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STUDY ON FLUORENE-BENZOTHIADIAZOLE COPOLYMER COMPOSITION AND APPLICABILITY AS A COLOR CONVERSION MATERIAL

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Abstract. A new photoluminescent polymer with a high thermal stability and superior color conversion ability was synthesized from a Suzuki coupling reaction, and its physical and optical properties were investigated. The applicability of the synthesized polymer as a color conversion material was also examined. A color filter was fabricated using a screen printing method and its optical properties were measured using a range of equipment after placing the fabricated color filter on the blue color light emission device.

Keywords: conducting photoluminescent polymer, color conversion, polyalkylfluorene(PAF), color filter, copolymer.

1. Introduction

Conducting photoluminescent polymers (PL) are very important compounds used in many fields.

Particularly, recent studies on these polymers have focused on their applicability as display materials such as organic EL devices or organic semiconductors. In addition, research on the synthesis of new conductive PL polymers has also been conducted very vigorously, and many types of PL polymers, including derivatives of polyalkylfluorene (PAF) [1-10], poly-*p*-phenylenevinylene (PPV) and polythiophene (PTh), have been presented. Of these, PAF derivatives are particularly attractive materials due to their high thermal and chemical stability, high processability, high fluorescence quantum efficiency and good solubility in a common organic solvent.

The principle of color conversion is that pigments release new light through self-luminescence by absorbing the light of certain wavelengths. These pigments are a very useful material since they can be used as a color filter.

Many inorganic substances with their color conversion properties have already been reported in the US patent [11]. However, it is very rare to find studies on the color conversion properties of organic substances. It is possible to do studies on the applicability of PL polymers as a substance for color conversion by manufacturing a simple color filter and measuring its optical properties. A general color filter is used to filter out light by absorbing certain wavelengths and allowing only a portion of the visible light to pass through. The color filter using color conversion differs from general color filters in that it absorbs certain wavelengths of light and emits new light through its self-luminous properties. According to a US patent [11], the color filter using color conversion refers to a display material using photoluminescence. This color filter was fabricated by forming a color conversion layer on top of a blue light device. Unlike general color filters, organic pigments absorb the light emitted from a blue light emission device and release new light through their self-luminous properties. Although previous color filters showed a decreased brightness compared to the original brightness of the back light, the color filter using color conversion is advantageous in that the brightness can be increased to more than the original brightness of the back light with low power consumption. Furthermore, it is considered a next-generation device with practical applications in a wide range of fields due to its simple production and easy pixel formation applicable to screen printing.

In this study, we synthesized a new PAF derivative with high PL efficiency and thermal stability and investigated its physical and optical characteristics. The applicability of the synthesized polymer as a color conversion material was also investigated.

2. Experimental

2.1. Instrumentation

The polymer molecular weight was determined using a Waters alliance 2000 gel permeation chromatography (GPC) instrument calibrated with polystyrene standards. ^1H - and ^{13}C -NMR spectra were recorded at 500 MHz on a Varian Unity Inova spectrometer in CDCl_3 solution. GC-Mass spectra were obtained using a Shimadzu Corporation QP-1000A spectrometer. Absorption and photoluminescence (PL) emission spectra of the polymer were measured using an Optizen 3220 UV/Vis spectrophotometer and a spectra pro 2150i spectrometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymer were carried out under a nitrogen atmosphere at a heating rate of $10^\circ/\text{min}$ using Setaram, Betsys 24 TG-DTA and Seiko, SSC5200H instruments, respectively.

2.2. Materials

The monomer, 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **5**, and the reaction precursor, 2,7-dibromo-9-fluorenone **2**, and two end capping reagents, 2-thiophene boronic acid and 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole, were purchased from Aldrich Chemical Co. and used without further purification.

2.3. Synthesis

9,9-Bis(4-hydroxyphenyl)-2,7-dibromofluorene **3** and 4,7-dibromo-2,1,3-benzothiadiazole **6** were obtained, as described previously [7, 8].

