Macromolecules

Transparent Aromatic Polyimides Derived from Thiophenyl-Substituted Benzidines with High Refractive Index and Small Birefringence

Pradip Kumar Tapaswi,[†] Myeon-Cheon Choi,[†] Keuk-Min Jeong,[†] Shinji Ando,[‡] and Chang-Sik Ha^{*,†}

[†]Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea [‡]Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-Ku, Tokyo 152-8552, Japan

Supporting Information

ABSTRACT: 2,2'-Bis(thiophenyl)benzidine (BTPB) and 2,2'-bis(4-chlorothiophenyl)benzidine (BCTPB) were synthesized via a benzidine rearrangement reaction of the corresponding hydrazobenzene derivatives obtained after the reduction of (3-nitrophenyl)(phenyl)sulfane and (4-chlorophenyl)(3-nitrophenyl)sulfane, respectively. Transparent polyimides (PIs) with high refractive indices and small birefringences as well as good thermomechanical stabilities were synthesized by the conventional two-step thermal polycondensation of BTPB and BCTPB with five different dianhydrides in *N*-methyl-2-pyrrolidone. 3,3',4,4'-Biphenylte-tracarboxylic dianhydride (BPDA)/BCTPB PI, a fully aromatic and non-fluorinated PI, with a highly distorted noncoplanar conformation of the main chain was transparent and colorless



with a transmittance of ~83% and >88% at 450 nm and in the visible region, respectively. In addition, all six non-fluorinated sulfur-containing aromatic PIs exhibited high average refractive indices (1.7112-1.7339), and small birefringences (0.0007-0.0022) at 633 nm, because of the high atomic polarizability of sulfur and the rigid bulky molecular structure of BTPB and BCTPB. The more effective steric effect caused by bulky 4-chlorothiophenyl in BCTPB improved the optical transparency but decreased the average refractive indices of BCTPB-based PIs compared to BTPB-based PIs.

INTRODUCTION

A high refractive index (*n*), small birefringence (Δn) , and high optical transparency along with good thermal-mechanical stability are the basic requirements of a polymer that can be used in various optical devices, such as organic light-emitting diodes (OLEDs),¹ microlens components for charge coupled devices (CCD), and high-performance CMOS image sensors (CISs), etc. $^{2-4}$ According to the Lorentz–Lorenz equation, the refractive index of optical polymers can be enhanced considerably by introducing a substituent with high molar refraction, low molar volume, high aromatic contents, or high density.⁵ Therefore, a range of functional moieties with high molar refractions, such as aromatic rings, heavy halogen (Cl, Br, and I) atoms, sulfur atoms, and metal atoms, have been introduced in polymers to enhance the refractive indices.⁶⁻¹¹ Among the various substituents, sulfur with a high atomic refraction is one of the most effective candidates. Many sulfurcontaining polymers, including poly(methacrylates),¹² episulfide,¹³ polyurethanes,¹⁴ and polyimides, have been used for advanced integrated optical applications.^{15–17} Aromatic polyimides (PIs) are among the most successful polymers used in advanced optical fabrications owing to their good thermal and

physical properties, high inherent refractive index, and excellent mechanical properties. On the other hand, the large birefringence and deep reddish-yellow coloration of conventional aromatic PIs need to be addressed first before they can be suitable for optical applications. The intra- and intermolecular charge-transfer (CT) interactions between the electrondonating diamine and electron-accepting aromatic dianhydride are considered the main reason behind the deep color of conventional aromatic PIs. A range of structural modifications, such as the introduction of bulky substituents with methyl groups at the ortho position of diamine, fluorine-containing substituents, alicyclic moieties, and noncoplanar or unsymmetrical structures in the polymer main chains, have been made to improve the transparency of conventional PIs.¹⁸ In many cases, however, these modifications result in a decrease in refractive index.¹⁹ Recently, the Ueda group developed a series of sulfur-containing aromatic PIs suitable for a range of optical applications.^{8-10,20-25} These PIs showed very high refractive

Received: March 1, 2015 **Revised:** April 30, 2015 Scheme 1. Synthetic Scheme of Benzidine Monomers (BTPB and BCTPB)



indices in the range 1.74–1.77 and a low birefringence of less than 0.0093; however, most of the corresponding 10–20 μ m thick PI films were not totally colorless, exhibiting pale to bright yellowish colors. This might limit their optical applications; hence, the quest for colorless and high refractive aromatic PIs still continues.

A previous study reported that noncoplanar 2,2',3,3'tetrachlorinated benzidine reacts with aromatic and alicyclic dianhydrides to form colorless PIs with a high refractive index, small birefringence, and good thermal-mechanical stability. This result proved three things: first, the high atomic polarizability of chlorine atoms can increase the refractive index of the polymer; second, even the presence of bulky chlorine atoms at the 2,2',3,3' position of benzidine, the rigidrod structure of the polymer main chain remains intact; and third, the optical transparency of the synthesized PIs can be improved by the judicious introduction of bulky substituents at the 2,2'-position of benzidine. Therefore, the introduction of both sulfur and halogen atoms to aromatic diamine or dianhydride monomers may lead to the synthesis of high refractive PIs. On the other hand, to weaken the color of the PI, it is essential to introduce some bulky substituents in the diamine or dianhydride monomers to minimize the intermolecular CT interaction between the PI chains. Care needs to be taken regarding the size of the bulky substituent because the introduction of a very bulky substituent will create a large free volume in the polyimide backbone; hence, packing will not be dense enough to induce a high refractive index in the PIs. This paper reports the synthesis of two new diamine monomers, 2,2'-bis(thiophenyl)benzidine (BTPB) and 2,2'-bis(4chlorothiophenyl)benzidine (BCTPB), with a bulky thiophenyl/4-chlorothiophenyl side group at the 2,2'-position of the benzidine system. The synthesis and properties of ten new PIs of BTPB and BCTPB with five different dianhydrides are also discussed. The 2,2'-disubstitution (thiophenyl/4-chlorothiophenyl) in BTPB and in BCTPB forced the phenyl rings of the biphenyl system into a non-coplanar rod-like twisted geometry, which is expected to hinder the close packing of the BTPB/BCTPB-based PIs chains and reduce both the intra- and intermolecular CT interactions. The CT interactions are considered the main reason behind the deep color of conventional aromatic PIs. Therefore, a decrease in CT interactions is expected to improve the optical transparency of the synthesized PI films. Again, the presence of sulfur and

chlorine atoms in BTPB and in BCTPB is expected to increase the refractive indices of BTPB- and BCTPB-based PIs.

EXPERIMENTAL SECTION

Materials and Characterization. Thiophenol (97%), 4-chlorothiophenol (97%), 1-iodo-3-nitrobenzene (99%), and cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA, ≥94%) were purchased from Aldrich and used as received. Pyromellitic dianhydride (PMDA, 97%), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, Aldrich, 97%), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich, 99%), and 3,3',4,4'-benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA, Aldrich, 96%) were dried at 120 °C for 1 day under vacuum prior to use. N-Methyl-2-pyrrolidone (NMP), which was obtained from the Aldrich Chemical Co., was dried with calcium hydride (CaH₂) and then distilled under reduced pressure. All other chemicals used in this study were supplied by Aldrich and used as received. The ${}^1\!\mathrm{H}$ and ${}^{13}\mathrm{C}$ NMR spectra were recorded on a Varian Unity Plus-400 NMR spectrometer. Viscosity measurements were performed using Cannon-Ubbelohde No. 100 and 200 viscometers at 30 °C after dissolving the PAAs in NMP. Elemental analysis was conducted with an elemental analyzer (EA, Vario EL, Elemental Analysen Systeme). The attenuated total reflection-Fourier transform infrared (ATR-FTIR, JASCO FT/IR-4100) spectra were obtained with 32 scans per spectrum at a 2 cm^{-1} resolution. A robust single reflection accessory (JASCO ATR Pr0450-S) with a germanium IRE (n = 4.0, incidence angle = 45°) was used for the ATR measurements. To examine the thermal stability of the PIs, thermogravimetric analysis (TGA) was performed under nitrogen using a TGA Q50 Q Series thermal analyzer at a heating rate of 10 °C/min from room temperature to 800 °C. Measurements of the glass transition temperature (T_g) were taken using a DSC Q 100 TA Instruments at a heating rate of 10 °C/min under a nitrogen atmosphere. The transparency of the PI films was measured from the ultraviolet-visible spectra recorded from one accumulation on a OPTIZEN 3220UV spectrometer optimized with a spectral width of 200-800 nm, a resolution of 0.5 nm, and a scanning rate of 200 nm/min. The thickness of each film was $\sim 20 \ \mu$ m. The excitation and fluorescentemission spectra of the PI films were characterized using a Hitachi F-4500 fluorescence spectrophotometer with a resolution of 0.2 nm and a scanning rate of 240 nm min⁻¹. The wide-angle X-ray diffraction (WXAD) measurements of the pulverized samples were conducted at room temperature in the reflection mode using a Rigaku diffractometer (Model Rigaku Miniflex). The Cu K α radiation (λ = 1.54 Å) source was operated at 50 kV and 40 mA. The 2θ scan data were collected at 0.01° intervals over the range $1.5-50^{\circ}$, at a scan rate of $0.58(2\theta)/\text{min}$. Dynamic mechanical analysis (DMA) was conducted using a DMA2980 (TA Instron) instrument. The storage modulus (E) and tan δ were determined as the sample was subjected to temperature

