Synthesis and Characterization of Soluble Polyimides Functionalized with Carbazole Moieties

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ABSTRACT: Here, we report the synthesis and characterization of new soluble polyimides that are functionalized using carbazole moieties in their side chain. As a monomer for synthesizing the polyimides, 4′-carbazole-9-yl-[1,1′;2′,1″]terphenyl-4′-diamine and 2-(3-carbazol-9-yl-propyl)-biphenyl-4,4″-diamine were synthesized and then characterized using 1H NMR, 13C NMR, FTIR, UV–visible and photoluminescence spectroscopy, differential scanning calorimetry (DSC), and elemental analysis. The polyimides synthesized via chemical imidization processes were characterized with X-ray photoelectron spectroscopy, gel permeation chromatography, wide angle X-ray diffraction, thermogravimetric analysis, DSC, tensile strength measurement, and dielectric property measurement. Results showed that the synthesized polyimides were soluble in a variety of organic solvents, optically transparent in a visible range, thermally stable, mechanically strong, and considerably low dielectric. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 8117–8130, 2008

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INTRODUCTION

Organic semiconducting materials have been highlighted as one of new class functional materials since their successful application to organic light-emitting device (OLED) displays.1–3 To date, most of these organic semiconducting materials being used in the actual manufacturing of OLED displays are limited to either thermally evaporable low-molecular-weight molecules4 or soluble polymers.3 Although the OLED displays made using these materials are now commercialized, their reliability (lifetime) is still inferior compared with liquid crystal display (LCD) and plasma display panel (PDP), which have major shares in flat panel display market.

The main effort of overcoming the low reliability of OLED displays was initially devoted to the development of thermally stable organic semiconducting materials.3–6 In case of low-molecular-weight materials, the key strategy was to introduce bulky and rigid aromatic groups into the skeleton structure of a molecule, irrespective of the type of materials. The similar idea has been adopted for various soluble conjugated polymers through introducing a rigid fluorine moiety. Beside this method, thermally and/or chemically curable polymer structures have been also attempted to improve the fundamental stability of organic layers.3,6,7 One of these structures was “imide,” and its corresponding semiconducting
polyimide (PI) has been reported to exhibit remarkably high thermal transition temperature over 200 °C. Additional advantages of semiconducting PIs include fairly wide band gap, excellent planarization (extremely stable down to several tens of nanometers in the layer thickness) and possible use of both wet and dry processes.

So far, these semiconducting PIs were made by thermal imidization process, at high temperatures, of corresponding precursor polymers that are soluble in organic solvents so that they can be wet-processed at room temperature. However, this high temperature process can give rise to additional cost, even though this could result in perfectly insoluble and stable nanolayers. In this regard, a thermally stable but soluble semiconducting PI is considered to be an alternative choice for low temperature processes. To date, however, no soluble semiconducting PIs have been reported though we previously studied a mixture of soluble insulating PI and semiconducting low-molecular-weight materials.

In this work, we synthesized two kinds of soluble semiconducting PIs containing newly synthesized carbazole diamine derivatives, 4’-carbazole-9-yl-[1,1’2’,1’] terphenyl-4,4’-diamine (CzTPDA) and 2-(3-carbazol-9-yl-propyl)-biphenyl-4,4’-diamine (CzHBPD). The carbazole derivatives were chosen and designed because of their rigidity, good chemical stability (owing to the in-plane resonance of carbazole ring), and moderately high oxidative potential suitable for hole transporting layer. In particular, the feature of these soluble PIs is on that the carbazole units are in the side part of main chain (backbone), which induces charge (hole) transport along with the side parts: here, one PI has the carbazole unit separated by aromatic rings from the backbone, and another PI has the carbazole group separated by aliphatic chain from the backbone.

**EXPERIMENTAL**

All chemicals including 4,4’-dinitro-biphenyl-2-ylamine, 1,4-dibromobenzene, 1,6-dibromo-hexane, hydrobromic acid, sodium nitrite, cuprous bromide, 18-crown-6, n-butyl lithium, triethylborate, trimethyl borate, tetrakis(triphenylphosphine) palladium, hydrazine monohydrate, 10% Pd on carbon, activated magnesium turnings, palladium(II)acetate, 2-(dicyclohexylphosphanyl) biphenyl were purchased from Aldrich Chemical Company. Prior to starting synthesis, carbazole was recrystallized from ethanol. 1-Methyl-2-pyrrolidinone (NMP) was vacuum distilled from calcium hydride, while pyromellitic anhydride (PMDA) and 2, 2’-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were used as received. 9H-Carbazole-3,6-diamine (CzDA) was used as received for polyimide synthesis. Two diamine compounds, 4’-Carbazol-9-yl-[1,1’2’,1’] terphenyl-4,4’-diamine (CzTPDA) and 2-(6-Carbazol-9-yl-hexyl)-biphenyl-4,4’-diamine (CzHBPD), were obtained by chemical reduction of corresponding dinitro-compounds that were synthesized as follows (see overall reactions in Scheme 1).

