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Original article

Phenothiazine과 2,1,3-Benzothiadiazole을 포함한 Copolymer의 합성 및 Side-chain 치환에 따른 Photovoltaic 특성 연구

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Synthesis, Photovoltaic Properties and Side-chain Effect of Copolymer Containing Phenothiazine and 2,1,3-Benzothiadiazole

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초 록

본 연구에서는 phenothiazine과 benzothiadiazole을 기반으로 하고, phenothiazine의 질소 위치에 다양한 side-chain을 치환한 고분자를 합성하였다. 합성된 고분자는 광학적, 전기화학적 분석 결과 300~700 nm에서 흡수를 보였고, -5.4 eV 정도의 이상적인 HOMO energy level를 갖는 특성을 확인하였다. 고분자와 $PC_{71}BM$을 광활성층으로 사용한 소자를 제작하였고, 측정결과 branched side-chain을 가지며 탄소수가 많은 P2HDPZ-bTP-OBT가 2.4%로 최대 광전변환효율을 갖는 것으로 확인되었다(V_{OC} : 0.74 V, J_{SC} : 6.9 mA/cm^2, FF : 48.0%).

Abstract

In this study, three kinds of polymers based on phenothiazine-benzothiadiazole were synthesized by a Suzuki coupling reaction, and the various side-chains were substituted at the nitrogen of phenothiazine. The optical and electrochemical properties of synthesized polymers were analyzed. The results indicate that their absorption ranged from 300 to 700 nm, and also confirmed the ideal highest occupied molecular orbital (HOMO) energy level was about -5.4 eV with low band-gap energy. Photovoltaic devices were fabricated using a photoactive layer composed of a blended solution of the polymer and $PC_{71}BM$ in ortho-dichlorobenzene The device with P2HDPZ-bTP-OBT containing the branched side-chain and long chain showed the best performance; the maximum power conversion efficiency of this device was 2.4% (with V_{OC} : 0.74 V, J_{SC} : 6.9 mA/cm^2, FF : 48.0%).

Keywords: *Phenothiazine derivative, Benzothiadiazole derivative, Organic photovoltaics (OPVs), Suzuki coupling, Push-pull structure*

1. Introduction

Recently, in response to the rapid growth of developing countries, such as those belonging to BRICS (Brazil, Russia, India, China, Republic of South Africa), and the development of the information and electronics industries, the energy demand has rapidly increased. The reserves of fossil energy are being exhausted, and the environmental issues, such as greenhouse-effect gases and atmospheric pollution resulting from the use of such fossil fuels, are steadily turning into global problems. As a means of overcoming this situation, competition is ongoing for the development of new and renewable sources of energy. One of them is solar energy, which is free from concerns of depletion [1-5].

Generally, solar energy that has been commercialized involves solar cells using silicone, with higher unit costs for power generation as compared to fossil fuels or nuclear energy. Therefore, it is difficult to install such equipment without governmental support. Furthermore, with the arrival of the information society, the interest in next-generation flexible displays has increased, and there is a need for a portable electric energy source for the operation of such displays. However, existing silicone solar cells are heavy and brittle, making them limited as regards meeting the requirement for lightweight batteries. In response to this problem, academic circles have been actively researching solar cells that are light, do not crack, and can pro-

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duce electricity through flexible organic materials[6-10]. Due to the possibility of a continuous process and manufacture in large sizes, organic solar cells have the advantage of lower manufacturing costs[11,12].

One of the decisive factors of organic solar cell efficiency is the photo-active layer. The donor materials used in the photo-active layer are usually polymers with good conjugation, whose range of photo absorption wavelengths matches the solar spectrum sufficiently well, with considerable photo absorbency. Also, electrical properties, such as electron mobility, must be excellent[13-15].

Due to their low ionization potential, phenothiazine derivatives work as stronger electron donors and are known to generate more stable radical cations. They are also characterized by electrical and thermal stability, with outstanding electro-optical characteristics in the device[16-18]. In this study, phenothiazine was used as the electron donor, with benzothiadiazole of a very strong electron affinity as the electron acceptor, with thiophene rich in electrons connected to each terminal to increase the effective π-conjugation length, thereby designing a basic molecular structure that gives the polymer a low band-gap. By substituting the various alkyl groups of phenothiazine, the optical and electrochemical characteristics of polymers by side-chain will be discussed, and the photovoltaic characteristics of a bulk heterojunction-type organic solar cell will be examined using the synthesized polymer materials.

2. Experimental

2.1. Materials

Phenothiazine, 2-ethylhexyl bromide, 2-hexyl-1-decanol, carbon tetrabromide, triphenylphosphine, n-butyllithium, aliquat 336, 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrahydrofuran (THF), pyrocatechol, 1-bromooctane, tin chloride, palladium-tetrakis(triphenylphosphine), bis(triphenylphosphine)-palladium(Ⅱ) dichloride, tributyl(thiophen-2-yl)stannane were purchased from Aldrich, whereas 1-bromododecane, triethylamine (TEA), N-bromosuccinimide (NBS) were bought from Alfa-Aesar, and were used without additional purification. Also, bromine was purchased from Junsei, and hexane, sodium hydroxide, toluene, acetic acid, nitric acid, magnesium sulfate, dimethylsulfoxide (DMSO), diethyl ether, acetone, potassium carbonate, thionyl chloride, methylene chloride (MC), ethanol, hydrochloric acid, chloroform, N,N-dimethylformamide (DMF) were bought from Samchun Pure Chemical.