scan mode at a programmed heating rate of 10 °C/min and a frequency of 1 Hz. The coefficient of thermal expansion (CTE) was measured using a TA Instruments thermal mechanical analyzer (TMA) with a fixed load of 0.05 N and a heating rate of 10 °C min⁻¹. The in-plane ($n_{\rm TE}$) and out-of-plane ($n_{\rm TM}$) refractive indices of the PI films were measured using a prism coupler (Metricon, PC-2000) at wavelengths of 404.0, 532.0, 632.8, and 829.0 nm at room temperature. The mean refractive indices ($n_{\rm av}$) were calculated using the equation $n_{\rm av}^2 = (2n_{\rm TE}^2 + n_{\rm TM}^2)/3$. The in-plane/out-of-plane birefringence (Δn) was calculated using the equation $\Delta n = n_{\rm TE} - n_{\rm TM}$. The thicknesses of the PI films were measured using a sensing-pin type surface profilometer (DEKTAK-III). The single crystal X-ray diffraction data were collected on a CCD area detector, Bruker SMART diffractometer ($\lambda = 0.71073$ Å). The structures were solved using the SHELXS program²⁷ and were refined by full-matrix least-squares on F 2 using the SHELXL program.²⁸

Synthesis. Benzidine derivatives containing thiophenyl and 4chlorothiophenyl side groups were synthesized through the benzidine rearrangement reactions of the corresponding hydrazobenzenes obtained after the reduction of (3-nitrophenyl)(phenyl)sulfane and (4-chlorophenyl)(3-nitrophenyl)sulfane, respectively, as shown in Scheme 1.

(3-Nitrophenyl)(phenyl)sulfane (1a). Thiophenol (25 g, 227 mmol), 1-iodo-3-nitrobenzene (56.6 g, 227 mmol), K₂CO₃ (62.6 g, 454 mmol), CuI (8.64 g, 45.4 mmol), and PEG-400 (5 mL) were added to approximately 200 mL of dry N,N-dimethylformamide (DMF) placed in a 500 mL round-bottomed flask in a N₂ atmosphere. The reaction mixture was heated at 120 °C for 12 h, cooled to room temperature, and filtered to give a wine red colored solution. The filtrate was concentrated using a rotary evaporator and then poured slowly into 400 mL of ice cooled H₂O and extracted with dichloromethane (DCM) $(3 \times 100 \text{ mL})$ to give a dark brown liquid after vacuum evaporation. This liquid was used directly for the next step without further purification. Yield: 49.9 g (95%); dark brown liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.02-7.97 (m, 3H, Ph-H), 7.50-7.45 (m, 3H, Ph-H), 7.42-7.37 (m, 3H, Ph-H) (Figure S1). $^{13}\mathrm{C}$ NMR (100 MHz, CDCl_3): δ 148.7, 143.4, 140.6, 134.2, 133.4, 129.9, 129.7, 128.9, 127.5, 123.1, 120.9 (Figure S2). Elemental analysis: Calculated for C12HoNO2S: C, 62.32; H, 3.92; N, 6.06. Found: C, 62.09; H, 4.03; N, 6.18. FTIR (neat, cm⁻¹): 3071, 1526, 1348, 732, and 691.

2,2'-Bis(thiophenyl)benzidine (BTPB). 46.3 g (200 mmol) of (3nitrophenyl)(phenyl)sulfane (1a) in 300 mL of EtOH was poured into 40 mL of a sodium hydroxide solution containing 40 g (1000 mmol) of sodium hydroxide. 36 g (550 mmol) of zinc powder was added slowly to the mixture over 0.5 h with stirring (to control the highly exothermic reaction), followed by heating under reflux for 1 day. The hot reaction mixture was filtered then washed with EtOH. The filtrate was poured into 500 mL of cold H_2O and extracted with DCM (3 × 100 mL) to give an orange liquid after vacuum evaporation by rotary evaporator. The diazene product (2a) was converted to the diazane product (3a) by further reduction with zinc dust and NH₄Cl. 5.24 g (80 mmol) of zinc dust was added slowly with stirring to the assynthesized diazene product (2a) dissolved in 150 mL of acetone under a nitrogen atmosphere followed by the slow addition of 80 mL of a saturated NH₄Cl solution. The reaction mixture was then stirred vigorously for 0.5 h at room temperature so that the reaction mixture becomes almost colorless (light yellow). The reaction mixture was made alkaline with a 10% aqueous ammonia solution and extracted with DCM (3×100 mL), giving a light yellow semisolid after solvent evaporation. Yield: 30.6 g (77%); light yellow semisolid. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (dd, J = 6.8 and 1.6 Hz, 4H, Ph-H), 7.31-7.24 (m, 6H, Ph-H), 7.10 (t, J = 8.0 Hz, 2H, Ph-H), 6.77-6.72 (m, 4H, Ph-H), 6.64 (dd, J = 8.0 and 1.6 Hz, 2H, Ph-H), 5.55 (s, 2H, -NH) (Figure S3). FTIR (KBr, cm⁻¹): 3338, 1594, 1478, 746, and 684.

The benzidine monomer, 2,2'-bis(thiophenyl)benzidine (BTPB), was obtained via a benzidine rearrangement reaction^{29,30} of the diazane (hydrazobenzene) product (**3a**). 30 g (75 mmol) of **3a** was dissolved in 350 mL of dry EtOH under a N_2 atmosphere. The mixture

was cooled to 0 °C in an ice bath. Subsequently, 150 mL of an EtOH-HCl (1:1) solution was slowly added to the diazane solution over an approximately 2 h period. Once the addition was completed, the ice bath was removed, and the mixture solution was stirred at room temperature for 3 h to allow a white solid to precipitate. The precipitated salt was filtered, washed several times with EtOH, and dissolved in 200 mL of water. The aqueous solution was made alkaline by a 10% aqueous sodium hydroxide solution, and the organic content was extracted with DCM (3 \times 75 mL). The DCM extract was evaporated to dryness to give a white solid. The benzidine monomer was purified further by recrystallization from a 50% EtOAc solution in hexane. The product yield was 18.1 g (60.0%); off-white crystalline solid; mp 152-154 °C (EtOAc:hexane = 1:1). ¹H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, J = 8.0 and 1.6 Hz, 4H, Ph-H), 7.25-7.19 (m, 6H, Ph-H), 6.98 (d, J = 8.0 Hz, 2H, Ph-H), 6.52 (dd, J = 8.4 and 2.4 Hz, 2H, Ph–H), 6.46 (d, J = 2.4 Hz, 2H, Ph–H), 3.56 (s, 4H, NH₂) (Figure S4). ¹³C NMR (100 MHz, CDCl₃): δ 146.3, 137.6, 135.8, 132.2, 131.9, 131.4, 129.0, 127.0, 116.5, 113.4 (Figure S5). Elemental analysis: Calculated for C24H20N2S2: C, 71.96; H, 5.03; N, 6.99. Found: C, 71.79; H, 5.13; N, 7.05. FTIR (KBr, cm⁻¹): 3454, 3420, 3331, 1621, 1594, 1464, 1272, 814, and 732.