**Synthesis of 4’-Carbazol-9-yl-[1,1’2’,1’] terphenyl-4,4’-diamine (CzTPDA)**

4,4’-Dinitro-biphenyl-2-ylamine (5.2 g, 20 mmol) was dissolved in a hot mixture of 40% hydrobromic acid (20 mL), water (80 mL), and acetonitrile (80 mL). The solution was cooled to 0 °C and then sodium nitrite (3.6 g, 52 mmol) in cold water (7 mL) was added with stirring, the temperature being kept below 10 °C. Cuprous bromide (6.5 g, 45 mmol) in hydrobromic acid (80 mL) was added to the cold diazonium compound with vigorous stirring, and after the mixture warmed up to the room temperature it was heated until the evolution of nitrogen ceased. The precipitate was extracted with chloroform, washed with water, chromatographed on alumina, and dried. Evaporation of the extract gave the crude product (6.2 g, yield = 96%). mp: 146–147 °C.

**FTIR (KBr):** 3161 (aromatic stretch), 1600 and 1475 (aromatic C=), 1550 and 1350 (C—NO2), 900–690 (aromatic out-of-plane bend) and 665 cm⁻¹ (C—Br). 1H NMR (300 MHz, CD2Cl2): δ ppm 7.25 (s, 1H), 7.63 (d, 2H), 8.19–8.42 (m, 4H). 13C NMR (75.45 MHz, CD2Cl2): δ ppm 133.6, 130.5, 128.3, 124.1, 122.9. Anal. Calcd for C19H13BrN2O4: C, 44.61; H, 2.18; N, 8.67; O, 19.81; Br, 24.73. Found: C, 45.04; H, 2.7; N, 8.88.

**Synthesis of 9-(4-Bromo-phenyl) carbazole (I2)**

A mixture of 1,4-dibromobenzene (14.2 g, 60 mmol), carbazole (10 g, 60 mmol), CuI (1.14 g, 6 mmol), 18-crown-6 (0.53 g, 2 mmol), and K2CO3 (16.6 g, 120 mmol) was suspended in 2 mL of DMF. The mixture was heated at 170 °C for 11 h under nitrogen and then cooled to room temperature followed by quenching with 1 N HCl and the
Scheme 1. Synthesis of new carbazole-containing diamines. (a) Synthesis of 2-bromo-4,4'-dinitro-biphenyl (I_1). (b) Synthesis of 9-(4-bromo-phenyl) carbazole (I_2). (c) Synthesis of carbazol-9-yl-4-benzeneboronic acid (I_3). (d) Synthesis of 9-(4,4'-dinitro-1,1',2',1''terphenyl-4''-yl)-carbazole (I_4). (e) Synthesis of 4''-carbazol-9-yl-[1,1',2',1''terphenyl-4''-yl]-carbazole (I_5). (f) Synthesis of 9-(9H-carbazol-9-yl)hexylboronic acid (I_6). (g) Synthesis of 2-(6-carbazol-9-yl-hexyl)-4,4'-dinitro-biphenyl (II_2). (h) Synthesis of 6-(9H-carbazol-9-yl)hexylboronic acid (II_3). (i) Synthesis of 2-(6-carbazol-9-yl-hexyl)-4,4'-dinitro-biphenyl (II_4). (j) Synthesis of 2-(6-carbazol-9-yl-hexyl)-4,4'-dinitro-biphenyl (II_5). (See the Supporting Information for more details of (a)–(i).)
precipitated thus obtained was filtered and washed with NH₂OH and water. The resulting gray residue was purified with column chromatography using hexane as eluant. (14 g, yield = 72%). mp: 327–328 °C.

IR (KBr): 3161 (aromatic stretch), 1600 and 1475 (aromatic C=C), 1350–1000 (C–N), 900–690 (aromatic out-of-plane bend) and 665 cm⁻¹ (C–Br). ¹H NMR (300 MHz, CD₂Cl₂): δ ppm 7.28–7.41 (m, 6H), 7.45 (d, 2H, J = 8.2 Hz) 7.72 (d, 2H, J = 8.2 Hz) 8.13 (d, 2H, J = 7.6 Hz). ¹³C NMR (75.45 MHz, CD₂Cl₂): δ ppm 139.4, 132.2, 130.8, 122.4, 121.7, 120.5, 119.6, 117.2, 111.0. Anal. Calcd for C₁₈H₁₂BrN: C, 67.10; H, 3.75; N, 4.35; Br, 24.80. Found: C, 67.91; H, 4.01; N, 4.39.