2.2. Measurements

^{1}H-NMR and ^{13}C-NMR spectrometer (Bruker AVANCE 250) were used to examine the molecular structure of the synthesized compounds, and the molecular weight of the synthesized polymers was measured using gel permeation chromatography (GPC, Shimadzu GPC system). Also, to examine thermal stability, thermogravimetric analysis (TGA, Q50) was used to measure decomposition temperature. As for UV-Vis spectra (Beckman Coulter DU730), the polymers were dissolved in chloroform for drop casting, manufacturing a film for absorbency measurements. As for cyclic voltammetry (Zahner IM6eX), the oxidation or reduction potential of the synthesized polymers were measured, with as can rate of 50 mV/s, and an Ag/AgCl reference electrode. The measured values were corrected with ferrocene as the correction value for calculation of energy level. The X-ray diffraction (XRD) pattern was used through SmartLab 3 kW (40 kV 30 mA, Cu target, wavelength : 1.541871 ang), Figaku, Japan. As for the topographic images of the photo active layer, atomic force microscopy (AFM, XE-100) was used in tapping mode.

2.3. Photovoltaic cell device fabrication

A photovoltaic cell device was fabricated with a structure of glass/ITO/PEDOT : PSS/polymer : $PC_{71}BM$ (weight ratio = 1 : 3, w/w)/BaF_2/Ba/Al. The devices were fabricated by spin-coating a PEDOT : PSS layer on top of ITO-coated glass substrates and annealed at 140 ℃ for 5 min. The photo active layer was spin-coated with polymer solution on top of PEDOT : PSS layer. The polymer solution was dissolved synthesized polymer and $PC_{71}BM$ in *ortho*-dichlorobenzene (ODCB). The devices were finished by deposition (10^{-6} torr or less) BaF_2, Ba and Al sequentially in a thermal evaporator. The devices were evaluated at 298 K in air using a Class A Oriel solar simulator (Oriel 96000 150 W solar simulator) having a xenon lamp that simulates AM 1.5 G irradiation (100 mW/cm^2) from 400 to 1100 nm. The instrument was calibrated with a Si photo diode at the National Renewable Energy Laboratory (NREL). All the characterization steps were carried out under ambient laboratory air.

2.4. Synthesis

2.4.1. 7-(Bromomethyl)pentadecane

In a 100 mL 2-neck flask, 16.25 mmol of 2-hexyldecan-1-ol and 21.125 mmol (1.3 eq) of carbon tetrabromide are completely dissolved in 32.5 mL of MC, then cooled to 0 ℃. 22.75 mmol (1.4 eq) of triphenylphosphine is dissolved in 8.5 mL MC, then dropwise is performed at 0 ℃. After 1 h of stirring at 0 ℃, and 1 h of stirring at room temperature, the reaction is terminated. The reactant is placed in 455 mL of ether/hexane (1/4), and any precipitate is filtered with silica gel, and cleansed with hexane. The solvent is evaporated to gain the product[19,20]. (yield : 92.8%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.89 (m, 6H), 1.28-1.39 (m, 24H), 1.57 (m, 1H), 3.45 (d, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.02, 22.59,22.62, 26.50, 26.53, 29.24, 29.41, 29.50, 29.65, 29.75, 31.76, 31.85, 32.58, 32.85, 39.56; GC-MS : 306.1 (calculated : 305.34).

2.4.2. 10-(Alkyl)-10H-phenothiazine

In a 3-neck flask, 14 mmol of phenothiazine is completely dissolved in 15 mL DMSO, then 87.5 mmol (6.25 eq) of sodium hydroxide is added. 18.2 mmol (1.3 eq) of alkyl bromide diluted in 3.5 mL DMSO is slowly added dropwise, and the reaction proceeds overnight. TLC monitoring is performed to decide the reaction completion. After the reaction is completed, if filtered for NaOH removal and extraction is performed with EA. (Washing with distilled water and brine) $MgSO_4$ is used for drying, then, after removing the solvent, purification is performed with column chromatography[21-24]. (Hexane/ethyl acetate =

20/1).

10-(Dodecyl)-10H-phenothiazine (yield : 97.6%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.92-0.94 (m, 6H), 1.28-1.32 (m, 18H), 1.76-1.90 (m, 2H), 3.85 (t, 2H), 6.85-6.95 (m, 4H), 7.13-7.14 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.1, 22.7, 26.9, 28.2, 28.8, 29.4, 30.0, 31.9, 32.8, 47.4, 115.2, 122.1, 124.9, 127.1, 127.4, 145.3; GC-MS : 367.3 (calculated : 367.59).

10-(2-Ethylhexyl)-10H-phenothiazine (yield : 96.7%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.93 (m, 6H), 1.27-1.49 (m, 8H), 1.95-1.97 (m, 1H), 3.74 (d, 2H), 6.88-6.97 (m, 4H), 7.14-7.19 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 10.5, 23.3, 24.1, 28.6, 30.8, 35.9, 51.1, 116.3, 122.3, 126.2, 126.8, 127.5, 145.8; GC-MS : 311.2 (calculated : 311.48).

10-(2-Hexyldecyl)-10H-phenothiazine (yield : 94.6%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.86-0.94 (m, 6H), 1.25-1.47 (m, 8H), 1.96-2.06 (m, 1H), 3.73 (d, 2H), 6.86-6.95 (m, 4H), 7.12-7.18 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.1, 22.7, 26.3, 27.9, 29.4, 29.6, 30.0, 31.7, 31.9, 34.6, 36.2, 51.6, 108.4, 115.9, 122.7, 126.0, 127.0, 127.5, 145.8, 150.3; GC-MS : 423.4 (calculated : 423.70).