(4-Chlorophenyl)(3-nitrophenyl)sulfane (1b). 4-Chlorothiophenol (21.69 g, 150 mmol), 1-iodo-3-nitrobenzene (37.35 g, 150 mmol), K₂CO₃ (41.4 g, 300 mmol), CuI (4.29 g, 22.5 mmol), and PEG-400 (5 mL) were added to approximately 200 mL of dry DMF taken in a 500 mL round-bottomed flask in a N2 atmosphere. The reaction mixture was heated at 120 °C for 12 h. The contents were then cooled to room temperature and filtered to give a wine red colored solution. The filtrate was concentrated by a rotary evaporator and then poured slowly into 400 mL of ice cooled H₂O to produce a white precipitate. The precipitate was collected after filtration and washed repeatedly with cold H₂O. The off-white solid was dried under vacuum at 40 °C for 12 h. The product was pure enough to use directly in the next step. Yield: 36.7 g (92%); off-white solid; mp 63-64 °C. ¹H NMR (400 MHz, DMSO- d_6): δ 8.11 (bd, J = 8.0 Hz, 1H, Ph-H), 7.98 (t, J = 2.0 Hz, 1H, Ph-H), 7.70 (d, J = 8.0 Hz, 1H, Ph-H), 7.65 (t, J = 8.0 Hz, 1H, Ph-H), 7.55-7.50 (m, 4H, Ph-H) (Figure S6). ¹³C NMR (100 MHz, CDCl₃): δ 148.7, 139.7, 135.2, 134.5, 134.4, 130.9, 130.0, 129.9, 123.4, 121.3 (Figure S7). Elemental analysis: Calculated for C12H8ClNO2S: C, 54.24; H, 3.03; N, 5.27. Found: C, 54.12; H, 3.10; N, 5.32. FTIR (KBr, cm⁻¹): 1518, 1347, 1087, 821, and 725.

2,2'-Bis(4-chlorothiophenyl)benzidine (BCTPB). 26.5 g (100 mmol) of (4-chlorophenyl)(3-nitrophenyl)sulfane (1b) dispersed in 200 mL of EtOH was poured into 20 mL of a NaOH solution containing 20 g (500 mmol) of sodium hydroxide. Zinc powder (18 g, 275 mmol) was added slowly to the mixture with stirring, followed by refluxing for 1 day. The hot reaction mixture was filtered followed by washing with EtOH. The filtrate was poured into 500 mL of cold H₂O with stirring, and the orange-yellow precipitate formed was filtered. The residue was washed several times with H₂O and dried under vacuum at 40 $^\circ C$ for 24 h. Yield 19.6 g (84%). The diazene product (2b) was converted to the diazane product (3b) by further reduction with zinc dust and NH₄Cl. 2.62 g (40 mmol) of zinc dust was added slowly with stirring to 18.7 g (40 mmol) of the diazene product $(\mathbf{2b})$ dissolved in 100 mL of acetone under a nitrogen atmosphere, followed by the slow addition of 40 mL of saturated NH₄Cl solution. The reaction mixture was then stirred vigorously for 1 h at room temperature until the reaction mixture became almost colorless (light yellow). The reaction mixture was made alkaline with a 10% aqueous ammonia solution and extracted with DCM, giving a light yellow solid after solvent evaporation. Yield: 17.7 g (94%); light yellow solid. ¹H NMR (400 MHz, DMSO- d_6): δ 8.31 (s, 2H, -NH), 7.81 (d, J = 7.5 Hz, 4H, Ph-H), 7.76 (br d, J = 3.0 Hz, 2H, Ph-H), 7.62 (t, J = 6.0 Hz, 2H, Ph-H), 7.48-7.41 (m, 8H, Ph-H) (Figure S8). FTIR (KBr, cm⁻¹): 3345, 1595, 1472, and 1089.

The benzidine monomer, 2,2'-bis(4-chlorothiophenyl)benzidine (BCTPB), like BTPB was obtained via a benzidine rearrangement reaction^{29,30} of the diazane product (**3b**). The diazane compound of 16.9 g (36 mmol) was dissolved in 200 mL of dry EtOH under a N₂ atmosphere. The mixture was cooled to 0 °C using an ice bath, and 80

Article



Figure 1. ORTEP diagram of a single crystal of BCTPB (CCDC 1047009).





mL of an EtOH-HCl (1:1) solution was added slowly to the diazane solution for approximately 2 h. Once the addition was complete, the ice bath was removed, and the mixture solution was stirred at room temperature for 6 h to allow a white solid to precipitate. The precipitated salt was filtered, washed several times with EtOH, and dissolved in 100 mL of water. This aqueous solution was made alkaline by adding a 10% sodium hydroxide solution, and the organic content was extracted with DCM. The DCM extract was evaporated to dryness to give a white solid. The benzidine monomer was purified further by recrystallization from a 50% EtOAc solution in hexane. The product yield was 12.2 g (72.0%); white crystalline solid; mp 168-169 °C (EtOAc:hexane = 1:1). ¹H NMR (400 MHz, DMSO- d_6): δ 7.20 (bs, 8H, Ph-H), 6.98 (d, J = 6.4 Hz, 2H, Ph-H), 6.55 (dd, J = 6.4 and 2.0 Hz, 2H, Ph-H), 6.48 (d, J = 2.0 Hz, 2H, Ph-H), 3.63 (s, 4H, NH₂) (Figure S9). $^{13}{\rm C}$ NMR (100 MHz, DMSO- d_6): δ 146.6, 136.7, 134.5, 133.1, 133.0, 132.9, 132.1, 131.9, 131.6, 129.2, 129.1, 129.0, 116.8, 116.7, 113.8, and 113.7 (Figure S10). Elemental analysis: Calculated for C24H18Cl2N2S2: C, 61.40; H, 3.86; N, 5.97. Found: C, 61.27; H, 3.91; N, 6.05. FTIR (KBr, cm⁻¹): 3327, 3078, 3020, 1600, 1470, 1277, 1225, 1089, 1011, and 824. A single crystal of BCTPB was obtained from a mixed solvent solution of BCTPB in EtOH, EtOAc, and DCM by the slow evaporation of solvents at room temperature for several

days. Crystal data: $0.22 \times 0.13 \times 0.07 \text{ mm}$, $C_{24}H_{18}Cl_2N_2S_2$, light yellow, $f_w = 469.42$; orthorhombic, P2(1)2(1)2(1); a = 9.3298(4) Å, b = 12.8039(6) Å, c = 18.0035(8) Å, $\alpha = \beta = \gamma = 90^{\circ}$; V = 2150.66(17) Å³, Z = 4; T = 200(2) K, R indices $[I > 2\sigma(I)]$: $R_1 = 0.0510$, $wR_2 = 0.0947$; R indices (all data): $R_1 = 0.0918$, $wR_2 = 0.1583$; GOF = 1.136. The torsion angle of the two central nitrogen-connected phenyl rings (plane 1: C7–C12; plane 2: C6–C5) was 55.07°, whereas the torsion angle of two C–S bonds (plane 3: C1–S1; plane 4: C12–S2) was 130.24° (Figure 1). The torsion angle between the 1,4-disubstituted phenyl ring (plane 5: C24–C19 and C13–C14) was 49.03°.

RESULTS AND DISCUSSION

Monomer Synthesis. The diamine monomers, namely, BTPB and BCTPB, were synthesized via a benzidine rearrangement reaction of the hydrazo (diazane) compounds (3a/3b) obtained after the reduction of *meta-substituted* nitrobenzene derivatives (1a/1b), as illustrated in Scheme 1. The *meta-substituted* nitrobenzene derivatives namely, (3nitrophenyl)(phenyl)sulfane (1a) and (4-chlorophenyl)(3nitrophenyl)sulfane (1b), were synthesized via the CuIcatalyzed cross-coupling reaction of 1-iodo-3-nitrobenzene

D



Figure 2. Molecular orbital (MO) diagrams of the representative polyimides.

with thiophenol and 4-chlorothiophenol, respectively, using K_2CO_3 as a base in dry DMF. Careful optimization showed that better yields could be achieved in the presence of PEG 400, which might act as both a ligand and mediator. Both BTPB and BCTPB were synthesized from the meta-substituted nitrobenzene derivatives (1a/1b) via a three-step reaction, as shown in Scheme 1. In the first step, 1a and 1b were reduced to the corresponding diazene compounds (2a and 2b) by reactions with sodium hydroxide and zinc powder in EtOH. The diazene compounds (2a and 2b) were then converted to the corresponding hydrazo compounds (3a and 3b) by zinc and aqueous ammonium chloride in acetone in excellent yield. Finally, BTPB and BCTPB were obtained by the benzidine rearrangement reaction of hydrazo compounds (3a and 3b) by EtOH-HCl (1:1). To ensure a higher yield of BTPB and BCTPB, it was necessary to carry out the benzidine rearrangement reactions immediately after the synthesis of the relatively less air stable hydrazo compounds (3a and 3b). In the benzidine rearrangement, various isomers were formed, but not all could be isolated in high purity. The reactions were optimized to obtain a higher yield of the benzidine derivatives (BTPB/BCTPB) only. Both BTPB and BCTPB were purified by repeated crystallization from a 50% EtOAc solution in hexane.