9,9-Bis(4-*n*-octyloxyphenyl)-2,7-dibromofluorene 4. In a nitrogen atmosphere, 1-bromooctane **1** (4.56 g, 23.6 mmol) was added to a solution of 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene **3** (3.00 g, 5.90 mmol) in DMSO (45 ml), and the reaction mixture was stirred. After confirming that the mixture had been melted sufficiently, 0.942 g of NaOH was added and the reaction mixture was heated to 339 K, held at that temperature for approximately 7 h, and cooled to room temperature. The reaction mixture was poured into water and extracted with EA. The organic extracts were dried over MgSO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography (silica gel, Hexane/EA (2:1, v/v), R_f 0.85) to provide 4.01g (5.48 mmol) of the title compound as a light brown solid. Yield: 93 %. Mass m/z 732. ^1H -NMR (CDCl_3 , ppm) δ : 7.52(*d*, 2H), 7.46(*s*, 2H), 7.43(*d*, 2H) 7.04, 6.75, 3.87, 1.74~1.26, 0.87. ^{13}C -NMR (CDCl_3 , ppm) δ : 114.30, 121.46, 128.94, 130.67, 136.20, 153.73, 158.20, 67.88, 64.34, 31.77, 29.22, 26.02, 22.622, 14.07.

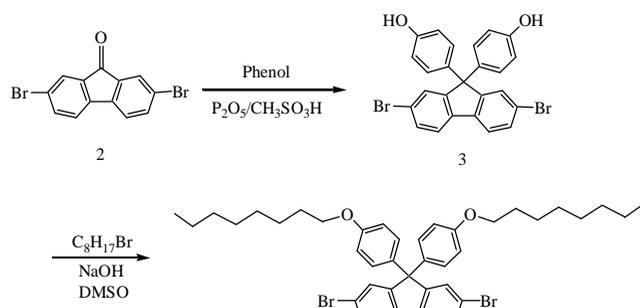
Polymerization. The polymer was synthesized by Suzuki cross-coupling polymerization. The phase transfer catalyst, aliquat 336 (0.70 g), tetrakis(triphenylphosphine)palladium (0.02 g) and 2 M aqueous sodium carbonate (25 ml) were added sequentially to a mixture of 9,9-bis(4-*n*-octyloxyphenyl)-2,7-dibromofluorene **4** (1.63 g, 2.24 mmol), 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **5** (2.50 g, 4.48 mmol), and 4,7-dibromo-2,1,3-benzothiadiazole **6** (0.653 g 2.24 mmol) in toluene (35 ml) under nitrogen. The solution was stirred vigorously and heated under gentle reflux for 1 h until a viscous reaction mixture was observed. An additional 10 ml of toluene was added, and the reaction allowed to continue for further 48 h. Subsequently, the polymer was capped by adding 0.05 g of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole and heating for 6 hours, followed by the addition of 0.15 g of 2-thiophene boronic acid and heating for 6 h. The reaction mixture was cooled to 323 K and added slowly to a stirred solution containing 500 ml of methanol and 50 ml of deionized water. The polymer fibers were collected by filtration and washed with methanol. The crude product was dissolved in toluene and reprecipitated with methanol-acetone (1:1). The solid material was washed with acetone for 24 h in a Soxhlet apparatus and dried in a vacuum oven at 333 K for 24 h. The polymer weighed 3.12 g (approximately 94 % yield). ^1H -NMR (CDCl_3 , ppm) δ : 8.09~6.81, 3.91~3.43, 2.16~2.04, 1.74~1.68, 1.33~1.15, 0.79~0.76. ^{13}C -NMR (CDCl_3 , ppm) δ : 157.99, 154.37, 152.93, 151.79, 140.90, 138.91, 138.86, 137.8, 136.47, 133.62, 132.06, 128.47, 126.70, 124.68, 123.97, 121.44, 120.06, 114.16, 67.90, 64.47, 61.47, 55.36, 48.82, 40.27, 31.80, 30.78, 29.23, 26.31, 26.08, 23.92, 22.58, 14.08.