2.4.3. 3,7-Dibromo-10-(alkyl)-10H-phenothiazine

In a 3-neck flask, 12 mmol of 10-(alkyl)-10H-phenothiazine is completely dissolved in 32 mL DMF, then 31.2 mmol (6.25 eq) of NBS diluted in 10 mL DMF is slowly added dropwise at 0 ℃. The reaction proceeds at room temperature and TLC monitoring is performed to decide the reaction completion. After the reaction is completed, extraction is performed with EA and the organic layer washed with distilled water and $NaHCO_3$ solution. The collected organic layer dried with $MgSO_4$ and the solvent was removed through vacuum evaporation. Then, purified by using column chromatography to obtain the product[22,25,26]. (eluent : $CHCl_3$/hexane = 1/1).

3,7-Dibromo-10-(dodecyl)-10H-phenothiazine (yield : 85.5%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.86-0.92 (m, 3H), 1.25-1.41 (m, 18H), 1.67-1.79 (m, 2H), 3.74 (t, 2H), 6.64-6.69 (m, 2H), 7.19-7.25 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.1, 22.6, 26.7, 29.6, 31.6, 47.6, 115.2, 116.6, 126.4, 129.6, 130.0, 144.1.

3,7-Dibromo-10-(2-ethylhexyl)-10H-phenothiazine (yield : 84.3%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.83-0.88 (m, 6H), 1.25-1.42 (m, 8H), 1.83-1.88 (m, 1H), 3.59 (d, 2H), 6.67-6.71 (m, 2H), 7.22-7.28 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 10.5, 14.0, 23.3, 24.1, 28.5, 30.7, 36.1, 51.4, 115.2, 117.1, 127.3, 130.0, 144.6; GC-MS : 469.0 (calculated : 469.28).

3,7-Dibromo-10-(2-hexyldecyl)-10H-phenothiazine (yield : 89.7%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.83-0.91 (m, 6H), 1.21-1.31 (m, 24H), 1.85-1.92 (m, 1H), 3.61 (d, 2H), 6.67-6.71 (m, 2H), 7.22-7.24 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.1, 22.6, 29.4, 29.6, 29.9, 31.6, 34.5, 51.8, 114.8, 117.1, 127.4, 130.0, 144.6.

2.4.4. 10-(Alkyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboraolan-2-yl)-10H-phenothiazine (M1a-c)

In a 2-neck flask, 6 mmol of 3,7-dibromo-10-(alkyl)-10H-phenothiazine is completely dissolved in 50 mL THF and stirred at -78 ℃ under nitrogen. 13.2 mmol (2.2 eq) of n-BuLi was added slowly to the solution over 30 min, and the mixture stirred for 1 h. 18 mmol (3.0 eq) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane added quickly to the solution and kept overnight at room temperature. The mixture was poured into water, extracted with ether, and dried with $MgSO_4$. The crude product was purified by recrystallization with ethanol[22,26,27].

10-Dodecyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine(M1a) (yield : 62.4%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.85-0.90 (m, 3H), 1.24-1.39 (m, 42H), 1.75-1.77 (m, 2H), 3.76-3.87 (m, 2H), 6.78-6.83 (m, 2H), 7.22-7.51 (m, 1H), 7.51-7.57 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.0, 22.6, 24.8, 26.6, 29.5, 31.8, 47.5, 83.6, 114.6, 116.5, 123.2, 123.9, 127.3, 129.6, 133.9, 134.3, 143.9, 147.2.

10-(2-Ethylhexyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine(M1b) (yield : 42.5%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.80-0.88 (m, 6H), 1.22-1.42 (m, 33H), 3.73 (d, 2H), 6.81 (d, 2H), 7.54-7.58 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 10.5, 14.0, 23.3, 24.1, 28.5, 30.7, 36.1, 51.4, 115.2, 117.1, 127.3, 130.0, 144.6.

10-(2-Hexyldecyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine(M1c) (yield : 68.9%), ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.88-0.91 (m, 6H), 1.20-1.62 (m, 48H), 1.85-2.04 (m, 1H), 3.72-3.75 (m, 2H), 6.80-6.84 (m, 2H), 7.54-7.57 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) : δ (ppm) 14.1, 22.6, 24.8, 26.2, 29.3, 29.9, 31.6, 34.6, 51.5, 82.7, 83.6, 115.2, 125.1, 133.8, 147.9.

2.4.5. 1,2-Bis(octyloxy)benzene

In a 2-neck flask, 0.18 mol of pyrocatechol, 0.72 mol (4.0 eq) of 1-bromooctane and 0.72 mol (4.0 eq) of K_2CO_3 was dissolved in 180 mL of DMF and stirred at 100 ℃ for 4 days under nitrogen. The mixture was poured into distilled water, extracted with MC. The organic layer was removed solvent and purified by column chromatography to give product[28-30]. (eluent : $CHCl_3$/hexane = 1/1) (yield : 96.8%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.88-0.93 (m, 6H), 1.31-1.52 (m, 20H), 1.78-1.89 (m, 4H), 4.01 (t, 4H), 6.86-6.90 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ (ppm) 14.0, 22.6, 26.2, 29.3, 31.8, 69.4, 114.9, 121.1, 149.4; GC-MS : 334.3 (calculated : 334.29).