Polyimides Synthesis and Characterization. Ten new PIs were prepared by the thermal imidization of their corresponding precursors, poly(amic acid)s (PAAs). The PAAs were synthesized by the addition polymerization of equimolar amounts of either BTPB or BCTPB and five different dianhydrides (6FDA, CBDA, BPDA, BTDA, and PMDA) in NMP (Scheme 2). Each dianhydride was added to a diamine solution, dissolved without heating, and stirred at room temperature for 2 days. For all the precursor solutions prepared, the solid contents were 30 wt %. All procedures were carried out in a glovebox purged with nitrogen. The NMP solutions of the PAA precursors were spin-coated onto glass

conditions, where they were dried at 80 °C for 8 h, 150 °C for 2 h, 200 °C for 2 h, 250 °C for 1 h, and 300 °C for 1 h under flowing nitrogen. After curing, the glass plate was immersed in water to facilitate the removal of the flexible, freestanding PI films. For poly(amic acid)s (PAAs), intrinsic viscosities at 30 $^{\circ}$ C were in the range of 0.92–1.26 dL/g (Table S1). All the PAA solutions (except CBDA/BTPB and CBDA/ BCTPB) were highly viscous, indicating that their molecular weights were relatively high. This shows that both BTPB and BCTPB had high reactivity, even in the presence of bulky thiophenyl/4-chlorothiophenyl substituents at the 2,2'-position. Normally, diamines with bulky side groups exhibit lower reactivity in the polycondensation reaction. The observed higher reactivity of BTPB/BCTPB might be due to electron donation from the sulfur atom of the thiophenyl side group. The relatively lower viscosity of CBDA-based PAAs might be due to the lower reactivity of the alicyclic CBDA. All the PI films except for CBDA/BTPB and CBDA/BCTPB were transparent and free-standing. CBDA/BTPB and CBDA/ BCTPB were quite brittle. PI films derived from 6FDA (6FDA/BTPB and 6FDA/BCTPB) were soluble in both polar and nonpolar organic solvents such as chloroform (CHCl₃), dichloromethane (CH₂Cl₂), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and NMP, but all other PI films were completely insoluble in most of the common organic solvents (Table S1).

plates and imidized thermally under programmed curing

FTIR and NMR Characterization of the PIs. The chemical structures of the synthesized PIs were confirmed by ATR FTIR and NMR spectroscopy. Figure S11 presents the ATR FTIR spectra of the synthesized PIs. The absence of absorption peaks around 1700 cm⁻¹ corresponding to the amide carbonyl stretching of PAAs indicates that the resulting PI films had been imidized completely. Typical absorption bands of aromatic PIs appeared in the range of 1782–1774 cm⁻¹ (C=O, asymmetric), 1721–1716 cm⁻¹ (C=O,

Macromolecules

symmetric), 1362–1354 cm⁻¹ (C–N), and 1090–1084 (C– $S_{aromatic}$). Figure S12 shows the ¹H NMR spectrum of 6FDA/BCTPB in CDCl₃. The most downfield protons were assigned to 6FDA (8.04, 7.94, and 7.86 ppm), whereas the remaining aromatic protons were attributed to BCTPB (7.38 and 7.24 ppm). In the ¹³C NMR spectrum of 6FDA/BCTPB (Figure S13), the presence of a very sharp imide carbon peak at 165 ppm and the absence of carboxylic peaks at approximately 200 ppm confirmed the complete imidization.

Molecular Structures. Figure S14 shows the threedimensional molecular structures of the model compounds for the synthesized PIs. The geometries were optimized by density functional theory (DFT) calculations using a relatively large basis-set function. $^{5,31-35}$ Figure 2 provides more details of the quantum-chemical calculations, molecular orbital (MO) diagrams, and calculated electronic transitions of models for the four PIs at the optimized S_0 geometry (Table S2). Irrespective of the nature of the dianhydrides, the calculated dihedral angles between the two benzene rings in the diamine moieties (BTPB and BCTPB) of the synthesized PIs were $\approx 80^{\circ}$ (79°-85), which are significantly larger than the dihedral angles observed in the unsubstituted benzidine/biphenyl-tetracarboxylic acid dianhydride-based PIs ($\approx 40^{\circ}$).²⁶ Consequently, the steric hindrance caused by the bulky thiophenyl or 4-chlorothiophenyl substituents attached to the 2,2'-positions of BPDA or BCTPB forces the benzene rings of the biphenyl system to be almost perpendicular, thereby causing significant conformational distortion of the PI backbones. Interestingly, X-ray diffraction of a single crystal of BCTPB revealed a dihedral or torsional angle of 51° between the two benzene rings of the biphenyl system of BCTPB. Therefore, the significantly larger dihedral angles in the BCTPB-based PIs originate mainly from the molecular geometries of the polyimide chains. The calculated dihedral angles obtained in the BTPB and BCTPBbased PIs were similar to the dihedral angles observed in the 2,2'-dichlorobenzidine-based PIs.²⁶ This might be due to the similar atomic size of the chlorine (99 pm) and sulfur (102 pm) atoms.

Crystallinity. Figure S15 shows the wide-angle X-ray diffraction (XRD) patterns of four representative aromatic PIs (BPDA/BTPB, BPDA/BCTPB, PMDA/BTPB, and PMDA/ BCTPB), where it can be seen that the PIs are completely amorphous. The polymer backbones with bulky thiophenyl/4-chlorothiophenyl side groups at the 2,2'-position of the noncoplanar biphenyl structures of BTPB/BCTPB would increase the disorder of the polymer chains, weaken the interchain interactions, and reduce the chain packaging efficiency to hinder polymer crystallization.

Optical Properties. The optical transparency of the PI films in the visible region was considered to be a crucial factor for a range of optical applications. Generally, aromatic PI films exhibit intense colors, ranging from light yellow to deep brown, depending on their structures, due to the formation of intra- or intermolecular charge-transfer complexes (CTC).³⁶ Figure 3 presents the experimental UV–vis absorption spectra of the PI films (~20 μ m thick). PI films of 6FDA/BTPB, 6FDA/BCTPB, CBDA/BTPB, CBDA/BCTPB, and BPDA/BCTPB were transparent and colorless, whereas the PI films of BPDA/BTPB were transparent with a slightly yellowish tint. All the PI films derived from PMDA and BTDA were deep yellow in color. Table 1 lists the absorption edges (λ_E) estimated from the point where the absorption curve intersects a bisected line drawn through the intersection of the extrapolations of the two

Article



Figure 3. UV-vis absorption spectra of (a) BTPB-based polyimides and (b) BCTPB-based PIs.

slopes. The absorption edges ($\lambda_{\rm E}$) of the films were in the range of 321–453 nm. The absorption edges ($\lambda_{\rm E}$) of all the PI films derived from CBDA, 6FDA, and BPDA were below 400 nm, which explains why these films are mostly colorless. The absorption edges (λ_E) of BPDA/BTPB and BPDA/BCTPB were 387 and 379 nm, respectively, which are shifted to significantly shorter wavelengths compared to those of conventional aromatic PIs ($\lambda_{\rm E}$ of PI derived from BPDA and *p*-phenylenediamine was observed at \sim 413 nm).²⁶ The steric hindrance caused by bulky thiophenyl/4-chlorothiophenyl side groups of BTPB and BCTPB distorts the main chain conformations of the PIs significantly. This is evident from the large dihedral angles of 84°-85° between two benzidine phenyl groups in BTPB- and BCTPB-based PIs (Figure S14), which inhibits the conjugation of imide-phenyl and phenylphenyl bonds in the PI chains and weakens the intra- or intermolecular CT interactions. Therefore, the reduced CT interactions exhibited by the BTPB- and BCTPB-based PIs shifted their absorption edges to shorter wavelengths. In addition, the absorption edges of the BCTPB-based PI films shifted toward shorter wavelengths compared to the BTPBbased PIs containing PMDA and BPDA dianhydride. On the other hand, the dihedral angles between the phenyl rings of the biphenyl system did not change much in the BTPB- and BCTPB-based PIs. The introduction of electronegative chlorines to the skeletal structure of BCTPB reduces the