**Synthesis of Carbazol-9-yl-4-benzeneboronic acid (I₁)**

Thiry milliliter of n-butyl lithium (30 mL, 75 mmol) was added to a solution of 9-(4-bromo-phenyl) carbazole (BPC) (9.7 g, 30 mmol) in anhydrous ether (100 mL) at –78 °C. The mixture was stirred at room temperature for 3 h. After the reaction mixture was cooled to –78 °C, 144 mmol (21.02 g) of triethylborate was added to the reaction mixture. After stirring for 8 h, the reaction mixture was added to 2 N aqueous HCl solution. The mixture was stirred for 1 h to produce a solid. The solid was filtered and washed several times with ether and finally was recrystallized in ethyl acetate to get 3.9 g (yield: 45%); mp = 320–322 °C.

IR (KBr): 3600–3400 cm⁻¹ (broad B–OH). ¹H NMR (300 MHz, CD₂Cl₂): δ ppm 2.0 (–OH), 7.08 (s, 4H), 7.2 (2H), 7.4 (4H), 7.55 (2H). ¹³C NMR (75.45 MHz, CD₂Cl₂): δ ppm 140, 130.8, 129, 125, 121.7, 120, 117.2, 110.0. Anal. Calcd for C₁₈H₁₄BNO₃: C, 74.22; H, 3.94; N, 8.61; O, 13.18. Found: C, 74.0; H, 3.9; N, 8.61; O, 13.5.

**Reduction to CzTPDA from I₄**

In a 500-mL round-bottom flask equipped with a stirring bar, a mixture of 0.70 g (1.5 mmol) of dinitro compound I₄, 0.02 g of 10% Pd/C, 0.5 mL of hydrazine monohydrate, and 15 mL of ethanol was heated at reflux for 10 h. After being cooled to room temperature, 15 mL of THF was added to dissolve the precipitate. The solution was filtered to remove Pd/C catalyst, and the filtrate was distilled to remove the solvent. The crude product was washed with methanol and recrystallized from toluene in nitrogen and dried in vacuum at 100 °C to give 0.51 g (yield: 80%).

IR (KBr): 3161 (aromatic stretch), 3400 (N–H), 1600 and 1475 (aromatic C=C), 1350–1000 (C–N), 900–690 cm⁻¹ (aromatic out-of-plane bend). ¹H NMR (300 MHz, CD₂Cl₂): δ ppm 4.0 (4H, –NH₂), 6.48–6.74 (m, H₆,₈,₁₀,₁₂), 7.23 (d, H₆,₈,₁₀,₁₂), 7.30 (d, H₆,₈,₁₀,₁₂), 7.4 (s, H₆,₁₀), 7.5–7.55 (m, H₈,₁₃,₁₄,₁₆). ¹³C NMR (75.45 MHz, CD₂Cl₂): δ ppm 148.1, 145.3, 131.3, 130.4, 129.8, 128.2, 127.0, 124.7, 123.5, 117.2, 114.8, 113.0. Anal. Calcd for C₃₀H₂₄N₃: C, 84.68; H, 5.45; N, 9.87. Found: C, 84.59; H, 5.50; N, 9.85.

**Synthesis of 9-(6-Bromo-hexyl)-9H-carbazole (I₁₂)**

To a mixture of carbazole (10 g, 60 mmol), KOH (3.5 g, 60 mmol), and DMF (200 mL) was added 1,6-dibromo-hexane (29.2 mL, 180 mmol) at 0 °C.
The reaction mixture was stirred at room temperature for 48 h, diluted with water (300 mL), and extracted with ether (150 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated. Pure product was obtained after column chromatography (SiO₂, hexane-dichloromethane, 4:1). (16.5 g, yield = 83%). mp: 264–265 °C.

IR (KBr): 3161 (aromatic stretch), 3000–2850 (C–H stretch), 1600 and 1475 (aromatic C=C), 1465 (−CH₂− bend), 1350–1000 (C–N), 900–690 cm⁻¹ (aromatic out-of-plane bend) and 665 cm⁻¹ (C–Br). 1H NMR (300 MHz, CD₂Cl₂): δ ppm 8.13 (d, 2H, J = 7.6 Hz), 7.45–7.34 (m, 4H), 7.28–7.2 (m, 2H), 3.95 (t, 2H, J = 6.9 Hz), 3.28 (t, 2H, J = 6.9 Hz), 1.90–1.70 (m, 4H). 13C NMR (75.45 MHz, CD₂Cl₂): δ ppm 140.3, 125.6, 122.8, 120.5, 118.6, 111.0, 43.2, 33.7, 32.5, 28.8, 27.9, 26.4. Anal. Calcd for C₁₈H₂₀BrN: C, 65.46; H, 6.10; N, 4.24; Br, 31.24. Found: C, 65.3; H, 7.8; N, 4.22.

