# Synthesis of $\pi$ -Conjugated Copolymers Composed of Benzo[2,1,3]thiadiazole and Thiophene Units Bearing Various Alkyl Groups and Their Application to Photovoltaic Cells

# KWANG-HOI LEE,<sup>1</sup> HO-JIN LEE,<sup>2</sup> KOUJI KURAMOTO,<sup>3</sup> YOHEI TANAKA,<sup>3</sup> KAZUHIDE MORINO,<sup>1</sup> ATSUSHI SUDO,<sup>1</sup> TATSUO OKAUCHI,<sup>3</sup> AKIHIKO TSUGE,<sup>3</sup> TAKESHI ENDO<sup>1</sup>

<sup>1</sup>Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka Prefecture 820-8555, Japan
<sup>2</sup>Research Fellow Laboratories Yokkaichi, JSR Corporation, 100 Kawajiri-cho, Yokkaichi, Mie Prefecture 510-8552, Japan
<sup>3</sup>Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu, Fukuoka Prefecture 804-8550, Japan

Received 22 December 2010; accepted 21 May 2011 DOI: 10.1002/pola.24790 Published online 14 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:**  $\pi$ -Conjugated polymers, **PTOTBT**, **PTEHTBT**, and **PTt-BTBT**, composed of benzothiadiazole as an electron accepting unit and terthiophene as an electron donating unit in the backbone were prepared. **PTOTBT**, **PTEHTBT**, and **PTt-BTBT** contained side chain groups of *n*-octyl, 2-ethylhexyl, and *t*-butyl groups, respectively. Solubility, optical and thermal properties of the polymers showed strong dependences on their side chain groups. **PTEHTBT** having 2-ethylhexyl groups in the side chain exhibited absorption maximum ( $\lambda_{max}$ ) at longer wavelength (565 nm) than **PTOTBT** 

**INTRODUCTION** Photovoltaic devices based on  $\pi$ -conjugated polymers have attracted much attention due to the potential application to low-cost, flexible, and large-area solar cells. Currently, bulk heterojunction (BHJ) type has been utilized for polymer solar cells (PSCs). The BHJ cell involves the blend film of a  $\pi$ -conjugated polymer as an electron donor and a fullerene derivative as an electron acceptor between the electrodes. Very high power conversion efficiencies (5-7% PCEs) have been achieved by BHJ solar cells.<sup>1-7</sup> PCE is determined by short circuit current  $(J_{sc})$ , open circuit current  $(V_{\rm oc})$ , and fill factor (FF). For attaining enhanced  $J_{\rm sc}$ , the polymers should have a broad absorption in the solar spectrum to ensure effective harvesting of the solar photons and high charge carriers mobility.<sup>8-10</sup> Recently,  $\pi$ -conjugated polymers composed of electron donating and electron withdrawing units in the polymer backbone have been prepared with expecting that the absorbance can be shifted to longer wavelength due to a formation of inter- and/or intramolecular charge-transfer complex. In addition, morphology of the donor-acceptor blend film plays very important role in an enhancement of  $J_{\rm sc}$ .  $V_{\rm oc}$  of OPV is proportional to the gap between highest occupied molecular orbital (HOMO) energy level of donor polymer and lowest unoccupied molecular orbital (LUMO) energy level of the acceptor fullerene

(534 nm) and **PTt-BTBT** (495 nm). **PTOTBT** showed higher thermal stability than the others. The prepared polymers were employed to polymer solar cells (PSCs) with a configuration of ITO/PEDOT-PSS/ polymer: PC<sub>61</sub>BH/LiF/AI. Power conversion efficiency of the PSC-based on **PTEHTBT** was 1.32%. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3543–3549, 2011

**KEYWORDS**: conjugated polymers; copolymerization; functionalization of polymers; photovoltaic; solar cell; UV-vis spectroscopy

material.<sup>11,12</sup> Hence, employing polymers with lower HOMO energy level is well-known method to give high  $V_{oc}$ .