Table 1. Absorption Edges ($\lambda_{\rm E}$), Optical Transmittance, and Excitation and Emission Peaks ($\lambda_{\rm ex}$, $\lambda_{\rm em}$) in the Fluorescence Spectra of the Synthesized PIs with Calculated Molecular Orbital Energies (ε) of HOMO and LUMO and Energy Band Gaps ($\delta\varepsilon$) for Monomeric Models of the PIs

polyimide	$\lambda_{\rm E}~({\rm nm})$	%T at 400 nm	%T at 450 nm	$\lambda_{\mathrm{ex}} (\mathrm{nm})$	$\lambda_{\rm em}~({\rm nm})$	$\varepsilon_{ m HOMO}~(m eV)$	$\varepsilon_{ m LUMO}~(m eV)$	$\Delta \varepsilon$ (eV)
PMDA/BTPB	431	7	55	452	576	-7.42	-2.31	5.10
PMDA/BCTPB	425	14	61	451	574	-7.64	-2.45	5.19
BPDA/BTPB	387	50	81	391	503	-7.19	-1.79	5.40
BPDA/BCTPB	379	66	83	384	482	-7.38	-1.85	5.53
CBDA/BTPB	322	76	81	339	413	-7.48	-0.31	7.16
CBDA/BCTPB	321	83	85	335	402	-7.64	-0.42	7.22
6FDA/BTPB	366	75	85			-7.19	-1.72	5.46
6FDA/BCTPB	363	76	85			-7.37	-1.74	5.63
BTDA/BTPB	453		28			-7.36	-2.13	5.23
BTDA/BCTPB	450		28			-7.47	-2.14	5.33

highest occupied molecular orbital (HOMO) energy level of BCTPB. Therefore, the energy band gap, the difference between the MO energies of HOMO and LUMO, for the BCTPB-based PIs are slightly larger than the BTPB-based PIs derived from the same dianhydride (Table 1), which shifts the absorption edges of the BCTPB-based PIs toward shorter wavelengths. In addition, the more bulky and spatially extended 4-chlorothiophenyl side groups in BCTPB increase the free volumes further compared to the thiophenyl group in BTPB. Consequently, the intermolecular CT interactions are weakened in the BCTPB-based PIs, which can induce hypsochromic shifts of the absorption edges of the BCTPB-based PIs.

Figure 4 presents the calculated absorption spectra of the PIs using the TD-DFT method. The spectra of the PIs containing



Figure 4. Calculated UV-vis absorption spectra of the representative PIs.

6FDA and BTDA could not be calculated due to the very large number of constituent atoms. The optical absorption patterns of CBDA/BTPB and CBDA/BCTPB are well reproduced, and the hypsochromic shifts observed by BPDA/BCTPB and PMDA/BCTPB compared to that of BPDA/BTPB and PMDA/BTPB were partly reproduced, but the experimental absorption edges for the latter PIs were shifted to significantly longer wavelengths. The contributions from intermolecular CT interactions were not included because the TD-DFT calculations were performed for single model molecules. Therefore, the mismatch between the calculated and experimental $λ_E$ values was caused mainly by an underestimation of the CT interactions. Figure 5 shows the optical transmission spectra of the PI films synthesized in this study. The spectral shapes of the PI



Figure 5. Optical transmission spectra of (a) BTPB-based polyimide films and (b) BCTPB-based PI films.

films vary considerably depending on the nature of the dianhydrides. As shown in Figure 5, the optical transmission spectra of the PI films derived from the alicyclic dianhydride CBDA and fluorinated dianhydride 6FDA show high transparency in the visible range (%T at 400 nm are 76% for CBDA/BTPB, 83% for CBDA/BCTPB, 75% for 6FDA/BTPB, and 76% for 6FDA/BCTPB). The higher optical transparencies of these PI films can be attributed to the lower electron affinity of CBDA and the presence of a bulky hexafluoroisopropylidene moiety in 6FDA, both of which inhibit charge transfer complex formation considerably. The transparency of the PI film of



Figure 6. Excitation and fluorescent emission spectra of the PIs: (a) BPDA/BTPB; (b) CBDA/BTPB; (c) PMDA/BTPB; (d)BPDA/BCTPB; (e) CBDA/BCTPB; (f) PMDA/BCTPB.

BPDA was improved significantly by replacing BTPB with BCTPB (from 50% of %T for BPDA/BTPB to 66% of %T for BPDA/BCTPB at 400 nm).

Fluorescent Properties. Fluorescence spectroscopy is used widely to examine the electronic structures and aggregation states of polymers owing to its high sensitivity to microenvironmental changes in the polymer matrices.³⁶ Figure 6 shows the one-dimensional excitation and emission spectra of thin films of six representative PIs. All these PI films showed apparent fluorescence emission in the visible region between 402 and 576 nm. Table 1 lists the wavelengths of the maxima of the excitation and emission spectra of these PIs. First, CBDA/ BTPB and CBDA/BCTPB showed fluorescent emission originating from their locally excited $\pi - \pi^*$ (LE($\pi - \pi^*$)) state at the diamine moieties, which is characterized by the short excitation wavelengths of 339 and 335 nm as well as by the Stokes shifts of 0.51 and 0.56 eV, respectively, as estimated from the difference in the wavelength between the excitation and emission maxima. The excitation peak of CBDA/BTPB at

339 nm was red-shifted slightly compared to that of CBDA/ BCTPB PI (335 nm), which can be explained by the smaller calculated band gap for the CBDA/BTPB (7.16 eV) than that for CBDA/BCTPB (7.22 eV). Second, PMDA/BTPB and PMDA/BCTPB showed very weak fluorescence because the lowest excited states of the PIs derived from the dianhydrides with localized π conjugation could be attributed to LE(n $-\pi^*$) or CT(n $-\pi^*$) states, which emit very weak fluorescence.^{37,38} Third, BPDA/BTPB and BPDA/BCTPB showed excitation peaks at 391 and 384 nm and emission peaks at 503 and 482 nm, and the Stokes shifts were 0.85 and 0.75 eV, respectively, which can be understood as CT interactions inducing efficient energy transfer from the LE state to the exited CT state. Therefore, the relatively intense fluorescence was emitted from the lowest excited states attributable to the CT($\pi-\pi^*$) states.

The calculated band gaps for BPDA/BTPB, BPDA/BCTPB, PMDA/BTPB, and PMDA/BCTPB were 5.40, 5.53, 5.10, and 5.19 eV, respectively, which coincides well with their respective Stokes shifts.

Table 2. Refractive Indices $(n_{\text{TE}}, n_{\text{TM}}, n_{\text{av}})$, Birefringence (Δn) of the PIs Measured at 633 nm, Abbe Numbers (ν_{D}) , Refractive Indices at Infinite Wavelength (n_{∞}) , and Coefficients of Wavelength Dispersion (D) of the PIs

PI	n _{TE}	$n_{\rm TM}$	n _{av}	Δn	$ u_{\mathrm{D}}$	n_{∞}	$D(10^{-3})$
6FDA/BTPB	1.6623	1.6611	1.6619	0.0012	16.47	1.6087	21.36
6FDA/BCTPB	1.6489	1.6482	1.6487	0.0007	20.77	1.6087	16.55
BTDA/BTPB	1.7162	1.7146	1.7157	0.0016	17.93	1.6651	21.17
BTDA/BCTPB	1.7116	1.7104	1.7112	0.0012	15.37	1.6477	24.40
CBDA/BCTPB	1.6900	1.6878	1.6893	0.0022	12.66	1.6148	28.83
PMDA/BTPB	1.7255	1.7236	1.7249	0.0019	15.97	1.6665	24.16
PMDA/BCTPB	1.7175	1.7158	1.7169	0.0017	13.11	1.6439	29.06
BPDA/BTPB	1.7342	1.7334	1.7339	0.0008	24.52	1.6948	15.83
BPDA/BCTPB	1.7284	1.7277	1.7282	0.0007	31.47	1.6981	12.22

