetic routes of the PBVT copolymers are shown in Scheme 2.

Film Fabrication. The PBVT copolymer films were prepared by spin-coating on glass substrates at 3000 rpm for 30 s from the copolymer/chloroform solution (0.01 g/mL). The films were dried to remove the solvent in a  $N_2$  atmosphere at room temperature.

### **Results and Discussion**

Solubility and Molecular Weight.  $([(BVT)_n-(OT)_m]_y)$  and  $([(BVT)_n-(BET)_m-OcCz_2]_y)$  copolymers were completely soluble in common organic solvents such as CHCl<sub>3</sub>, THF, and



Scheme 1. Synthetic procedure of the BVT monomer.



Scheme 2. Synthetic routes of the PBVT copolymers.

DMF. The weight-average molecular weights  $(M_w)$  of the ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) and ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymers were 29 500 and 32 100 with polydispersity index (PDI) of 2.5 and 2.68. The number-average molecular weights  $(M_n)$  were 11 400 and 12 000. However, the ([(BVT)<sub>n</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymer was only partially soluble in the common organic solvents.

<sup>1</sup>H-NMR Analysis. Figure 1(a) shows the <sup>1</sup>H-NMR spectrum of BVT monomer. The strong peaks at around 7.3–8.1 ppm were assigned. This was attributed to a new bond that was formed between the two aromatic groups and an aromatic group. It can be reasonably concluded that the polymerization of vinylene occurs at positions a and b.<sup>13–15</sup> Figure 1(b) shows the <sup>1</sup>H-NMR spectrum of ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) copolymer. The typical peaks of the OT were observed at 7–7.2 and 0.8–2.8 ppm. The characteristic peaks of the BVT monomer were also assigned at 7.3–8.1 ppm. This shows that ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) copolymer was successfully polymerized. Figure 1(c) shows the <sup>1</sup>H-NMR spectrum of ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymer. The characteristic peaks of the BVT, BET, and OcCz monomers were observed at 7.3–8.1 ppm, 3.5–5.0 ppm, and 0.8–1.9 ppm, respectively.

**Thermal Properties.** Figure 2 shows the results of thermogravimetry (TGA) analysis of the PBVT copolymers and poly-BET. Three consecutive mass degradation steps were observed for the PBVT copolymers.<sup>16–19</sup> The first mass degradation of the PBVT copolymers in the temperature range 200–250 °C is related to the destruction of the bond between the two aromatics and aromatic. The second mass degradation that occurred between 300 °C and 400 °C could be attributed to the decomposition of the vinylene chains. The third mass degradation of the two copolymers at about 430 °C is due to the decompositions of the main chain.

**Optical Properties.** Figure 3 shows the PL spectra and UV–vis spectra of the PBVT copolymers and polyBET. The PL spectrum of polyBET and  $([(BVT)_n-(OT)_m]_y)$  copolymer showed that their maximum emission was at 598 and 620 nm, respectively. The emission of  $([(BVT)_n-(BET)_m-OcCz_2]_y)$  copolymer (662 nm) was red-shifted by about 64 nm compared to that of polyBET. This is probably because the vinylene spacer in  $([(BVT)_n-(BET)_m-OcCz_2]_y)$  played a role in balancing the electron and hole transporters in the light-emittinglayer.<sup>20</sup>

Also, solid-state UV–vis spectra gave further insight into the extent of polymer conjugation and structure, as well as the electronic effects of the polymeric materials in the solid state. As shown in Figure 3, the  $\pi$ – $\pi$ \* transition of ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) and ([(BVT)<sub>n</sub>-(BET)<sub>n</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymers and polyBET were characterized by absorption maxima ( $\lambda$ <sub>max</sub>) at around 453, 462, and 440 nm, respectively.<sup>21–24</sup>





Figure 2. TGA analysis of the PBVT copolymers and polyBET.



Figure 3. Optical properties of the PBVT copolymers and polyBET.

The optical bandgaps calculated from UV band edge were 2.11, 2.06, and 2.24 eV for the  $([(BVT)_n-(OT)_m]_y)$ ,  $([(BVT)_n-(BET)_m-OcCz_2]_y)$  copolymer and polyBET.

**Cyclic Voltammogram.** Figure 4 shows the cyclic voltammograms of the PBVT copolymers and polyBET. The cyclic



Figure 4. Cyclic voltammogram of the PBVT copolymers and polyBET.

voltammograms of these can be calculated by the following equation:

HOMO (eV) = 
$$-4.8 - (E_{\text{onset}} - E_{1/2}(\text{Ferrocene}))$$

The highest occupied molecular orbital (HOMO) levels of the ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) and ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymers and polyBET were -5.25, -5.27, and -5.36 eV, respectively.<sup>25–28</sup> The lowest unoccupied molecular orbital (LUMO) levels were calculated from the optical bandgaps estimated from UV–vis spectra and the HOMO levels. The LUMO levels of ([(BVT)<sub>n</sub>-(OT)<sub>m</sub>]<sub>y</sub>) and ([(BVT)<sub>n</sub>-(BET)<sub>m</sub>-OcCz<sub>2</sub>]<sub>y</sub>) copolymers and polyBET were -3.14, -3.21 and -3.12 eV, respectively.

# Conclusion

For improving their solubility and optical properties, PBVT copolymers containing alkyl, electron-transporting, and hole-transporting groups were copolymerized. Especially,  $([(BVT)_n-(BET)_m-OcCz_2)_y)$  copolymer containing both electron- and hole-transporting groups and  $([(BVT)_n-(OT)_m]_y)$  copolymer containing the alkyl groups were very well soluble in common organic solvents. The emission of  $([(BVT)_n-(OT)_m]_y)$  copolymers was red-shifted by about 64 and 22 nm, respectively, compared to that of the polyBET. Their HOMO and LUMO levels were -5.27, -5.25 and -3.21, -3.14 eV, respectively. The optical bandgaps were 2.06 and 2.11 eV, respectively.

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