Color filter fabrication. The applicability of the synthesized polymer as a color conversion material was examined using the following procedure. The color filter solution was produced by mixing PVC binder with 10 % toluene solution at a mixing weight ratio of 1:1. The solution for the color filter was printed on a PET film by screen printing and dried for 3 h at 333 K. The optical properties of the color filter were measured using a range of equipment after placing the produced color filter on the blue color light emission device.

3. Results and Discussion

Reaction monomers 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene **3** and 4,7-dibromo-2,1,3-benzothiadiazole **6** were synthesized using the procedure reported previously [7, 8]. The structural analytical results corresponded to the literary data. As shown in Scheme 1, 9,9-bis(4-*n*-octyloxyphenyl)-2,7-dibromofluorene **4** was

synthesized by the reaction of 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene **3** with 1-bromooctane **1** in an aqueous NaOH solution.

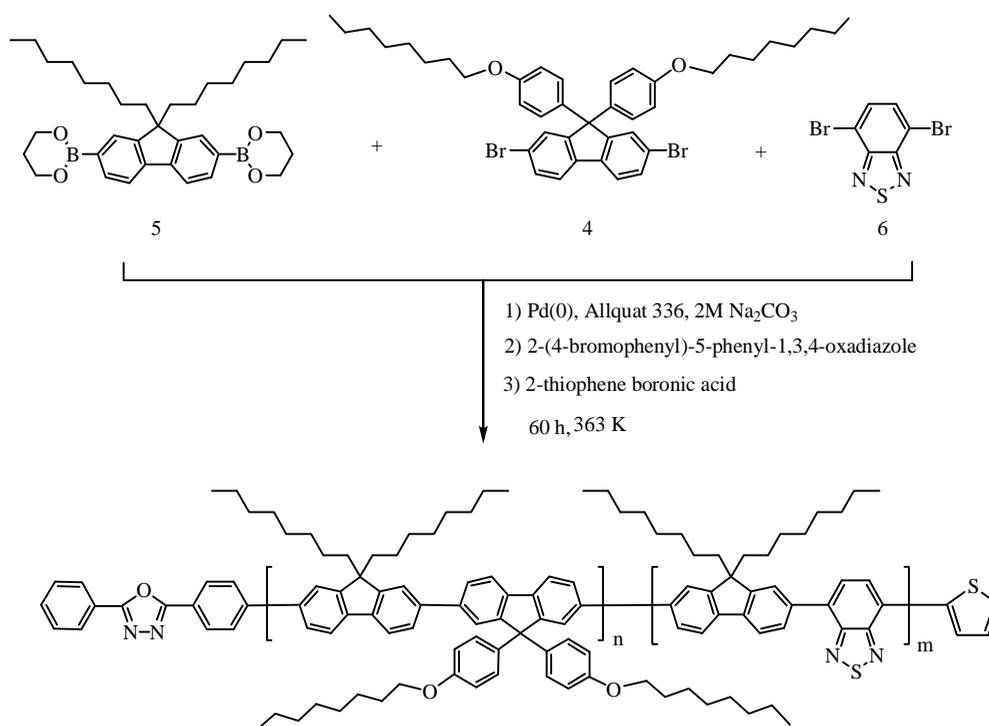


Scheme 1. Synthetic route of monomer **4**

The structure was characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy, and mass spectrometry. In the mass spectrum, the base peak was observed at $732(\text{M}^+)$ and a typical fragmentation pattern was noted. $^1\text{H-NMR}$ spectra of 9,9-bis(4-n-octyloxyphenyl)-2,7-dibromofluorene **4** showed the following δ values: 7.52(*d*, 2H), 7.46(*s*, 2H), 7.43(*d*, 2H) ppm for H atoms on the fluorene benzene ring, 7.05~6.75 ppm for H atoms on the phenyl ring adjacent to C-9, 3.87 ppm for H atoms on $-\text{OCH}_2-$, and 1.74~0.85 ppm for H atoms on $-\text{OC}_8\text{H}_{17}$,

except for $-\text{OCH}_2-$. The $^{13}\text{C-NMR}$ spectra of monomer **4** showed the following δ values: 114.03~158.20 ppm for C atoms of the phenyl ring, 67.88 ppm for C atom adjacent to the oxygen of phenyl group, 64.34 ppm for C-9 atom of fluorene, and 31.77~14.07 ppm for C atoms of the octyl group.