Refractive Indices and Birefringence. Table 2 summarizes the in-plane refractive index $(n_{\rm TE})$, out-of-plane refractive index ($n_{\rm TM}$), average refractive index ($n_{\rm av}$), and in-plane/out-ofplane birefringence (Δn) of the PIs. The values of n_{TE} and n_{TM} for the BTPB-based PI films measured at 633 nm are in the range of 1.6623-1.7342 and 1.6611-1.7334, respectively, whereas those for the BCTPB-based PI films are in the range of 1.6489-1.7284 and 1.6482-1.7277, respectively. The facts that the values of n_{TE} were slightly higher than those of n_{TM} for all PI films reflected the preferential orientation of the main chains parallel to the film plane. The n_{av} of the BTPB-based PI films measured at 633 nm ranged from 1.6619 to 1.7339, whereas that for the BCTPB-based PI films ranged from 1.6487 to 1.7282. The $n_{\rm av}$ of the PIs depends on the nature of both the dianhydride and diamine. The n_{av} values of the 6FDA-based PIs (6FDA/BTPB and 6FDA/BCTPB) were much smaller than those of the non-fluorinated aromatic PIs, obviously due to the unique fluorine impact contribution (very low polarizability per atomic volume of fluorine). The PIs derived from CBDA (CBDA/BCTPB) showed significantly lower refractive indices than those from the non-fluorinated aromatic PIs, which was attributed to the aliphatic nature of CBDA. The n_{av} of the CBDA/BTPB film could not be measured because it was highly brittle in nature. As expected, all six non-fluorinated sulfur containing aromatic PIs exhibited high n_{av} values >1.71 at 633 nm due to the presence of sulfur atoms with very high atomic refraction and rigid molecular structures of BTPB and BCTPB. The PIs derived from BPDA (BPDA/BTPB and BPDA/ BCTPB) showed higher refractive indices than the PIs derived from PMDA and BTDA. The n_{av} of 1.7339 observed for BPDA/BTPB at 633 nm was the highest of the sulfurcontaining PIs synthesized in this study, whereas the n_{av} of 1.7282 observed for BPDA/BCTPB was significantly high for a colorless PI. On the other hand, the introduction of chlorine in BCTPB decreased the n_{av} of BCTPB-based PIs compared to the analogous BTPB-based PIs. This result can be explained by the more bulky structures of the BCTPB-containing PIs increasing their van der Waals volumes significantly compared to the BTPB containing PIs and inhibiting dense molecular packing. Consequently, the BCTPB containing PIs inherently have a larger intermolecular free volume, which is also consistent with the high optical transparency due to the significantly weakened intermolecular CT interactions, as discussed above. The navs of BPDA/BTPB, BPDA/BCTPB, PMDA/BTPB, and PMDA/BCTPB were larger than those of BTDA/BTPB and BTDA/BCTPB because of the rod-like polymer backbone of BPDA and PMDA, which will encourage dense molecular packing of the polyimide chains. The bent structure of BTDA will inhibit the dense molecular packing of the polyimide chains and reduce the refractive index. The n_{av} of PMDA-containing PIs were lower than the BPDA-containing PIs due to the lower percentage of aromatic moieties in the polyimide network of the former than the latter.^{5,39}

The calculated refractive indices for PMDA/BTPB, PMDA/ BCTPB, BPDA/BTPB, BPDA/BCTPB, and CBDA/BCTPB at 633 nm were 1.6645, 1.6724, 1.7154, 1.7227, and 1.6210, respectively, assuming a constant molecular packing coefficient (K_p) of 0.6.^{21,35} The calculated $n_{\rm av}$ values were all slightly smaller than their experimental $n_{\rm av}$ s at 633 nm (Table 2). In contrast to the experimental average refractive indices, the calculated refractive indices of the BCTPB-containing PIs are larger than those of the BTPB-containing PIs. This suggests that the linear polarizability (α) per its van der Waals volume $(V_{\rm vdw})$ of BCTPB is larger than that of BTPB, even though the effects of molecular packing practically have a more dominant influence over the experimental $n_{\rm av}$ values. The practical K_p values of the PIs were estimated from the calculated values of $V_{\rm vdw}$ and α (Table 3) and the observed refractive indices of

Table 3. Calculated van der Waals Volumes (V_{vdw}) , Molecular Polarizabilities (α) , and Estimated Packing Coefficients (K_p) of the PIs^{*a*}

polyimide	$V_{\rm vdW}$ (Å ³)	α (Å ³)	$\alpha/V_{\rm vdW}$	$K_{ m p}$ at λ_∞
PMDA/BTPB	483.0	67.97	0.1407	0.6740
PMDA/BCTPB	510.8	72.54	0.1420	0.6622
BPDA/BTPB	554.1	81.84	0.1477	0.6480
BPDA/BCTPB	581.9	86.6	0.1488	0.6395
CBDA/BTPB	468.5	61.96	0.1326	
CBDA/BCTPB	496.3	66.69	0.1344	0.6787
6FDA/BTPB	633.5	85.51	0.1350	0.6546
6FDA/BCTPB	661.3	90.26	0.1365	0.6372
BTDA/BTPB	573.6	81.86	0.1427	0.6581
BTDA/BCTPB	601.4	86.64	0.1441	0.6485

^{*a*}The packing coefficients (K_p) were calculated as $(n_{av}^2 - 1)/(n_{av}^2 + 2) = (4\pi/3)K_p(\alpha_{av}/V_{vdW})$, where n_{av} , α_{av} , and V_{vdW} are the average refractive index, the average polarizability, and the van der Waals volume of the PIs, respectively.²¹

BCTPB and BTPB containing PIs.³⁹ K_p can be used to be a measure of the molecular packing density of a PI. When the dianhydride structure is fixed, the K_p values estimated for the BCTPB-containing PIs (e.g., 0.6395 for BPDA/BCTPB) were significantly smaller than those of the BTPB-containing PIs (e.g., 0.6480 for BPDA/BTPB), which agrees well with the tendency of the smaller experimental refractive indices of the BCTPB-containing PIs. This also shows that the increase in free volume caused by the substitution of chlorine in BCTPB

Macromolecules

was sufficient to loosen the molecular packing and lower the refractive indices of the BCTPB-based PIs.

The anisotropy in the refractive index, also known as "birefringence", is an important optical property for applications in lenses and waveguide devices, in which a large birefringence can cause aberrations or polarization-dependent losses. All the PIs synthesized in this study showed significantly small and positive in-plane/out-of-plane birefringence (Δn) , ranging from 0.0022 to 0.0007, despite their rigid molecular structures and high refractive indices. Conventional PIs with rigid structures generally show large birefringence.²⁶ The bulky and highly polarizable thiophenyls at the 2,2'-position of the non-coplanar biphenylene structure of BTPB and BCTPB direct almost normal to the biphenyl linkage and endow large free volumes among the polymer chains and weaken the intermolecular packing between the polymer chains. These factors reduce the Δn . BPDA/BCTPB PI can be a promising candidate for various optical applications owing to the high transparency, large refractive indices, and very small birefringence.

The experimental refractive indices were measured at four different wavelengths: 404, 532, 632.8, and 829 nm. The refractive index at infinite wavelength (n_{∞}) and the coefficient of wavelength dispersion (D) were calculated using the simplified Cauchy's formula:

$$n_{\lambda} = n_{\infty} + (D/\lambda^2)$$

Figure 7 shows the wavelength dispersion of the refractive indices. The Abbe's number ($\nu_{\rm D}$), which is commonly used to estimate the wavelength dependence of the refractive indices of optical materials, is given by the equation

$$\nu_{\rm D} = (n_{\rm D} - 1) / (n_{\rm F} - n_{\rm C})$$

where n_{D_1} , n_{C_2} and n_{C_2} are the refractive indices of the material at the wavelengths of the sodium D (589.3 nm), hydrogen F (486.1 nm), and hydrogen C (656.3 nm) lines, respectively. Table 2 lists the values of n_{∞} , ν_D , and D. Figures 7 and 8 show the wavelength dispersion of the experimental and calculated $n_{\rm av}$ values of the synthesized PIs, respectively. The smaller $\nu_{\rm D}$ value corresponds to a higher degree of wavelength dispersion, whereas a large $\nu_{\rm D}$ value indicates low wavelength dispersion. BPDA/BTPB and BPDA/BCTPB exhibited large $\nu_{\rm D}$ values of 24.52 and 31.47, respectively. In general, the refractive index and Abbe numbers are in a trade-off relation because optical absorption in the UV-vis region causes an increase in refractive index at shorter visible wavelengths.⁴⁰ In addition, one of the coauthors reported that BPDA-derived PIs exhibited high refractive indices with large wavelength dispersion, which corresponds to small Abbe numbers, among 11 kinds of PIs.⁴¹ Therefore, the fact the Abbe numbers for BPDA-derived PIs are the highest in all the PIs seems to be unusual. One essential reason may be due to their very good transparency, though the exact reason is unclear at moment. More systematic investigation on this point should be further performed in our future work. The PIs derived from 6FDA and CBDA (6FDA/BTPB, 6FDA/BCTPB, and CBDA/BCTPB) showed smaller $\nu_{\rm D}$ values (16.47, 20.77, and 12.66, respectively) owing to their smaller n_{av} values despite having higher optical transparency, whereas BTDA/BTPB, BTDA/BCTPB, PMDA/BTPB, and PMDA/BCTPB exhibited smaller $\nu_{\rm D}$ values (17.93, 15.37, 15.97, and 13.11, respectively) owing to their lower optical transparencies in the UV/vis region despite having higher refractive indices. As shown in Figure 8, the



Figure 7. Wavelength dispersion of the n_{av} values of (a) BTPB-based PI films and (b) BCTPB-based PI films.