Benzothiadizaole (BT) unit is very frequently employed as an electron acceptor unit in the electron donor-acceptor polymers for PSCs, because of its planar skeleton to extend  $\pi$ -conjugated length and electron accepting characteristic. A large number of solar cells based on the polymer involving BT units have been reported.<sup>1-3,13-22</sup> Good solubility of conjugated polymer in organic solvents is necessary for the solution processing. The solubility can be generally tailored by the length and bulkiness of alky chains in the side chains. The selection of appropriate alkyl chain is very important because the electronic and optical properties of the polymer are influenced by the side chains.

Herein, we report a new design and synthesis of  $\pi$ -conjugated polymers composed of benzothiadiazole as electron accepting unit and terthiophene as an electron donating unit in the backbone (Scheme 1). We examined and compared the optical and thermal properties of the polymers by varying alkyl side groups in the side chain. The photovoltaic characteristics of the polymers were investigated by employing them to the solar cell with a configuration of ITO/ PEDOT-PSS/polymer: PC<sub>61</sub>BH/LiF/Al.

Correspondence to: T. Endo (E-mail: tendo@mol-eng.fuk.kindai.ac.jp)

Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3543-3549 (2011) © 2011 Wiley Periodicals, Inc.



SCHEME 1 Structures of polymers.

#### **EXPERIMENTAL**

# Materials

THF and toluene were dried over sodium/benzophenone ketyl. Chloroform and DMF were distilled over CaH<sub>2</sub>. Methanol and dichloromethane were used as received. 3,4-dibromothiophene, 2-tributylstannyl thiophene, Pd(PPh<sub>3</sub>)<sub>4</sub>, Ni(dppp)Cl<sub>2</sub>, magnesium, *n*-octyl bromide, 2-ethylhexyl bromide, trimethylstannyl chloride, a hexane solution of *n*-BuLi, *N*-bromosuccinimide (NBS) were used without purification.

#### **Measurements and Characterization**

<sup>1</sup>H NMR spectra were recorded on a Varian INOVA 400 NMR spectroscopy using tetramethylsilane as an internal standard in chloroform-d (CDCl<sub>3</sub>). IR spectrum was recorded on Thermo fishier Scientific NICOLET iS10. UV-vis spectroscopy was measured in chloroform (1.0  $\times$  10<sup>-5</sup> M) on a JASCO V570 spectrometer. Polymer films for UV-vis measurement were prepared on a glass substrate with a spin coater (700 rpm for 10 sec. and then 3000 rpm for 60 sec.) using 10 mg/mL chloroform solution. Numberaverage  $(M_n)$  and weight-average  $(M_w)$  molecular weights were determined by size exclusion chromatography with TOSOH HLC-8120GPC using a calibration curve of polystyrene standards and THF as an eluent. Thermogravimetric analyses (TGA) were conducted with a TA instrument TG-DTA6200 at a heating rate of 10 °C/min under nitrogen. HOMO levels of polymers were measured using a photoelectron spectrometer AC-2 (Riken Keiki) by measuring of ionic potential of polymer film in air.<sup>23,24</sup>

#### **Device Fabrication and Characterization of PSC**

The photovoltaic cell structure used in this study is ITO/ PEDOT: PSS/active layer/LiF/Al, where the active layer is the blend film of a polymer as an electron donor and [6,6]phenyl C<sub>61</sub> butyric acid hexyl ether (PC<sub>61</sub>BH) as an electron acceptor in the weight ratio of 1:1 (w/w). PEDOT: PSS was spin coated on the pre-cleaned ITO glass substrate and heated at 150 °C for 10 min. Subsequently, active layer was prepared by spin casting of the blend solution of polymer and PC<sub>61</sub>BH in chlorobenzene (10 mg/mL) on the PEDOT: PSS layer. The thickness of active layer is about 100 nm. LiF (1 nm) and Al anode (100 nm) were deposited on the active layer to complete solar cell fabrication. Solar cell parameters were estimated from current density-voltage (J-V) characteristics under air mass 1.5 global solar simulated light (AM1.5G at 100 mW/cm<sup>2</sup>, highly uniform irradiation system using 150W Xe lamp as light source, Wacom Electric) irradiation. We calibrated the light intensity using a standard cell for amorphous silicon ( $\alpha$ -Si) solar cells. J-V characteristics were measured using a Current-Voltage Source Meter (Keithley 2410, Keithley) at room temperature in the glove box filled with inert gas.