Fluorene-benzothiadiazole copolymer **7** was synthesized by Suzuki cross-coupling polymerization between 9,9-bis(4-n-octyloxyphenyl)-2,7-dibromofluorene **4**, 4,7-dibromo-2,1,3-benzothiadiazole **6** and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **5**. Scheme 2 shows the synthetic route for copolymer **7**. Copolymer **7** was characterized and verified by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ with CDCl_3 as the solvent. $^1\text{H-NMR}$ spectra of copolymer **7** showed the following δ values: approximately 8.03~6.81 ppm for H atoms on the phenyl ring and benzothiadiazole ring, 3.91~3.43 ppm for H atoms on $-\text{OCH}_2-$, and 2.16~0.76 ppm for H atoms on the octyl groups, except for $-\text{OCH}_2-$. From $^{13}\text{C-NMR}$ spectra, signals were observed at approximately 158~114 ppm for C atoms of the phenyl ring and benzothiadiazole ring, approximately 48~14 ppm and 67.90 ppm for the octyl groups, and 64~55 ppm for C-9 atoms of the fluorene ring. Figs. 1 and 2 show $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of copolymer **7**, respectively.



Scheme 2. Synthetic route of copolymer **7**

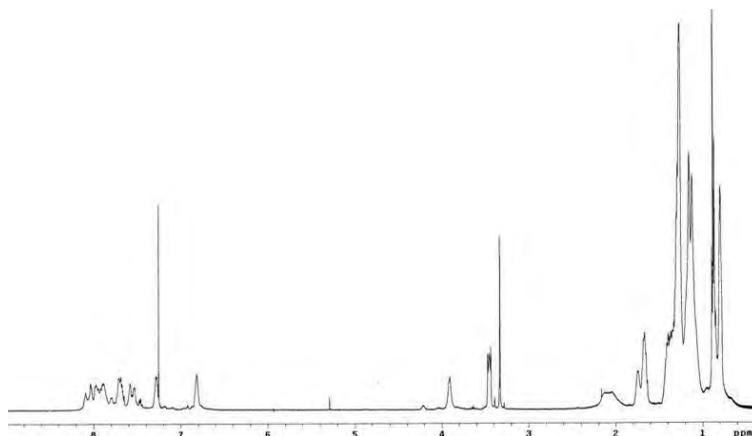


Fig. 1. ^1H -NMR spectra of fluorene-benzothiadiazole copolymer 7

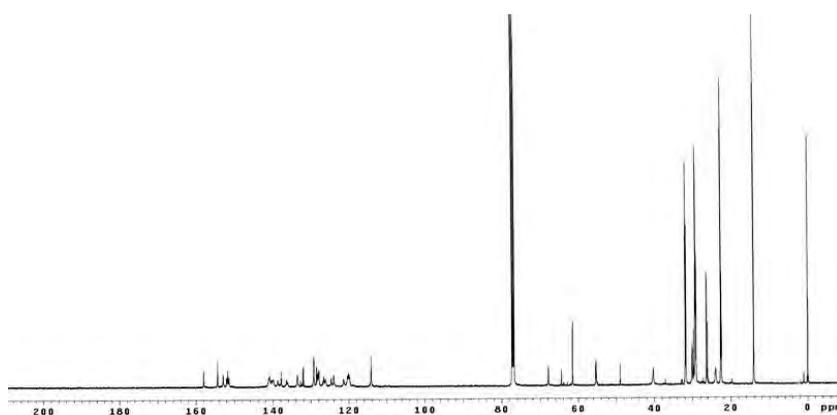


Fig. 2. ^{13}C -NMR spectra of fluorene-benzothiadiazole copolymer 7

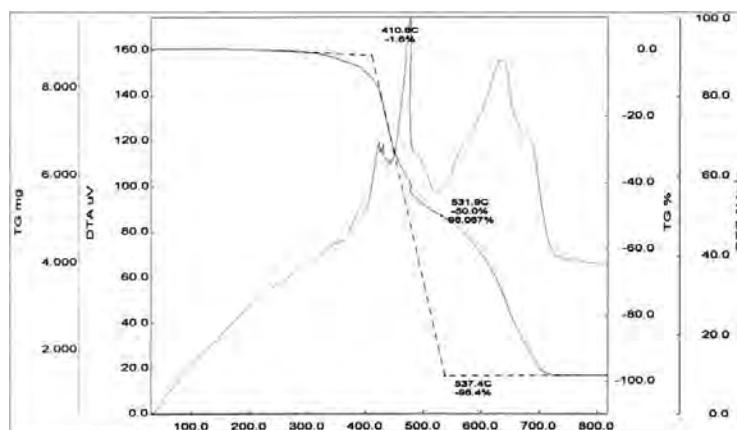


Fig. 3. TGA thermogram of copolymer 7

Table 1

Physical and optical properties of copolymer 7

M_n^a	M_w^a	$PDI^a (M_w/M_n)$	T_g, K	T_d^b, K	$\lambda_{\text{maxabs}}, \text{nm}$	λ_{PL}, nm	E_g^c, eV
18055	37927	2.10	105	410.8	345	545	2.46

Notes: aM_n , M_w and PDI of the polymer were determined by gel permeation chromatography (GPC) using polystyrene standards. b Temperature of 1.6 % weight loss measured by TGA in nitrogen. c Estimated from the onset of the absorption edge responsible for the copolymer.