**Synthesis of 6-(9H-Carbazol-9-yl)hexylboronic acid (II₃)**

Activated magnesium turnings (8.7 g, 32 mmol) were suspended in 5 mL of anhydrous ether in a 250-mL three-necked RB flask equipped with reflux condenser and dropping funnel. The magnesium is activated with few crystals of Iodine along with a calculated amount of compound II₂ (0.33 g, 1 mmol). After ~10 min, the mixture starts refluxing and the remaining II₂ (7.6 g, 24 mmol) dissolved in 10 mL of diethyl ether was added drop-wise to the flask and the reaction mixture was kept under gentle reflux for about 5 h. Trimethyl borate (2.6 g, 3 mL, 25 mmol) was taken in a separate flask and was dissolved in 15 mL of diethyl ether. The brown solution of initially prepared Grignard was transferred to this flask through a nitrogen pressured canula at −78 °C over a period of 30 min. The flask of Grignard reagent was washed with an additional 2 mL of ether to ensure complete transfer. During the addition, the temperature rose and it was carefully maintained below −60 °C. This reaction mixture was then stirred overnight and was allowed to warm up to RT in the due course. The brownish yellow precipitate formed was diluted with additional diethyl ether (20 mL), the mixture was cooled to 0 °C in an ice-water bath, and 10%aq. H₂SO₄ was added dropwise until the clear pale-yellow solution was obtained. It was then stirred at room temperature for 1 h and the ether layer was separated and aqueous was extracted three times with diethyl ether. The combined organic layer was washed with water and brine, dried over MgSO₄. Filtration and concentration afforded the compound II₃ as a pale-yellow solid which was used as such in the continuing steps without further purification. (5 g, yield = 68%). mp: 269–270 °C.

IR (KBr): 3600–3400 cm⁻¹ (Broad B–OH), 3161 (aromatic stretch), 3000–2850 (C–H stretch), 1600 and 1475 (aromatic C=C), 1465 (−CH₂− bend), 1350–1000 (C–N), and 900–690 cm⁻¹ (aromatic out-of-plane bend). ¹H NMR (300 MHz, CD₂Cl₂): δ ppm 8.13 (d, 2H, J = 7.6 Hz), 7.45–7.34 (m, 4H), 7.28–7.2 (m, 2H), 3.95 (t, 2H, J = 6.9 Hz), 3.28 (t, 2H, J = 6.9 Hz), 2.00 (−OH), 1.80–1.70 (m, 4H). ¹³C NMR (75.45 MHz, CD₂Cl₂): δ ppm 133.4, 121.6, 120.5, 118.6, 111.0, 50.2, 33.7, 32.5, 28.8, 27.9, 26.4. Anal. Calcd for C₁₈H₂₂BNO₂: C, 73.24; H, 7.51; N, 4.75; O, 10.84; Br, 6.36. Found: C, 73; H, 7.5; N, 4.69; O, 10.9.

**Synthesis of 2-(6-Carbazol-9-yl-hexyl)-4,4'-dinitro-biphenyl (II₄)**

All catalysts and reagents and the reactions were handled under a purified nitrogen atmosphere. A mixture of 6-(9H-carbazol-9-yl) boronic acid (2.92 g, 10 mmol) and 2-Bromo-4,4'-dinitro-biphenyl (BDNBP) (3.2 g, 10 mmol) was taken in 250 mL degassed and flamed Schlenk flask. To this 20 mL of distilled toluene was added followed by 15 mL of 3 M solution of potassium phosphate (K₃PO₄) through syringes to the mixture and it was further degassed and refilled with nitrogen. Finally, 0.045 g of palladium(II) acetate (Pd(OAc)₂) as catalyst and 0.078 g of 2-(dicyclohexylphosphanyl) biphenyl as ligand was added to the reaction flask. The mixture was vigorously refluxed under flowing nitrogen for 48 h. When the reaction mixture was cooled down to room temperature the mixture was filtered and the filtrate was extracted three times with diethyl ether. The combined organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography CH₂Cl₂/petroleum ether giving 3.22 g (yield: 65%) of the title product as a pale yellow sticky solid. mp: 3 °C.
7.45–7.34 (m, 4H), 7.28–7.15 (m, 3H), 3.95 (t, 2H), 3.28 (t, 2H), 1.90–1.70 (m, 4H). 13C NMR (75.45 MHz, CD2Cl2): δ ppm 140.3, 133.6, 130.5, 128.3, 125.6, 124.1, 122.9, 121.8, 120.5, 118.6, 111.0, 43.2, 33.7, 32.5, 28.8, 27.9, 26.4. Anal. Calcd for C30H27N3O4: C, 73.01; H, 5.51; N, 8.51; O, 12.97. Found: C, 72.8; H, 5.47; N, 8.5; O, 13.