# 4,7-Bis(5-trimethylstannylthiophen-2-yl) benzo[2,1,3]thiadiazole (3)

To a THF solution of LDA prepared from the reaction of diisopropylamine (0.519 g, 0.363 moL) and *n*-BuLi (0.206 mL, 0.323 mmol) (1.57 M hexane solution) in THF (1 mL) at -78 °C was added **1** (0.303 g, 0.101mmol) in THF (2 mL) at -78 °C. After stirring the solution for 1 h at -78 °C, trime-thylstannyl chloride (90.5 mg, 0.454 mmol) was added to the solution. After 1 h, the reaction was quenched by water and the organic layer was extracted with ethyl acetate, washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (alumina) using hexane as an eluent to give 63.0 mg (100%) of **3** as a reddish solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.43 (s, -CH<sub>3</sub>, 18H), 7.27 (d, J = 3.6 Hz, Th-H, 2H), 7.85 (s, Ph-H, 2H), 8.17 (d, J = 3.6 Hz, Th-H, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) -8.2, 125.8, 125.9, 128.4, 136.1, 140.2, 145.1, 152.7.

### 3,4-Di-(2-ethylhexyl)thiophene (5)

To a solution of **4** (0.64 g, 26.29 mmol) and Ni(dppp)Cl<sub>2</sub> (0.71 g) in THF (100 mL) was slowly added 2-ethylhexyl magnesium bromide solution prepared from the reaction of 2-ethylhexyl bromide (12.0 g, 62.5 mmol) and magnesium (1.52 g, 62.5 mmol) in ethyl ether (31.3 mL) at 0 °C. After stirring overnight at room temperature, the reaction mixture was poured into water and extracted with diethyl ether. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration volatiles were removed under reduced pressure, and the resulting residue was purified by distillation to afford 0.76 g (94%) of **5** as colorless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.87 (m, -CH<sub>3</sub>, 12H), 1.32 (m, -CH<sub>2</sub>-, 16H), 1.56 (m, -CH-, 1H), 2.43 (d, -CH<sub>2</sub>-, 4H), 6.85 (s, Th-H, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 10.8, 14.1, 23.1, 25.8, 28.9, 32.7, 33.3, 39.4, 120.7, 141.2.

# 2,5-Dibromo-3,4-di-(2-ethylhexyl)thiophene (7)

To a solution of **5** (0.76 mg, 24.56 mmol) in DMF (50 mL) was added NBS (0.87 g, 49.11 mmol). After stirred overnight at room temperature the solution was poured into water and extracted with ethyl acetate. The combined organic layer was washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After organic solvent was removed under reduced pressure the residue was purified by column chromatography (silica gel) using hexane as an eluent to give 0.97 g (85%) of **7** as colorless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.87 (m, -CH<sub>3</sub>, 12H), 1.24-1.54 (m, 18H), 2.48 (d, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 11.1, 14.1, 23.1, 25.7, 28.9, 32.5, 33.4, 39.6, 108.5, 141.0.

# 3,4-Di-tert-butylthiophene (10)

To a solution of **9** (1.22 g, 5.25 mmol) in benzene (100 mL) was added *p*-TsOH (0.20 g, 1.16 mmol). After refluxing for 1 h, the solution was washed with aqueous sodium bicarbonate and dried over  $Na_2SO_4$ . The mixture was filtrated and concentrated under reduced pressure, and the resulting residue was purified by column chromatography (silica gel) using hexane as an eluent to give 0.74 g (72%) of **10** as colorless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 1.47 (s, -CH<sub>3</sub>, 18H), 7.16 (s, Th-H, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 33.5, 35.3, 122.3, 150.6.