The molecular weight of copolymer **7** was measured by calibrated with polystyrene standards. Table 1 lists the weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI). The thermal properties of the resulting polymer **7** were measured by TGA and DSC under a nitrogen atmosphere. The glass transition temperature (T_g) of polymer **7** was approximately 378 K, which is higher than that of the poly(9,9-disubstitutedfluorene) derivatives (~328 K) [9] due to the attachment of two 4-octyloxyphenyl groups to C-9 position of the fluorene unit. As shown in Fig. 3, the TGA thermogram of copolymer **7** exhibited two weight-loss plateaus. At lower temperatures, almost no weight loss was observed. The side chain in the copolymer decomposed first at 593–783 K; its onset temperature for thermal bond cleavage was approximately 683 K. The polymer backbone was subjected to decomposition at 783–983 K, where the onset temperature for thermal bond cleavage was at 805 K. These findings demonstrated the good thermal stability of the resulting polymer.

The optical properties of copolymer **7** were analyzed by UV-Vis and PL spectroscopy. Fig. 4 shows the UV-Vis and photoluminescence (PL) spectra of copolymer **7**, which was measured in methylene chloride at room temperature. Copolymer **7** showed an absorption band at $\lambda_{max} = 345$ nm (shoulder at 440 nm). From the onset of the absorption peak, the optical band gap of copolymer **7** was estimated to be 2.46 eV. The PL spectra of copolymer **7** in thin film were taken under excitation of 325 nm line of He-Cd laser. A thin film of copolymer **7** was prepared from a toluene solution by spin-coating on a quartz plate. Copolymer **7** exhibited the maximum emission band at 545 nm, indicating that the synthesized polymer emitted yellowish-green light.

The applicability of the synthesized polymer as a color conversion material was also examined. A color filter solution was produced by mixing the PVC binder with 10 % toluene solution. The color filter was fabricated by printing the color filter solution on a PET film based on the screen print method. The optical properties of the color filter were also measured using a range of equipment after placing the fabricated color filter on top of the blue color light emission device. Table 2 lists the optical properties of the color filter during color conversion.