2.4.6. 1,2-Dinitro-4,5-bis(octyloxy)benzene

In 1000 mL 3-neck flask, 62.77 mmol of 1,2-dioctlyoxybenzene and 90 mL of acetic acid was dissolved 90 mL of MC and stirred at 0 ℃ for 1 h under nitrogen atmosphere. The solution was added slowly 144 mL of nitric acid (69%) and stirred at room temperature for 40 h. The mixture was poured into ice water to complete the reaction, and was extracted with MC, brine and distilled water. Concentration under reduced pressure gave the crude product, then the product was obtained as a yellow powder by recrystallization with ethanol[28-30]. (yield : 85.7%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.86-0.92 (m, 6H), 1.25-1.48 (m, 20H), 1.56-1.90 (m, 4H), 4.07-4.12 (t, 4H), 7.19 (s, 2H)

2.4.7 4,5-Bis(octyloxy)benzene-1,2-diaminium chloride

In a 1000 mL 2-neck flask, hydrochloric acid (37 %, 140 mL) was

added 1,2-dinitro-4,5-bis(octyloxy)benzene (23.55 mmol) and tin (II) chloride (188.4 mmol, 8 eq) in ethanol (350 mL). The mixture was refluxed under a nitrogen atmosphere overnight. After the removal of the solvent, the residue filtered off under reduced pressure. The precipitate was washed distilled water and methanol, then the product as a white powder obtained[28-30]. (yield : 98.5%).

2.4.8. 5,6-Bis(octyloxy)benzo[c][1,2,5]thiadiazole

In a 1000 mL 3-neck flask, 4,5-bis(octyloxy)benzene-1,2-diaminium chloride (23.2 mmol) and triethylamine (236 mmol) was dissolved MC (340 mL) under a nitrogen atmosphere. The solution of thionyl chloride (59 mmol) in MC (50 mL) was added slowly into the mixture and refluxed for 20 h. After the removal of the solvent, the residue was washed distilled water (400 mL) and filtered off under reduced pressure. Then, the product as a brown powder obtained by recrystallization with ethanol[28-31]. (yield : 82.3%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.92 (m, 6H), 1.30-1.55 (m, 20H), 1.86-1.94 (m, 4H), 4.07-4.12 (t, 4H), 7.13 (s, 2H).

2.4.9. 4,7-Dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole

In a 500 mL 3-neck flask, 5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (7 mmol) and acetic acid (93.75 mL) was dissolved 175 mL of MC under a nitrogen atmosphere. The diluted bromine (47.6 mmol) in 30 mL of MC added dropwise and stirred for 48 h. The mixture was quenched with 200 mL of distilled water and extracted with MC and 1 M Na_2SO_3 sol'n. The solvent was removed by reduced pressure evaporation, the product as a brown powder was obtained by recrystallization with ethanol[28-30,32]. (yield : 78.9%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.92 (m, 6H), 1.30-1.57 (m, 20H), 1.83-1.91 (m, 4H), 4.13-4.19 (t, 4H).

2.4.10. 5,6-Bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole

In a 250 mL 2-neck flask, to a solution of 4,7-dibromo-5,6-bis(octyloxy) benzo[c][1,2,5]thiadiazole (4.36 mmol) in 109 mL of anhydrous THF, 0.48 mmol of Pd $(PPh_3)_4$ and 13.08 mmol of 2-(tributylstannyl)thiophene was added. The mixture was refluxed under a nitrogen atmosphere for 48 h. After the reaction is complete, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent : $CHCl_3$/n-hexane = 1/1) to obtain product[28-31]. (yield : 82.1%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.95(m, 6H), 1.30-1.55 (m, 20H), 1.86-1.98 (m, 4H), 4.08-4.14 (t, 4H), 7.22-7.25 (m, 2H), 7.50-7.52 (m, 2H), 8.46-8.48 (m, 2H).

2.4.11. 4,7-Bis(5-bromothiophen-2-yl)-5,6-Bis(octyloxy)benzo[c] [1,2,5]thiadiazole (M2)

In a 250 mL 2-neck flask, 5,6-Bis(octyloxy)-4,7-di(thiophen-2-yl) benzo[c][1,2,5]thiadiazole (2.51 mmol) and acetic acid (55 mL) were dissolved in 55 mL of chloroform under nitrogen. N-bromosuccinimide (6.02 mmol) added by portion into the mixture and stirred at room temperature for 24 h. The mixture was poured into 100 mL of distilled water and extracted with chloroform. The organic layer was separated and dried with $MgSO_4$. After the solvent was removed under vacuum, and the crude product was purified by column chromatography (eluen t : $CHCl_3$/n-hexane = 1/4). A orange solid compound was obtained after removing solvents and drying in vacuum[28-30]. (yield : 64.1%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.93(m, 6H), 1.30-1.55 (m, 20H), 1.91-1.97 (m, 4H), 4.09-4.15 (t, 4H), 7.17-7.19(d, 2H), 8.36-8.38(d, 2H).

2.4.12. General synthesis method of polymer

In a 3-neck flask, 1.0 equiv of monomer 4, and 1.0 equiv of monomer 12 are placed and dissolved in toluene. 1.5 mol% palladium-tetrakis(triphenylphosphine) was added to give 2M K_2CO_3. After adding aliquat 336, the mixture was allowed to react for at 90 ℃ 48 h. After completion of the reaction, end-capping was performed with bromobenzene. Soxhlet extraction of methanol, acetone and chloroform was performed in sequence on the reaction product for purification, after with the chloroform fraction was collected for solvent removal and reprecipitation with methanol to give the product[28,33,34].