# 2,5-Dibromo-3,4-di-tert-butylthiophene (11)

To a solution of **10** (0.74 g, 3.77 mmol) in DMF (10 mL) was added NBS (0.14 mg, 7.92 mmol). After stirring for 3h at room temperature, the solution was poured into water and extracted with ethyl acetate. The organic layer was washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtrated and concentrated under reduced pressure, and the resulting residue was purified by column chromatography (silica gel) using hexane as an eluent to give 1.09 g (82%) of **11** as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 1.59 (s, -CH<sub>3</sub>, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 33.6, 37.8, 107.0, 149.0.

# **PTOTBT**

To a mixture of 8 (233 mg, 0.50 mmol), 2 (313 mg, 0.50 mmol), and  $Pd(PPh_3)_4$  (58 mg, 0.050 mmol), which was dried in vacuo for 10 min, toluene (40 mL) and DMF (10 mL) were added. Argon gas bubbled into the solution for 10 min, and then the solution was stirred at 110  $^{\circ}$ C for 20 h. The resulting solution was cooled to room temperature and then poured into methanol (150 mL). The resulting precipitate was collected by filtration, dissolved in chloroform (150 mL), and then the solution was passed through a column (silica gel, PSQ100) using chloroform as an eluent. The obtained solution was concentrated under reduced pressure. To the resulting residue, methanol (300 mL) was added to give a solid, which was collected by filtration to afford 71 mg (24%) of **PTOTBT** as a purple solid ( $M_w$ 1300,  $M_w/M_n$ 1.63). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 0.80 (br-s, -CH<sub>3</sub>, 6H), 1.20-1.59 (m, --CH2--, 24H), 2.30-2.76 (m, --CH2--, 4H), 6.82-7.89 (m, Ar-H, 6H)

#### PTEHTBT

To a mixture of **7** (233 mg, 0.50 mmol), **3** (313 mg, 0.50 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (25 mg, 0.016 mmol), which was dried *in vacuo* for 10 min, toluene (8 mL) and DMF (2 mL) were added. Argon gas was bubbled into the solution for 10 min, and then the solution was stirred for 2 h at 120 °C. The resulting solution was cooled to room temperature and then poured into methanol (150 m). The resulting precipitate was collected by filtration, dissolved in chloroform (150 mL) and then the solution was passed through a column (silica gel, PSQ100) using chloroform as an eluent. The obtained solution was concentrated under reduced pressure. To the resulting residue methanol (300 mL) was added to give a solid, which was collected by filtration to afford 180 mg (60%) of

**PTEHTBT** as a purple solid ( $M_w$  23,000,  $M_w/M_n$  PDI 4.95). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.80-0.92 (m, -CH<sub>3</sub>,12H), 1.20-1.68 (m, -CH- and -CH<sub>2</sub>-, 18H), 2.28-2.86 (m, -CH<sub>2</sub>-, 4H), 7.17-7.56 (m, Ar-H, 2H), 7.86-7.89 (m, Ar-H, 2H), 8.07-8.10 (m, Ar-H, 2H)

# **PTt-BTBT**

To a mixture of 11 (177 mg, 0.50 mmol), 3 (313 mg, 0.50 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (25 mg, 0.016 mmol), which was dried in vacuo for 10 min, toluene (8 mL) and DMF (2 mL) were added. Argon gas was bubbled into the solution for 10 min, and then the solution was stirred at 120 °C for 3 h. The resulting solution was cooled to room temperature and then poured into methanol (150 m). The resulting precipitate was collected by filtration, dissolved in chloroform (150 mL), and then the solution was passed through a column (silica gel, PSQ100) using chloroform as an eluent. The obtained solution was concentrated under reduced pressure. To the resulting residue, methanol (300 mL) was added to give solid, which was collected by filtration to afford 130 mg (53%) of **PTt-BTBT** as a black solid ( $M_w$  2800,  $M_w/M_n$  1.68). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 1.46-1.69 (m, *t*-Bu,18H), 7.14-7.29 (m, Ar-H, 2H), 7.85 (br-s, Ar-H, 2H), 8.03-8.09 (m, Ar-H, 2H)