**Reduction to CzHPDPA from II4**

In a 500-mL round-bottom flask equipped with a stirring bar, a mixture of 0.99 g (2 mmol) of dinitro compound II4, 0.023 g of 10% Pd/C, 0.55 mL of hydrazine monohydrate, and 15 mL of ethanol was heated at reflux for 12 h. After being cooled to room temperature, 15 mL of THF was added to dissolve the precipitate. The solution was filtered to remove Pd/C catalyst, and the filtrate was distilled to remove the solvent. The crude product was washed with methanol and recrystallized from toluene in nitrogen and dried in vacuum at 100 °C to give 0.51 g (yield: 74%). mp: 308–310 °C (DSC in air).

**Synthesis of Soluble Polyimides**

To make polyimides, 0.4 mmol of diaminodichlorobenzene was dissolved into 1.5 mL of NMP. To this solution, 0.4 mmol of dianhydride (PMDA or 6FDA) was added together with additional 1.5 mL of NMP. This solution was stirred at room temperature under nitrogen atmosphere for 48 h to yield a viscous polyamic acid (PAA) solution. To this PAA solution, for chemical imidization reaction, 2 mL of acetic anhydride and 1 mL of pyridine were added and stirred for 12 h at room temperature and 6 h at 90 °C. Finally the solution was poured into methanol (200 mL). The precipitate was collected by filtration and then dissolved in THF (10 mL). This solution was poured into methanol (500 mL), leading to precipitates (solid PI) which were then filtered and dried at 70 °C under vacuum. Scheme 2 summarizes the synthesis process and resulting polyimides.

**Preparation of Thin Films**

**For the Measurement of Mechanical and Thermal Properties**

Polyimide solutions (solid concentration: 5–7 wt. %) were prepared using THF as a solvent and were purified by using 13 mm, 0.45 μm PTFE syringe filter to remove nondissolved residues and/or dust particles. These pure solutions were poured onto a Petri dish and held for about 8 h at room temperature. The casting films were dried in an oven at 40 °C for 6 h without vacuum and again for another 6 h with vacuum. The dried film samples were softbaked at 80 °C for 6 h and at 100 °C for 10 h. The thickness of these films was around 150 μm.

**For the Measurement of UV–visible Spectra and Dielectric Constant**

Quartz substrates were cleaned with diluted water and then with hot piranha solution (7:3 M ratio of conc. H2SO4 and 30% H2O2). Indium-tin oxide (ITO) coated glass substrates were cleaned using a detergent in an ultrasonication bath for ~30 min, rinsed thoroughly with distilled water, dried at 60 °C in vacuum, and finally stored in a nitrogen-filled glove box. Before spin-coating of the polyimide solutions, the ITO side of the substrates was pretreated with plasma (Harrick Plasma Cleaner, PDC-32 G). Onto these pre-cleaned ITO-coated glass substrates, the polyimide films were spin-coated for dielectric constant measurements, while quartz substrates were used to deposit the polyimide films for optical property measurements. The drying and softbaking condition was the same as described earlier.

**Measurements**

Infrared spectra (KBr disks) were measured using a FTIR spectrometer (Shimadzu IR Prestige-21 spm) equipped with a Ge-KBr beam splitter. 1H and 13C NMR spectra were measured using a NMR spectrometer (Varian Unity Plus-300–300 MHz: Standard: tetramethylsilane). Elemental analysis was conducted with an elemental analyzer (EA, Vario EL, Elemental Analysen Systeme). The surface composition of polymers was measured using X-ray photoelectron spectroscopy.
(XPS, ESCALAB 250, Thermo Electron Corporation) equipped with monochromatic Al Kα (hν = 1486.6 eV) X-ray source (15 kV, 150 W, 500 μm X-ray spot size, 45° incident angle and 90° of sample to analyzer angle). Inherent viscosities were measured using a Cannon Fenske viscometer with solutions in NMP (0.5 g/dL, 25 °C). Number-average molecular weight (Mn) and polydispersity (PDI) of soluble PIs synthesized were measured using a gel permeation chromatography (GPC, Waters 515) equipped with a differential refractometer, HPLC pump (Waters 410), and two Styragel HR 5E columns in DMF (0.1 mg/L) solvent at 42 °C which were calibrated with polystyrene standards. Solubility test was performed using equal amounts of polymers in matched quantities of commonly used solvents.