Poly[(N-10'-dodecyl-phenothiazine-3,7-ylene)-alt-(4,7-bis(thiene-2-yl)-5,6-dioctyloxyl-2,1,3-benzothiadiazole)-2',2"-diyl] (PDDPZ-bTP-OBT) (yield : 27.8%) ^{1}H NMR (250 MHz, $CDCl_3$) : 0.85-1.02 (m, 9H), 1.26-1.50 (m, 40H), 1.83-2.12 (m, 4H), 3.87 (m, 2H), 4.17 (m, 4H), 6.79-6.96 (m, 2H), 7.14-7.48 (m, 6H), 8.38-8.49 (m, 2H).

Poly[(N-10'-(2-ethylhexyl)-phenothiazin-3,7-ylene)-alt-(4',7'-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole)] (P2EHPZ-bTP-OBT) (yield : 56.5%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.92 (m, 12H), 1.24-1.55 (m, 28H), 1.93-1.97 (m, 5H), 2.72-2.82 (m, 2H) 4.06-4.15 (m, 4H), 6.78-6.89 (m,2H) 7.10-7.48 (d, 4H), 8.24-8.35 (d, 4H).

Poly[(N-10'-(pentadecan-7-yl)-phenothiazin-3,7-ylene)-alt-(4',7'-bis (thiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole)] (P2HDPZ-bTP-OBT) (yield : 74.5%) ^{1}H NMR (250 MHz, $CDCl_3$) : δ (ppm) 0.87-0.91 (m, 12H), 1.26-1.56 (m, 52H), 1.96-1.99 (m, 5H), 2.61-2.80 (m, 2H) 4.06-4.17 (m, 4H), 6.89-6.93 (m,2H) 7.17-7.53 (d, 4H), 8.37-8.47 (d, 4H).

3. Results and discusstion

3.1. Synthesis and characterization

The polymers were synthesized by the Suzuki coupling reaction based on phenothiazine and 2,1,3-benzothiadiazole. Figure 1 show the synthesis paths for the polymers. To examine the performance in response to side-chain effect, linear and branched chains were applied to the nitrogen positions of the phenothiazine, and the carbon number of the branched chains was increased to improve solubility. Polymer molecular weight and poly dispersity index were measured using GPC. THF was used as the eluent, and polystyrene was used as the standard. For each polymer, the umber-average molecular weights (M_n) were 2,300, 4,700 and 5,800 for PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT, respectively; the poly dispersity indexes were 1.73, 1.81 and 1.31, respectively. P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT showed high solubility in the common organic solvents chloroform, chlorobenzene, toluene, etc., while PDDPZ-bTP-OBT did not dissolve

Table 1. Physical Properties of Synthesized Polymers

polymer	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Yield (%)	T_d^a (℃)
PDDPZ-bTP-OBT	2,292	3,971	1.73	27.8	329.9
P2EHPZ-bTP-OBT	4,701	8,487	1.81	56.5	333.6
P2HDPZ-bTP-OBT	5,801	7,620	1.31	74.5	337.5

[a]Temperature for 5% weight loss.

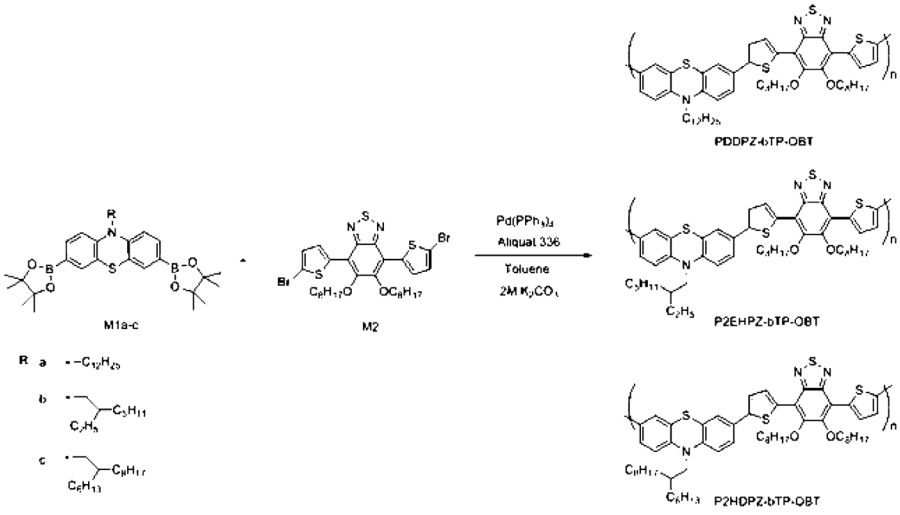


Figure 1. Synthetic route of polymers.