#### **RESULTS AND DISCUSSION**

#### Synthesis and Characterization of Polymers

The synthetic methods of monomers are shown in Scheme 2. 4,7-Bis(thiophenyl-2-yl)benzo[2,1,3]thiadiazole (1) was prepared as described in the literature.<sup>25,26</sup> 4,7-Bis(5-bromothiophen-2-yl)benzo[2,1,3]thiadiazole (2) was synthesized by bromination of **1** using NBS in 66% yield.<sup>26</sup> Dilithiated **1** prepared by using LDA was reacted with trimethylstannyl chloride to gave 4,7-bis(5-trimethylstannylthiophen-2-yl)benzo[2,1,3]thiadiazole (3), quantitatively. 3,4-Dialkylthiophenes **5** (R = 2-ethylhexyl) and **6** (R = n-octyl)<sup>27</sup> were prepared from the reaction of 3,4-dibromothophene with the corresponding alkylmagnesium bromide in the presence of Ni(dppp)Cl<sub>2</sub> as a catalyst. Bromination of **5** by NBS gave **7** in 84% yield. We attempted to prepare 2,5-bis(trimethylstannyl)-3,4-di(2-ethylhexyl)thiophene as a monomer from the reaction of 2,5-dilithio-3,4-di(2-ethylhexyl)thiophene with trimethylstannyl chloride. However, the reaction afforded complex products, produced probably by the decomposition of the target compound during a work-up process. 2,5-Dilithio-3,4-dioctylthophene prepared from the reaction of 6 with *n*-BuLi was reacted with trimethylstannyl chloride to afford  $\mathbf{8}^{28}$  3,4-Bis(*t*-butyl)thiophene **10** was prepared from  $9^{29}$  in the presence of *p*-toluenesulfonic acid in 74% yield. Monomer **11** was prepared by bromination of **10** using NBS in 84% vield.

The target polymers were prepared by the Stille cross-coupling polymerization in DMF/toluene using  $Pd(PPh_3)_4$  as a catalyst (Scheme 3). After the polymerization was terminated the resulting solution was precipitated into methanol. The methanol-insoluble fraction was subsequently dissolved in chloroform and passed through a column (silica gel, PSQ100B) using chloroform as an eluent to remove the metal catalyst. First, the polycondensation of **8** and **2** was



performed. In this case, a significant amount of a chloroform-insoluble fraction was given, implying that the polymer PTOTBT would have intrinsically less soluble nature. Only the chloroform-soluble fraction was passed through a silica

gel column to obtained purified PTOTBT, of which weight average molecular weight  $M_{\rm w}$  was estimated to be 1300. IR spectra of both the chloroform-soluble and -insoluble fractions were indicated identical signal patterns, implying that





 TABLE 1
 Synthesis and Characterization of PTOTBT, PTEHTBT, and PTt-BTBT

		Molecular Weight <sup>b</sup>		TGA (°C) <sup>c</sup>	
	Yield (%) <sup>a</sup>	M <sub>w</sub>	$M_{\rm w}/M_{\rm n}$	$T_{d5}$	<i>T</i> d10
РТОТВТ	24	1300	1.68	396	420
РТЕНТВТ	60	23000	4.95	387	421
PTt-BTBT	53	2800	1.68	255	266

<sup>a</sup> Insoluble part in methanol.

<sup>b</sup> Measured by GPC (THF).

<sup>c</sup> Under N<sub>2</sub>, 10 °C/min.

the repeating units in the polymer main chain were identical. Hence, the insoluble part may be **PTOTBT** with large molecular weights. Next, we designed PTOTBT analogues bearing branched alky groups in the side chain to increase the solubility and molecular weight. A polymer bearing 2ethylhexyl groups in the side chain was designed as a target polymer **PTEHTBT**. The synthetic strategy for **PTEHTBT** is rather different from that for PTOTBT. As described earlier, the synthesis of a distannyl substituted 3,4-di(2-ethylhexyl)thiophene was not successful. Therefore, we prepared distannyl substituted monomer 3 and dibromothiophene 7 for the preparation of PTEHTBT. The polycondensation of 3 and 7 afforded PTEHTBT in 60% yield after purification by silica gel column. PTEHTBT exhibited increased solubility and molecular weights ( $M_w$  23,000,  $M_w/M_n$  4.95) compared with PTOTBT. PTEHTBT showed a good solubility in chloroform, THF, chlorobenzene, and dichlorobenzene. We also designed **PTt-BTBT** bearing more bulky *t*-butyl groups in the side chain. The polycondensation 3 and 11 gave PTt-BTBT in 53% yield after silica gel column purification. The molecular weight and yield of soluble **PTt-BTBT** ( $M_w$  2800,  $M_{\rm w}/M_{\rm n}$  1.68) were higher than those of **PTOTBT**, implying t-butyl group enhanced solubility more efficiently than noctyl group did.