Thermogravimetric analysis (TGA) was performed under nitrogen using a thermogravimetric analyzer (TGA Q50 Q Series) at a heating rate of 10 °C/min from 50 to 600 °C. Thermal transition behavior of samples was carried out using a differential scanning calorimetry (DSC, TA instrument Q 100) at a heating rate of 20 °C/min from 50 to 500 °C. Tensile properties were measured using a universal testing machine (UTM, KSU 05, Kyungsang Instrument) with a load cell of 10 kgf at room temperature: gauge length and strain rate were 2 cm and 0.5 cm/min, respectively. Optical properties were measured using UV–visible spectrophotometer (HITACHI U-2010) (thickness of each film was ~1 μm), while photoluminescence (PL) spectra were measured using a fluorescence spectrometer (HITACHI F-4500). Wide-angle X-ray diffraction (WAXD) measurements of the pulverized samples were conducted using a X-ray diffractometer (Rigaku, Miniflex): Cu Kα radiation (λ = 1.54 Å) source was operated at 50 kV and 40 mA. Capacitance (C) of films was measured using an impedance analyzer (HP4194A)

Scheme 2. Polymerization of carbazole-containing polyimides from constituent monomers.
and then corresponding dielectric constants (at a frequency of 1 MHz) were calculated using 
\[ K = \frac{Cd}{A\varepsilon_0} \]
where \( d \) is the film thickness (each film was 1.0 ± 0.05 \( \mu \)m), \( A \) is the area, and \( \varepsilon_0 \) is the permittivity in vacuum.

RESULTS AND DISCUSSION

Characterization of Diamines

The synthesized diamines, CzTPDA and CzHBPDA, were characterized in various ways as given in the experimental section (also note that detailed data for each intermediate are provided in the supporting information: Figs. S1–S4). As a representative data, here we discuss with NMR spectra as shown in Figure 1. As given in Fig. S1, \(^1\)H NMR spectra of \( I_1 \) and \( I_2 \) gave all peaks corresponded to expected chemical structures, whereas the transformation of \( I_2 \) to \( I_3 \) was confirmed by the appearance of B–OH peaks around 2.0 ppm. \( I_4 \) that is obtained by the Suzuki coupling reaction of \( I_3 \) and \( I_1 \) showed the peaks of biphenyl hydrogens together with those of 9-phenyl carbazole. Finally, the formation of CzTPDA was confirmed from the appearance of \( \text{\text{N-H}}_2 \) peaks at ~4.0 ppm [see Fig. 1(a)]. Similarly, the formation of CzHBPDA was also confirmed from Figure 1(a): note the appearance of alkyl hydrogen peaks at 1–2 ppm instead of aryl hydrogens observed in CzTPDA. As shown in Figure 2(b), \(^{13}\)C NMR spectra also support that the diamines were successfully synthesized: for CzTPDA, the characteristic peaks of aryl carbons are found at 148–113 ppm, whereas those of alkyl carbons are observed at 59–28 ppm.

Characterization of Polyimides

Viscosity and Molecular Weight

The viscosity, molecular weight, and distribution of polyimides synthesized are summarized in Table 1. The viscosity ranges from 0.52 to 0.63 dL/g, implying that they have an appreciable molecular weight.\(^\text{19}\) The GPC data showed that \( M_n \) ranges from 37,000 to 58,000, while PDI was 1.3–1.9. This indicates that the present polyimides have relatively narrower molecular weight distribution, meaning the reduced portion of far lower and higher molecular fractions, which could affect negatively the performance of thin films prepared finally.

![Figure 1. \(^1\)H NMR (a) and \(^{13}\)C NMR (b) spectra of CzTPDA and CzHBPDA.](image)

![Figure 2. Representative FTIR spectra of PAA, PI, and PI\(_2\).](image)
FTIR Spectra

Figure 2 shows the FTIR spectra of the polyimides synthesized, in which the carbonyl peaks of imide groups were measured at around 1783 and 1724 cm\(^{-1}\), whereas those of amide groups (typically found at 1650 cm\(^{-1}\)) were not observed (see Fig. S5 in the supporting information). This indicates that the imidization of precursor moiety (PAA) was completed during polycondensation step. In more detailed peak assignment is as follows: the characteristic absorption bands of PAA appear at 3400–2400 (OH in carboxylic), 3500–3100 (NH in amide), 1660 and 1535 (C\(\equiv\equiv\)O in imide), and 1513 cm\(^{-1}\) (C\(\equiv\equiv\)C in \(\text{C}_6\text{H}_5\)),\(^{20}\) whereas those of fully cured PIs appear at 1780 (C\(\equiv\equiv\)O in phase), 1720 (C\(\equiv\equiv\)O out of phase), 1513 (C\(\equiv\equiv\)C in \(\text{C}_6\text{H}_5\)), 1380 (C\(\equiv\equiv\)N in imide), and 730 cm\(^{-1}\) (imide ring deformation).\(^{21}\) Here, we note that C\(\equiv\equiv\)H stretching (2800–2900 cm\(^{-1}\)), \(\text{CH}_2\) bending (1465 cm\(^{-1}\)), and \(\text{CH}_3\) bending (1375 cm\(^{-1}\)) arising from the alicyclic moieties of the polymer were clearly seen for PIs derived from CzHBPDA.