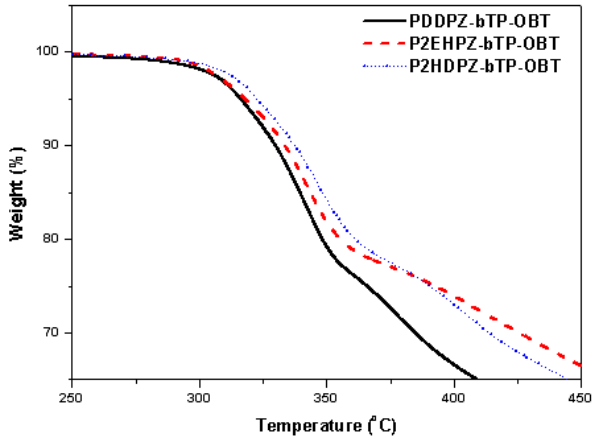


Figure 2. Thermogravimetric analysis (TGA) curve of PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT at a heating rate of 10 ℃/min under a nitrogen atmosphere.

well. Various alkyl chains were adapted to the rigid phenothiazine to increase solubility, but it is generally assumed that the solubility of polymers with linear structures is lower compared to branched chains [35,36]. The thermal stability of the synthesized polymers were measured and examined with a TGA (see Figure 2 for the results). As seen in the TGA profile, PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT had decomposition temperatures of at least 300 ℃, demonstrating high stability, with the weight loss (%) at 300 ℃ being 1.9, 1.5 and 1.2%, respectively. The data describing the physical characteristics of the polymer are shown in Table 1.

3.2. Optical and Electrochemical properties

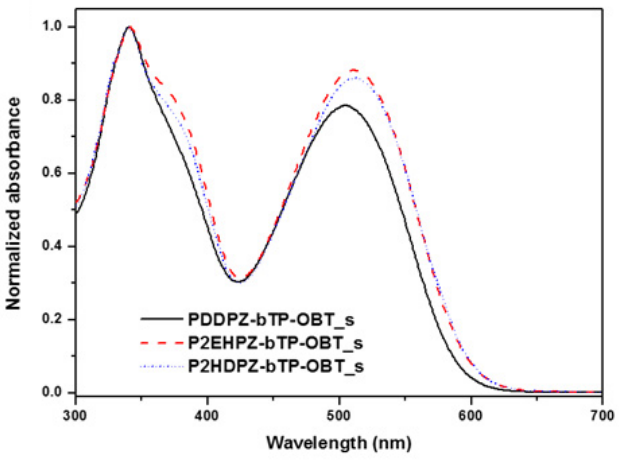
The UV-Vis absorption spectra of the polymer were measured in solution and film state (see Figure 3); the measured data are shown in Table 2. In solution state, the polymer was dissolved in a chloroform solution for measurement, while, for the film state, the polymer solution was drop-cast on a quartz plate for measurement. For all polymers, a red shift was observed for the film state relative to the solution state. This was observed because the maximum absorption was shown due to the increased π-π stacking of the polymer backbone in the solid polymer state[35,37,38]. The optical band gap of the polymers was calculated from the edge of the absorbance spectra, and amounted to 1.95, 1.98, and 1.90 eV for PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT, and P2HDPZ-bTP-OBT, respectively. The synthesized polymers were donor-acceptor type, with the LUMO energy level influenced by the acceptor unit, and the HOMO energy level decided by the donor unit. As the three polymers synthesized in this study were used to examine performance variations according to the changes in the substituted alkyl groups, the band gap was influenced by the structure of the electron donor compound[36,37].

Table 2. UV-Visible Absorption Wavelength, Band-gap Energy, and Ionization Potential of Synthesized Polymers

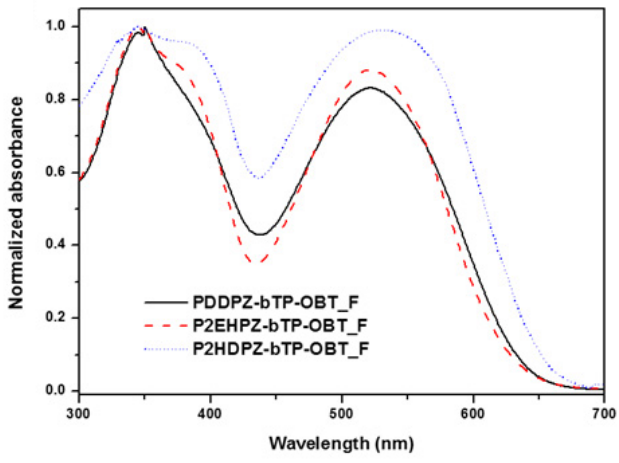
polymer	λ_{max} (nm)		λ_{edge} (nm)	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)
	Solution	Film	Film			
PDDPZ-bTP-OBT	505	522	634.5	1.95	-5.58	-3.58
P2EHPZ-bTP-OBT	510	521	626.5	1.98	-5.43	-3.45
P2EHPZ-bTP-OBT	512	530	652.7	1.90	-5.48	-3.58

Table 3. Photovoltaic Properties of the Synthesized Polymer : $PC_{71}BM$ (1 : 3) Devices

polymer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PDDPZ-bTP-OBT	0.68	4.2	39.3	1.1
P2EHPZ-bTP-OBT	0.70	6.0	46.4	1.9
P2EHPZ-bTP-OBT	0.74	6.9	48.0	2.4



(a)



(b)

Figure 3. Normalized absorption spectra of PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT in (a) chloroform and (b) as thin films.

The electrochemical properties of the polymers were examined by measuring the oxidation-reduction potential through cyclic voltammetry. Since, due to the structural characteristics of the polymers, reduction characteristics are not exhibited, LUMO energy level was calculated using the optical band gap (Table 2). The HOMO energy levels for the synthesized polymers PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ- bTP-OBT were -5.58, -5.43 and −5.48 eV, respectively, and LUMO energy levels were -3.63, -3.45, and −3.58 eV. The LUMO energy levels of the polymers synthesized are in the ideal energy range for high efficiency in solar cells. Therefore, excitons are efficiently separated at the interface between polymer and PCBM[39,40]. Furthermore, the measured HOMO energy levels of the synthesized polymers were high due to the plentiful electrons in phenothiazine.