Thermal properties of the obtained polymers were investigated by TGA.  $T_{d5}$ s of **PTOTBT**, **PTEHTBT**, and **PTt-BTBT** 



FIGURE 2 UV-vis spectra of PTOTBT, PTEHTBT, and PTt-BTBT in chloroform.

were observed at 396, 387, and 255 °C, respectively (Table 1 and Fig. 1). **PT-tBTBT** bearing *t*-butyl groups in the side chain gave significantly poor thermal stability compared with **PTOTBT** and **PTEHTBT** having *n*-octyl and 2-ethylhexyl groups, respectively.

# **Optical Properties of Polymers**

Optical properties of the polymers were investigated by UVvis spectroscopy in dilute chloroform solution and in film state. Absorption maxima of PTOTBT, PTEHTBT, and PTt-BTBT in chloroform were observed at 534, 565, and 495 nm, respectively (Figure 2). PTEHTBT showed absorption maximum ( $\lambda_{max}$ ) at longer wavelength than **PTOTBT** and PTt-BTBT, probably due to the much larger molecular weight of **PTEHTBT** than the others. Interestingly, despite the molecular weight of PTt-BTBT was about two times larger than that of **PTOTBT**,  $\lambda_{max}$  of **PTt-BTBT** appeared at shorter wavelength than that of **PTOTBT**. This result can be attributed to steric effect of polymer side chain; bulky *t*-butyl group may disturb the planarity of polymer backbone to shorten  $\pi$ -conjugation length. UV-vis spectra of polymer films prepared by spin casting were measured as well.  $\lambda_{max}$ s of PTOTBT, PTEHTBT, and PTt-BTBT films were observed at 549, 637, and 510 nm, respectively, which were red-shifted compared to those of polymer solutions indicating the



FIGURE 1 TGA curves of PTOTBT, PTEHTBT, and PTt-BTBT.



FIGURE 3 UV-vis spectra of PTOTBT, PTEHTBT, and PTt-BTBT films.

	UV-vis (n	UV-vis (nm)			
	$\lambda_{\max} \operatorname{CHCl}_3^a (\varepsilon)^b$	$\lambda_{\max}$ film	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	$E_{g.opt}$ (eV) <sup>e</sup>
РТОТВТ	534 (19,400)	549	-4.97	-3.32	1.65
РТЕНТВТ	565 (22,300)	637	-5.21	-3.62	1.59
PTt-BTBT	495 (17,500)	510	-5.43	-3.45	1.98

TABLE 2 Optical Properties and Energy Levels of Polymers

 $^{a}$  Conc. = 1.0  $\times$  1  $0^{-5}$  M.

<sup>b</sup> Molar absorption coefficient.

<sup>c</sup> Measured with AC-2.

<sup>d</sup> Calculated from the equation,  $E_g = |HOMO - LUMO|$ .

<sup>e</sup> Calculated from the onset absorption,  $E_{\rm g}=1240/\lambda_{\rm onset}$ .

effective planarization and  $\pi$ - $\pi$  interaction of the polymer backbone in the solid state (Figure 3). Especially, **PTEHTBT** showed larger shift of  $\lambda_{max}$  by 72 nm in the solid state compared with the others (by 15 nm). We investigated the HOMO energy levels of the polymers with a photo-electron spectrometer AC-2 (Riken Keiki) by measuring ionic potential of polymer film in air.<sup>23,24</sup> The HOMO energy levels were estimated to be -4.97, -5.21, and -5.43 eV for **PTOTBT**, **PTEHTBT**, and **PTt-BTBT**, respectively. The band gaps obtained from onset absorptions of polymer films were 1.65, 1.59, and 1.98 eV for **PTOTBT**, **PTEHTBT**, and **PTt-BTBT**, respectively (Table 2).