Figure 8. Wavelength dispersion of the calculated refractive indices of the PI films.

trends of the wavelength dispersion of the experimental $n_{\rm av}$ values could not be reproduced by the wavelength-dependent calculated $n_{\rm av}$ values, but the DFT calculations correctly predicted that the $n_{\rm av}$ values of BPDA/BTPB and BPDA/BCTPB could be >1.74 at the shorter visible wavelengths (ca. 400–550 nm).

Thermal Properties. The thermal decomposition and deformation behavior of the PIs were evaluated by TGA, DSC, and DMA measurements under nitrogen. The results are listed in Table 4. As shown in Figure 9 (TGA), all the PIs showed good thermal stability, such as 5% weight-loss

Table 4. Thermal and Mechanical Properties of the PIs^a

	$T_{\rm g}$ ((°C)				
PIs	DSC	DMA	$T_{\rm d}^{5}$ (°C)	$T_{\rm d}^{10}$ (°C)	CTE (ppm/K)	E' (GPa)
PMDA/BTPB	279	278	489	509	10.0	10.74
PMDA/BCTPB	282	306	494	512	23.9	18.00
BPDA/BTPB	209	227	483	501	38.8	5.64
BPDA/BCTPB	234	243	485	505	39.7	6.14
CBDA/BTPB		228	446	461		1.94
CBDA/BCTPB		257	453	467		2.58
6FDA/BTPB	214	245	486	498	56.4	3.54
6FDA/BCTPB	236	244	487	507	60.8	6.43
BTDA/BTPB	207	220	468	495	61.4	2.88
BTDA/BCTPB	221	239	485	506	63.0	5.35

 ${}^{a}T_{g}$: glass transition temperature; T_{d}^{5} , T_{d}^{10} : temperature at 5% and 10% weight loss, respectively; CTE: coefficient of thermal expansion; E': storage modulus measured at 25 °C.



temperatures (T_d^5) in the range 453–494 °C and a 10% weight-loss temperatures (T_d^{10}) in the range 461–512 °C. The weight residues at 800 °C ranging from 41% to 54% were observed in nitrogen. The PIs derived from BCTPB exhibited higher T_d^5 and T_d^{10} compared to the BTPB-based PIs containing the same dianhydride. Decomposition of the dianhydride segments of the PI chains generally occurs at a lower temperature than that of the diamine segments, and the introduction of chlorine with a higher atomic density than hydrogen reduces the decomposition rate of BCTPB-based PIs.

CBDA/BTPB and CBDA/BCTPB with alicyclic dianhydride exhibited lower T_d^{5} and T_d^{10} than the aromatic PIs. All aromatic PIs showed good thermal stability without significant weight loss up to 400 °C. PMDA/BTPB and PMDA/BCTPB with relatively ordered, linear, and rod-like polymer chains showed the highest T_d^{5} and T_d^{10} .

The glass transition temperatures (T_{gs}) were determined by DSC (Figure S16) and DMA (Figure 10). In DMA, T_{g} was



Figure 10. Temperature dependence of the storage modulus and tan δ for PIs; filled square and filled circle symbols denote the change of storage modulus and the change of tan δ , respectively, as a function of temperature.

determined to be the peak temperature of the tan δ curve. The DMA thermograms (Figure 10) showed α -relaxations (main peaks) between 220 and 306 °C, whereas the T_{gs} estimated by DSC analysis were in the range 207-282 °C. The T_{gs} estimated from DMA were slightly higher (except PMDA/ BTPB) than those estimated from DSC. These differences in the T_{g} values estimated by DMA and DSC may be due to the different frequency responses of the PIs, i.e., f = 0 Hz for DSC and 2 Hz for DMA. One of the most important key parameters is the T_{σ} of optical device fabrication. All the PIs showed high T_{g} s, exceeding 200 °C suitable for applications to optoelectronic devices. The PIs derived from BCTPB exhibited higher T_{o} s than the analogous BTPB-based PIs, which can be attributed to the bulkier 4-chlorothiophenyl moiety stiffening the polymer backbone more effectively than the thiophenyl unit by introducing a barrier to segmental rotation. The PIs derived from PMDA possessed the highest $T_{g}s$, which are significantly higher than those of the other PIs synthesized in this study. The significantly high $T_{\rm g}$ s of the PMDA-based PIs could be attributed mainly to the ordered, linear, rigid-rod-like polymer backbone that increases the intermolecular CT interactions between the polymer chains. CBDA/BTPB and CBDA/ BCTPB exhibited no $T_{\rm g}$ s below 300 °C, which was the measuring limit of the DSC machine. This might be due to the higher $T_{\rm g}$ of these two PIs than their decomposition temperatures.

Figure S17 presents the TMA thermograms of the representative PIs. Table 4 lists the CTE values of all the synthesized PIs. The PMDA/BTPB and PMDA/BCTPB films displayed small CTEs of 10.0 and 23.9 ppm/K, whereas BPDA/BCTPB and BPDA/BTPB with high refractive indices and high optical transparencies exhibited CTEs < 40 ppm/K. The pseudo rigid-rod-like structures of PMDA and BPDA increased the interchain packing densities of their PIs and thereby reduced the CTE values. The interchain packing density in BPDA/BTPB and BPDA/BCTPB decreased to some extent due to the rotational vibration motion of the two phenyl rings of BPDA, and their CTEs also increased slightly compared to the PMDA-based PIs. In turn, the bent structure of BTDA and bulky hexafluoroisopropylidene group in 6FDA prevent dense chain packing and result larger CTEs in PIs derived from BTDA and 6FDA.42 The PIs derived from BCTPB showed smaller CTEs than analogous BTPB-based PIs. This can be attributed to the bulkier 4-chlorothiophenyl moiety, which inhibits dense polymer chain packing. A small CTE is highly advantageous to apply as a substrate material in optically transparent and thermally stable PIs for flexible displays, in which the polymer substrates need to be exposed to higher temperatures (>200 °C) during the vacuum deposition processes of inorganic thin films. In this regard, BPDA/BTPB and BPDA/BCTPB could be promising candidates for various optical applications owing to the high transparencies, high refractive indices, low birefringences, and CTEs < 40 ppm/K.

Figure 10 shows the variations in the storage modulus (E')and loss factor (tan δ) at various temperatures. Figure 10 shows that the storage modulus of the PIs remained almost constant upon heating below their glass transition temperatures, but after their T_g s, the modulus decreased dramatically. The storage modulus (E') of the aromatic PIs measured at 25 °C were in the range 18.0 to 3.54 GPa, which reflects the very high mechanical strength of all synthesized aromatic PIs. PMDA/ BTPB and PMDA/BCTPB registered higher storage moduli than the other aromatic PIs due to the relatively ordered, linear, rigid-rod-like polymer backbones, whereas the alicyclic CBDAbased PIs showed lower storage moduli.

These results suggest that the presence of bulky thiophenyl and 4-chlorothiophenyl groups at the 2,2'-position of BTPB and BCTPB, respectively, do not deteriorate the thermal stability of their PIs significantly. Therefore, 2,2'-bis-(thiophenyl)- and 2,2'-bis(4-chlorothiophenyl)-substituted benzidines (BTPB and BCTPB) in a para-linked polyimide chain do not change the rod-like structure of the polyimide backbone considerably but reduce the interactions between the polymer chains by incorporating bulky thiophenyl and 4chlorothiophenyl side groups between the polymer chains. This can explain the higher thermomechanical stabilities as well as the higher transparencies of these PIs.