XPS Spectra

The XPS survey spectra of PIs synthesized here show carbon, nitrogen, and oxygen (binding energy at 281, 397, and 528 eV, respectively) (see Fig. 3). In case of fluorinated PIs, a fluorine peak is observed at a binding energy of 686 eV. From the XPS spectrum that focuses on C\(_{1s}\) of PI\(_f\) (see Fig. S6 in the supporting information), it is disclosed that the polyimide has three characteristics peaks corresponding to C–C bonds (284.6 eV), C–N bonds (285.6 eV), and C–O bonds (288.6 eV). The observation of single C\(_{1s}\) peak at 288.6 eV (C=O) means that the carbon atom in the carboxyl group exists in the same electronic environment, indicating that all amic acid units were converted into imide groups by the dehydration reaction between carboxylic acid and amide groups of PAA. This is also supported by the absence of C–O peak that is typically measured for PAA.\(^{22}\)

Solubility and Crystallinity

The solubility of synthesized PIs was examined with various solvents as given in Table 2. PI\(_2\) and PI\(_f\) were readily soluble in organic solvents such as chloroform, THF, DMP, DMSO, NMP, and \(m\)-cresol, whereas PI\(_1\) and PI\(_f\) also showed good solubility in these organic solvents except a partial solubility in chloroform (note that PI and PI\(_f\) were insoluble in chloroform). The trend can be attributed to a rigidity factor: aliphatic moieties impart more flexibility than aromatic groups,

Table 1. Viscosity and Molecular Weights of Polyimides Synthesized in this Work

<table>
<thead>
<tr>
<th>Dianhydride</th>
<th>Diamine</th>
<th>Polyimides</th>
<th>(\eta) (dL/g)</th>
<th>(10^4 M_n)</th>
<th>PDI</th>
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</thead>
<tbody>
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<td>PMDA</td>
<td>CzDA</td>
<td>PI</td>
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<td>1.6</td>
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<td>CzHBPDA</td>
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<td>1.3</td>
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<tr>
<td>6FDA</td>
<td>CzDA</td>
<td>PI(_f)</td>
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<td>5.8</td>
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<tr>
<td>6FDA</td>
<td>CzHBPDA</td>
<td>PI(_f)</td>
<td>0.52</td>
<td>4.5</td>
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</table>

Figure 3. XPS survey spectra of PI\(_1\) and PI\(_f\).

leading to better solubility, while side chain units loosen the close chain packing of polymer chains leading to enhanced solubility for PIs derived from CzTPDA and CzHBPDA and 6FDA.

Figure 4 shows WAXD diffractograms of synthesized polyimides. PI showed peaks at a low angle region of 2θ < 9°, which is considered to be originated from highly ordered polycrystalline microdomains as typically observed in a rigid rod-like polyimide. The broad peak at 9° < 2θ < 40° can be attributed to the mixed diffraction of a poorly order domains and amorphous halo. For PI1, PI1′, and PI2′ broad amorphous halos are observed, indicating almost no ordered crystal structures. In contrast, PI2 exhibited a sharp peak at ~16.7° (d-spacing = 5.4 Å), suggesting existence of more ordered structure compared with PI2′.

**Thermal Stability and Transition Behavior**

Most of polyimides were decomposed at above 480 °C for 5% weight loss (see Table 3), whereas for 10% weight loss the decomposition temperature was in the range of 500–572 °C (see Fig. S7 in the supporting information). In particular, PIs based on CzDA exhibited highest decomposition temperatures, which can be related to the rigidity of polyimide backbone. In contrast, fluorine-containing PIs showed lower decomposition temperature than nonfluorinated PIs, indicating the influence of reduced chain–chain interaction. Furthermore, the presence of thermally fragile hexyl chain might affect the least stable PI2 and PI2′.

Figure 5 shows DSC thermograms (third run) of selected diamine and polyimide powders. The glass transition started at ~168 and 140 °C and then the glassy phase changed into amorphous states at 176 and 149 °C for CzTPDA and CzHBPDA, respectively. In particular, CzTPDA showed no melting behavior below 350 °C, whereas CzHBPDA exhibited clear melting at around 305 °C. As a result, all PIs showed high glass transition temperatures that range from 268 to 288 °C (see Table 3). However, we could not detect any transition for PI and PI′, which can be attributed to their highly ordered and rigid features.