The general color filter absorbs certain wavelengths of light, allowing only a proportion of the visible light to pass through. Therefore, the color filter blocks a considerable amount of light to present a much lower brightness than the original brightness of the back light. On the other hand, the color filter fabricated in this study presented higher brightness than the original brightness of the back light. The light transmittance of the color filter

was approximately 45 %, indicating that the brightness must have been decreased by approximately 55 % compared to that of the back light. On the other hand, according to the study results, the measured brightness (159 cd/m^2) was approximately 48.6 % higher than that (107 cd/m^2) measured for the device without a color filter. This was attributed to the self-luminosity of the PL polymer. The CIE coordinates were $x = 0.27$ and $y = 0.48$ (yellowish-green color). Fig. 5 shows the emission image when the color filter was placed on top of the blue color light emission device. The figure confirms that the yellowish-green color passed through the color filter.

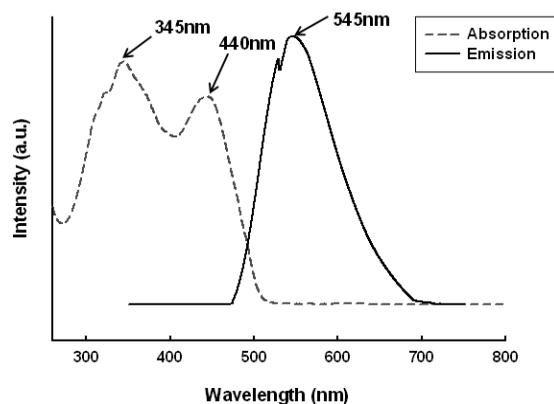


Fig. 4. UV-Vis and PL spectra of copolymer **7**

Table 2

Characteristics of the color filter produced by screen printing

Filter	x	y	Cd/m^2	Color	Transmittance*
X	0.16	0.18	107	Blue	-
O	0.27	0.48	159	Yellowish-green	45 %

Transmittance* refers to the value of color filter film measured by a UV-Vis spectrophotometer.

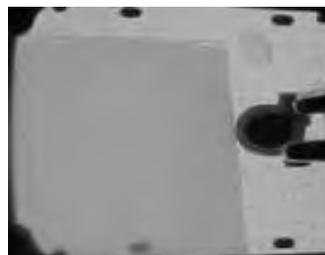


Fig. 5. Emission picture of the color filter

4. Conclusions

A new PL polymer was synthesized by a Suzuki coupling reaction and its optical properties and applicability

lity as a color conversion material were studied. The synthesized PL polymer showed good thermal stability and superior color conversion ability. The decomposition temperature (T_d) was 683.8 K, and the T_g was 378 K. The polymer exhibited M_w of 37927, M_n of 18055, and PDI of 2.10. The main absorption peak in the UV-Vis spectra of copolymer **7** was observed at 345 nm, followed by a shoulder peak at 440 nm. PL spectra of copolymer **7** in the thin film showed a maximum emission band at 545 nm. The applicability of this polymer for use as a color conversion material was also investigated. The color filter was fabricated by screen printing and its optical properties were measured using a range of equipment after placing the fabricated color filter on the blue color light emission device. The transmittance of the color filter was approximately 45 %. The brightness of the blue color light emission device without the filter was 107 cd/m². This was significantly lower than 159 cd/m² observed when the color filter fabricated in this study was placed on top of the device. This 48.6 % increase was attributed to the ability of the organic polymer on top of the blue light emission device to absorb the blue light released from the device and emit yellowish-green light through color conversion.

Acknowledgments

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ВИВЧЕННЯ СТРУКТУРИ ФЛУОРЕН-БЕНЗОТІАДІАЗОЛЬНОГО КОПОЛІМЕРУ ТА ЯК МАТЕРІАЛУ ЗДАТНОГО ПЕРЕТВОРЮВАТИ КОЛІР

Анотація. За реакцією Сузукі синтезовано новий фотолюмінесцентний полімер з високою термічною стабільністю і надзвичайною здатністю до перетворення кольору. Досліджено його фізичні і оптичні властивості. Показано можливість застосування синтезованих полімерів як матеріалу здатного перетворювати колір. З використанням методу трафаретного друку виготовлено кольоровий фільтр і виміряні його оптичні властивості, використовуючи широкий спектр обладнання.

Ключові слова: провідний фотолюмінесцентний полімер, перетворення кольору, поліалкілфлуор, кольоровий фільтр, кополімер.