CONCLUSIONS

Two new diamine monomers, namely 2,2'-bis(thiophenyl)benzidine (BTPB) and 2,2'-bis(4-chlorothiophenyl)benzidine

(BCTPB), were synthesized via the benzidine rearrangement reactions of the corresponding hydrazobenzene derivatives. The hydrazobenzene derivatives were obtained by the reduction of (3-nitrophenyl)(phenyl)sulfane and (4-chlorophenyl)(3nitrophenyl)sulfane, which were the cross-coupled products of thiophenol and 4-chlorothiophenol with 1-iodo-3-nitrobenzene, respectively. Ten new PIs were synthesized via the conventional two-step polycondensation of BTPB and BCTPB with five different dianhydrides in NMP. All the PIs except for CBDA/BTPB and CBDA/BCTPB were self-standing, tough, and flexible. The PI films except for PMDA/BTPB, PMDA/ BCTPB, BTDA/BTPB, and BTDA/BCTPB showed good optical transparency in the visible region. In particular, BPDA/ BCTPB, a fully aromatic, non-fluorinated PI, was colorless and transparent with a transmittance of \sim 83% at 450 nm and an average transmittance of >88% in the visible region. The PIs underwent 10% weight losses when subjected to thermal gravimetric analysis between 461 and 512 °C in a nitrogen atmosphere. All the PIs exhibited high thermal stability with glass transition temperatures ranging from 207 to 282 °C, as measured by DSC, and from 220 to 306 °C according to DMA. The CTE of the PIs films were between 10.00 and 63.00 ppm/ K. Most importantly, the BPDA/BCTPB PI film, a colorless PI film, exhibited CTE < 40 ppm/K between 50 and 200 °C as well as good pliability and toughness suitable for applications to flexible substrates. All six non-fluorinated, sulfur-containing aromatic PIs exhibited high average refractive indices >1.71 at 633 nm. The PIs synthesized in this study showed significantly small and positive birefringence ranging from 0.0007 to 0.0022. In particular, colorless BPDA/BCTPB with n_{av} of 1.7282 at 633 nm and birefringence of 0.0007 is highly suitable for applications as flexible films in advanced electronic and optical devices. The bulky thiophenyl and 4-chlorothiophenyl side groups at the 2,2'-position of BTPB and BCTPB, respectively, reduced the interactions between the polymer chains keeping the rod-like polyimide backbone intact, resulting in PIs with high thermal stabilities and high transparencies. In addition, PIs exhibited high average refractive indices and small birefringences owing to the large atomic polarizability of sulfur and the rigid bulky molecular structure of BTPB and BCTPB. The much stronger steric effect caused by bulky 4-chlorothiophenyl in BCTPB improved the optical transparency but decreased slightly the average refractive indices of the BCTPB-based PIs compared to the BTPB-based PIs.

ASSOCIATED CONTENT

S Supporting Information

Seventeen figures and two tables, including seven ¹H NMR spectra, five ¹³C NMR spectra, one ATR FTIR spectrum, molecular structures, WAXD patterns, and quantum-chemical calculation, DSC thermograms, and TMA curves. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b00432.

AUTHOR INFORMATION

Corresponding Author

*Fax +82-51-514 4331, Tel +82-51-510-2407, e-mail csha@ pnu.edu (C.-S. Ha).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the National Research Foundation of Korea (NRF). Grant funded by the Ministry of Science, ICT, and Future Planning, Korea (Acceleration Research Program (No. 2014 R1A2A111054584)); Pioneer Research Center Program (No. 2010-0019308/2010-001948); the Brain Korea 21 Plus Project. (21A2013800002)).

REFERENCES

(1) Ju, Y. G.; Almuneau, G.; Kim, T. H.; Lee, B. W. Jpn. J. Appl. Phys. 2006, 45, 2546–2549.

(2) Suwa, M.; Niwa, H.; Tomikawa, M. J. Photopolym. Sci. Technol. 2006, 19, 275–276.

(3) Nakai, J.; Aoki, T. US Patent 7087945, 2006.

(4) Regolini, J. L.; Benoit, D.; Morin, P. Microelectron. Reliab. 2007, 47, 739–742.

(5) Ando, S.; Fujigaya, T.; Ueda, M. Jpn. J. Appl. Phys. 2002, 41, L105–L108.

(6) Liu, J. G.; Nakamura, Y.; Terraza, C. A.; Suzuki, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromol. Chem. Phys.* **2008**, *209*, 195–203.

(7) Liu, J. G.; Nakamura, Y.; Suzuki, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromolecules* **200**7, *40*, 7902–7909.

(8) Terraza, C. A.; Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 1510–1520.

(9) Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromolecules* **2007**, *40*, 4614–4620.

(10) You, N.-H.; Suzuki, Y.; Yorifuji, D.; Ando, S.; Ueda, M. *Macromolecules* **2008**, *41*, 6361–6366.

(11) Maxwell, J. R.; Daniel, M. K. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 2453-2461.

(12) Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. J. Appl. Polym. Sci. 2000, 76, 45–49.

(13) Lu, C. L.; Cui, Z. C.; Wang, Y. X.; Yang, B.; Shen, J. C. J. Appl. Polym. Sci. 2003, 89, 2426-2430.

(14) Nebioglu, A.; Leon, J. A.; Khudyakov, I. V. Ind. Eng. Chem. Res. 2008, 47, 2155–2159.

(15) Nakamura, A.; Fujii, H.; Juni, N.; Tsutsumi, N. Opt. Rev. 2006, 13, 104–110.

(16) Nakamura, T.; Tsutsumi, N.; Juni, N.; Hujii, H. J. Appl. Phys. 2005, 97, 054505-054510.

(17) Mikami, A.; Koshiyama, T.; Tsubokawa, T. Jpn. J. Appl. Phys. 2005, 44, 608–612.

(18) Liaw, D.-J.; Wang, K.-L.; Huang, Y.-C.; Lee, K.-R.; Lai, J.-Y.; Ha, C.-S. Prog. Polym. Sci. 2012, 37, 907–974.

(19) Groh, W.; Zimmermann, A. Macromolecules **1991**, 24, 6660–6663.

(20) Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. Polym. J. 2007, 39, 543-550.

(21) Liu, J. G.; Nakamura, Y.; Ogura, T.; Shibasaki, Y.; Ando, S.; Ueda, M. Chem. Mater. 2008, 20, 273–281.

(22) You, N.-H.; Suzuki, Y.; Higashihara, T.; Ando, S.; Ueda, M. Polymer **2009**, *50*, 789–795.

(23) You, N.-H.; Fukuzaki, N.; Suzuki, Y.; Nakamura, Y.; Higashihara, T.; Ando, S.; Ueda, M. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 4428–4434.

(24) You, N.-H.; Nakamura, Y.; Suzuki, Y.; Higashihara, T.; Ando, S.; Ueda, M. J. Polym. Sci., Part A: Polym. Chem. **2009**, 47, 4886–4894.

(25) You, N.-H.; Higashihara, T.; Ando, S.; Ueda, M. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 656–662.

(26) Choi, M.-C.; Wakita, J.; Ha, C.-S.; Ando, S. *Macromolecules* 2009, 42, 5112-5120.

(27) Sheldrick, G. M. SHELXS-97, program for X-ray crystal structure solution, Göttingen University, Germany, 1997.

(28) Sheldrick, G. M. SHELXS-97, program for X-ray crystal structure refinement, Göttingen University, Germany, 1997.

(29) Hofmann, A. W. Proc. R Soc. London 1863, 12, 576.

(30) Schmidt, H.; Schultz, G. Chem. Ber. 1878, 11, 1754.

- (31) Gaussian 03, Revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (32) Slonimskii, G.; Askadskii, A.; Kitaigodorodskii, A. Polym. Sci. USSR 1970, A12, 556.
- (33) Bondi, A. J. Phys. Chem. 1964, 68, 441.
- (34) Ando, S. J. Photopolym. Sci. Technol. 2006, 19, 351-360.

(35) Terui, Y.; Ando, S. J. Photopolym. Sci. Technol. 2005, 18, 337–340.

(36) Hasegawa, M.; Horie, K. Prog. Polym. Sci. 2001, 26, 259-335.

(37) Wakita, J.; Sekino, H.; Sakai, K.; Urano, Y.; Ando, S. J. Phys. Chem. B 2009, 113, 15212-15224.

(38) Wakita, J.; Inoue, S.; Kawanishi, N.; Ando, S. *Macromolecules* **2010**, *43*, 3594–3605.

(39) Terui, Y.; Ando, S. J. Polym. Sci., Part B: Polym. Phys. 2004, 42, 2354-2366.

(40) Dislich, H. Angew. Chem., Int. Ed. Engl. 1979, 18, 49-59.

(41) Ando, S.; Watanabe, Y.; Matsuura, T. Jpn. J. Appl. Phys. 2002, 41, 5254-5258.

(42) Hougham, G.; Tesoro, G.; Vlehbeck, A. Macromolecules 1996, 29, 3453-3456.