3.3. Photovoltaic properties

As for the photovoltaic properties of the synthesized polymers, a bulk heterojunction device with the structure ITO/PEDOT : PSS/polymer : $PC_{71}BM/BaF_2/Ba/Al$ was created, and the measurements were performed under 100 mW/cm^2 AM1.5 illumination. The ITO substrate was surface treated using UVO (ultravioletozone), and PEDOT : PSS solution was spin-coated on top, then heat treated at 120 ℃ for 10 minutes. As for the active layer, the synthesized polymers and $PC_{71}BM$ were blended at 1 : 3 (w/w), and the result was spin-coated on the PEDOT : PSS layer. Then, the result was moved to a high vacuum chamber for thermal evaporation of BaF_2, Ba and Al in sequence. The J-V curves of the BHJ devices made with the blended film of polymer (PDDPZ-bTP-OBT, P2EHPZ-bTP-OBT and P2HDPZ-bTP-OBT) : $PC_{71}BM$ are shown in Figure 4. The open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE) of these devices are summarized in Table 3. The best PCE value of these devices was 2.4% in P2HDPZ-bTP-OBT : $PC_{71}BM$ (1/3, w/w), with the values of V_{OC}, J_{SC} and FF of 0.74 V, 6.9 mA/cm^2, and 48.0%, respectively. The PCE values were proportional to the V_{OC}, J_{SC} and FF values, with linear side chain structure exhibiting a higher performance compared to branched chain structures, and

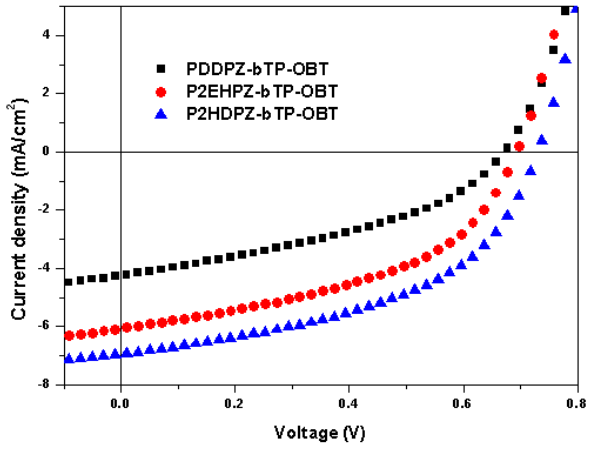


Figure 4. J-V curves of the BHJ devices based on the blend of synthesized polymer : $PC_{71}BM$ (1 : 3).

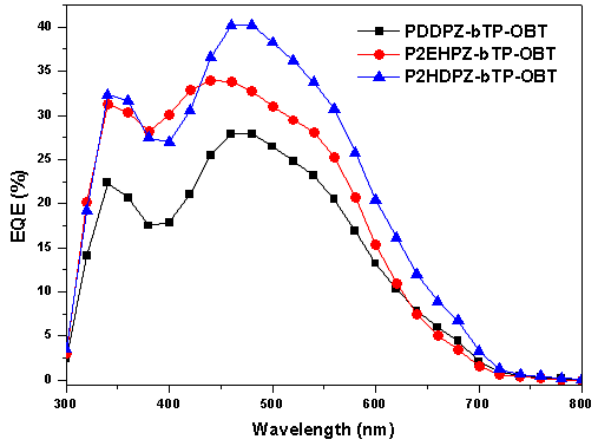


Figure 5. External quantum efficiencies (EQE) of the BHJ devices based on the blend of synthesized polymer : $PC_{71}BM$ (1 : 3).

there was a trend of increasing efficiency with increasing carbon number[36,41]. The produced EQE spectra of the device are shown in Figure 5. As for the P2HDPZ-bTP-OBT : $PC_{71}BM$ device, the highest photo conversion efficiency was seen at the 450~500 nm wavelength range, at least 35%, with a 40.2% EQE at 480 nm. The J_{SC} value calculated from the integrating of the EQE curve was 5.23 mA/cm^2 (in the wavelength range of 300~800 nm), showing an error of about 24% when compared with the 6.9 mA/cm^2 value measured for a device with the same specifications. The EQE values for PDDPZ-bTP-OBT and P2EHPZ-bTP-OBT were 27.9% at 460 nm and 33.9% at 440 nm, respectively, and the calculated values for J_{SC} at 3.5 mA/cm^2 and 4.27 mA/cm^2 were obtained from integrating of the EQE curve. This clearly showed that a large change was affected by the geometric structure of the polymer side chain[42,43].

3.4. Morphology

To examine the morphology and molecular organization of the polymer thin film in order to understand the effect on photovoltaic proper

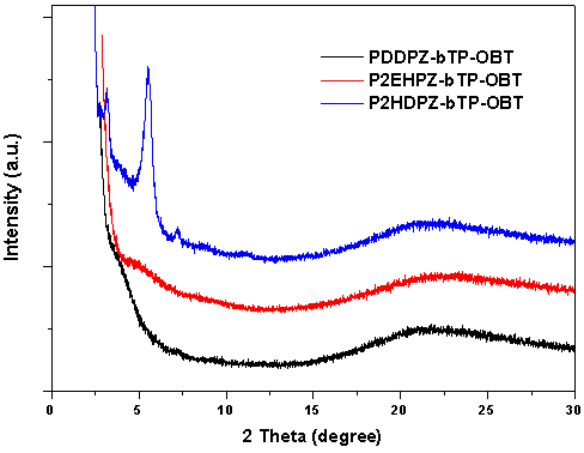


Figure 6. X-ray diffraction (XRD) patterns of spin-coated films of synthesized polymers on ITO glass.