**Mechanical and Dielectric Properties**

All polyimides synthesized here showed appreciable mechanical stiffness, tensile strength varying from 94 to 111 MPa, elongation at break from 9 to 14%, and tensile modulus in the range 1.6–2.0 GPa (see Table 3). Owing to the rigidity and high
ordering, PI and PI\textsuperscript{f} exhibited the highest tensile strength and lowest percentage of elongation at break. On the other hand, the flexible alkyl side chain made PI\textsubscript{2} and PI\textsubscript{f}\textsubscript{2} less mechanically stiff but induced larger elongation at break. The dielectric constant (\(\varepsilon\)) was varied according to the type of monomers: the lowest value was measured for PI\textsubscript{f}\textsubscript{2} (\(\varepsilon = 2.5\)), whereas the highest value was obtained for PI (\(\varepsilon = 3.1\)). The lowest dielectric constant for PI\textsubscript{f}\textsubscript{2} is attributed to the steric hindrance effect of bulky 6F moieties as well as the electrostatic repulsion among fluorine atoms.\textsuperscript{25} It is already well known that fluorinated polyimides often have higher free volume than unfluorinated ones, leading to lowered dielectric constant. In addition, the low dielectric constant for PI\textsubscript{2} and PI\textsubscript{f}\textsubscript{2}, compared with PI\textsubscript{1} and PI\textsubscript{f}\textsubscript{1}, is considered due to the alkyl chain that reduces the number of polarizable molecular units in a given volume.

### Optical Properties

Prior to studying the optical properties of polyimides, we discuss the optical absorption and PL spectra of diamines used for synthesizing polyimides. As shown in Figure 6, CzDA in acetone exhibited UV–visible absorption peaks at the wavelength of 327 and 338 nm which can be attributed to the carbazole moiety.\textsuperscript{26} CzHBPDA showed absorption peaks at around 307–339 nm which can be attributed to the carbazole moiety but is mixed with \(\pi-\pi^*\) transition of diphenylamine.\textsuperscript{27} CzTPDA showed similar two absorption maxima at the wavelength of 323 and 345 nm, which can be assigned to the carbazole group, in the presence of another broad peak at 368 nm that can be ascribed to the conjugation made between aromatic rings and carbazole group.\textsuperscript{28} However, because these data were obtained using a sample solution in acetone, we cannot see clear optical absorption characteristics of diamines in the wavelength below \(\sim 300\) nm owing to the overlapping of acetone absorption. Hence, we dropped the solutions on a quartz substrate and then dry off the solvent at room temperature, leading to solid powder-like films. As shown in Figure 7, three diamines show quite a similar absorption shape in this short wavelength range, which can be attributed to the absorption of the smallest unit “phenyl group” in either diphenyl part.
(CzTPDA and CzHBPDA) or carbazole part (CzDA). This will be discussed again below (Fig. 8) for the absorption spectra of corresponding polyimides. In particular, the PL spectra of these diamines showed an interesting trend that is related to the conjugation effect. CzTPDA showed the longest PL wavelength due to the extended conjugation length, whereas the shortest PL wavelength was observed from CzHBPDA owing to the alkyl space group to disconnect the conjugation between carbazole and diphenylamine moieties.

Figure 6. Optical absorption (a) and photoluminescence (b) spectra of diamines (CzDA, CzTPDA, and CzHBPDA) dissolved in acetone.

Figure 7. Optical absorption spectra of diamines (CzDA, CzTPDA, and CzHBPDA) coated on a quartz substrate by dropping solutions followed by drying at room temperature.

As shown in Figure 8, all polyimides show a broad absorption with two characteristic peaks. The huge peak below 270 nm can be assigned to the complex structure of main chain units that consist of diamines (see Fig. 7) and dianhydrides, whereas the smaller peak in the wavelength of 270–400 nm can be attributed to the carbazole chromophore as discussed in Figure 6.29 This result indicates that the present soluble PIs are optically transparent in the wide range of visible light (>400 nm). The films showed a yellowish tint which was minimum for aliphatic chain...
containing PIs, (PI$_2$ and PI$_6$) and the incorporation of fluorine decreased the yellowish color further. [see the optical transmission spectra of PIs in the supporting information (Fig. S8)]. However, all PIs synthesized showed almost undetectable PL (excitation at 350 nm). The disappearance of PL in PIs compared with corresponding diamines can be attributed to the nonradiative energy transfer process by the formation of intermolecular or intramolecular charge transfer complexes as usually observed in aromatic polyimides.22,30–32

CONCLUSIONS

We have synthesized carbazole based novel diamines and corresponding PIs that were soluble in organic solvents. The number average molecular weight of PIs was mostly higher than 4 x 10$^4$ g/mol with quite a narrow distribution. All PIs showed high mechanical strength (>1.5 GPa) and extremely high glass transition temperature (>260 °C). Interestingly, most of PIs exhibited low dielectric constant below 3, while the PI films were optically transparent in the visible range (>~400 nm). However, almost no PL was observed for all PI films due to the intrinsic charge transfer complex characteristics of typical polyimides. We expect that the present soluble and optically transparent PIs could be used as a hole-transporting layer for OLEDs.

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REFERENCES AND NOTES