#### **Photovoltaic Properties of Polymers**

The blend films of the new polymers as electron donors and [6,6]-phenyl C<sub>61</sub> butyric acid hexyl ester (PC<sub>61</sub>BH)<sup>30</sup> (Fig. 4) as an electron acceptor and applied to solar cells with a configuration of ITO/PEDOT-PSS/polymer: PC<sub>61</sub>BH/LiF/Al. Polymer and PC<sub>61</sub>BH were blended with a ratio of 1:1 in chlorobenzene (10 w/v%), which was spin-coated on PEDOT-PSS layer, pre-casted on ITO electrode. Finally, LiF and Al layers as top electrodes were deposited on the blend film. Figure 4 shows current density-voltage (J-V) curves of the solar cells estimated under AM1.5 at 100 mW/cm<sup>2</sup>. The associated pho-



FIGURE 4 Current density-voltage (J-V) characteristics of solar cells based on PTOTBT, PTEHTBT, and PTt-BTBT under the illumination of AM 1.5 G, 100 mW/cm<sup>2</sup>, and the structure of  $PC_{61}BH$ .

tovoltaic parameters  $V_{oc}$ ,  $J_{sc}$ , FF, and PCE are summarized in Table 3. Solar cells based on **PTEHTBT** and **PTt-BTBT** exhibited higher  $V_{oc}$  (0.82–0.85 eV) than that based **PTOTBT** (0.71 eV). This result can be attributed to the low-lying HOMO energy level of **PTEHTBT** (–5.21 eV) and **PTt-BTBT** (–5.43 eV), compared with **PTOTBT** (–4.97 eV).<sup>11,12</sup> In terms of  $J_{sc}$  the solar cell-based on **PTEHTBT** showed much higher value (4.54 mA/cm<sup>2</sup>) than others (0.99–1.24 mA/ cm<sup>2</sup>). Probably, **PTEHTBT** with  $\lambda_{max}$  at longer wavelength may harvest more photons to enhance  $J_{sc}$ . PCEs of the solar cells based on **PTOTBT**, **PTEHTBT**, and **PTt-BTBT** were 0.32, 1.32, and 0.21%, respectively.

#### **CONCLUSIONS**

Novel  $\pi$ -conjugated polymers composed of benzothiadiazole and terthiophene units in the backbone were synthesized. The polymers PTOTBT, PTEHTBT, and PTt-BTBT containing *n*-octyl, 2-ethylhexyl, and *t*-butyl groups, respectively, in the side chain exhibited significant differences in optical and thermal properties. The solution and film of PTEHTBT showed UV-vis  $\lambda_{max}$ s at longer wavelength than those of PTOTBT and PTt-BTBT, implying the optical properties of the polymer can be controllable by varying the side chain. **PTOTB** bearing linear alkyl chain showed higher thermal stability than others. The prepared polymers were employed into PSCs with a configuration of ITO/PEDOT-PSS/polymer: PC<sub>61</sub>BH/LiF/Al. PCS with PTEHTBT exhibited higher PCE (1.32%) than those based on **PTOTBT** (0.32%) and PTt-BTBT (0.21%), probably due to the fact that PTEHTBT with larger molecular weight exhibited UV-vis  $\lambda_{\max}$  at longer wavelength to effectively harvest the solar photons.

	TABLE 3	Characteristic	Properties	of Poly	vmer Sola	r Cells
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	J <sub>sc</sub> (mA/cm <sup>2</sup> )	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
РТОТВТ	1.24	0.71	0.36	0.32
PTEHTBT	4.54	0.82	0.35	1.32
PTt-BTBT	0.99	0.85	0.25	0.21

 $J_{\rm sc},$  short-circuit current density;  $V_{\rm oc},$  open-circuit voltage; FF, fill factor; PCE, power conversion efficiency.

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