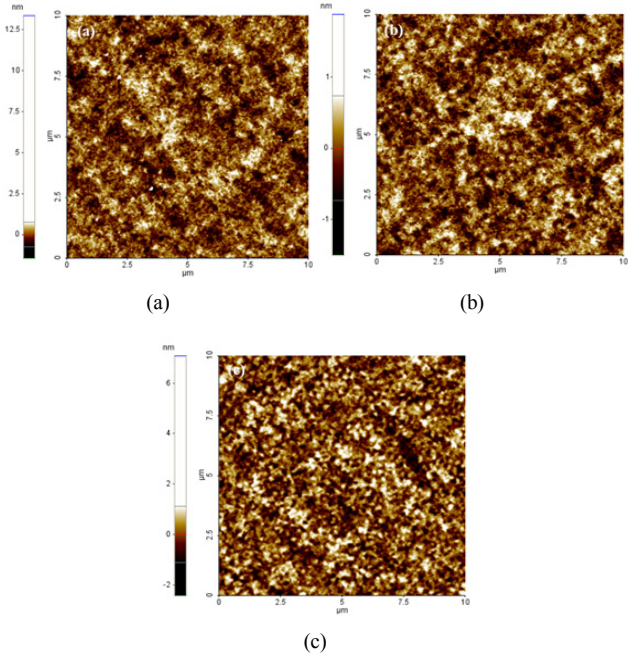


Figure 7. Atomic force microscope (AFM) tapping mode height images of thin films. Scan size is 10 μm X 10 μm. (a) PDDPZ-bTP-OBT : $PC_{71}BM$ (1 : 3, w/w), (b) P2EHPZ-bTP-OBT : $PC_{71}BM$ (1 : 3, w/w) and (c) P2HDPZ-bTP-OBT : $PC_{71}BM$ (1 : 3, w/w).

ties due to changes in the substituted side-chains of the synthesized polymers, X-ray diffraction (XRD) was used. As seen in Figure 6, sharp diffraction peaks were only shown for P2HDPZ-bTP-OBT, at 5.5°. Weak peaks were seen at 3.1° and 7.2°. No reflection peaks were shown in the XRD patterns in the thin film state of PDDPZ-bTP-OBT and P2EHPZ-bTP-OBT. As for P2HDPZ-bTP-OBT, calculation of d-spacing using Bragg's law ($\lambda = 2\,d\sin\theta$) yielded the result of 1.60 nm, from which it could be conjectured that π-π stacking edge-on in 1.60 nm intervals occurs when the polymer is in the thin film state. Previous research confirms that other polymers were amorphous in the

thin film state[44-46].

Figure 7 shows the AFM height images of the synthesized polymers. The measured sample was produced by coating ITO glass with a PEDOT : PSS layer, then spin coating polymers : $PC_{71}BM$ (1 : 3, w/w) dissolved in ODCB. For all polymers, images with smooth and flat surfaces with a root-mean-square (RMS) surface roughness of 0.35~0.54 nm were obtained. Among these, P2HDPZ-bTP-OBT had a relatively higher roughness value (0.54 nm), and it was judged that, when compared with the other polymers, electrons separated from excitons will be able to move more easily[47-50]. Also, PDDPZ-bTP-OBT and P2EHPZ-bTP-OBT showed similar roughness values, based on which, as with the XRD patterns, the two polymers can be assumed to be in amorphous state[45,46].

4. Conclusion

In this study, three phenothiazine and benzothiadiazole-based polymers were synthesized using the Suzuki coupling reaction. The synthesized polymers showed good solubility in common organic solvents, such as chloroform, *ortho*-dichlorobenzene, toluene, and hexane. As for the thermal stability of these polymers, TGA was measured in a nitrogen atmosphere, yielding high thermal stability of 300 ℃ and above. All polymers showed photo absorption in the range between 300~700 nm, with two strong peaks. While the peak at 300~430 nm is due to the delocalized π-π^* transition in the chain of the polymer, the 450~600 nm peak is due to the localized transition in the transfer of charge between the phenothiazine and benzothiadiazole units. Cyclic voltammetry was used to measure the oxidation characteristics of the polymers, giving ideal HOMO energy levels of -5.43~-5.48 nm. The device was produced using polymer : $PC_{71}BM$ (1 : 3, w/w) as the photo-active layer, and measurements using a solar simulator at AM 1.5G (100 mW/cm^2) illumination gave a maximum conversion efficiency for P2HDPZ-bTP-OBT at 2.4% (with V_{OC} : 0.74 V, J_{SC} : 6.9 mA/cm^2, FF : 48.0%). AFM was used to generally confirm smooth and flat images for the polymers, with P2HDPZ-bTP-OBT showing relatively high roughness with RMS at 0.54 nm. XRD measurements showed sharp diffraction peaks for P2HDPZ-bTP-OBT only, and no reflection peaks were shown for the other polymers. It is thought that synthesized polymers branched with long chains have good molecular arrangement properties in the thin film state, increasing the length of the electron transfer path, which, in turn, improves photon-to-electron conversion efficiency.

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