Synthesis and Properties of Organosoluble Polyimides Derived from 2,2′-Dibromo- and 2,2′,6,6′-Tetrabromo-4,4′-Oxydianilines

Jyh-Chien Chen,[1] Yuan-Tsai Liu,[1] Chyi-Ming Leu,[2] Hsueh-Yi Liao,[2] Wen-Chin Lee,[2] Tzong-Ming Lee[2]

[1]*Department of Polymer Engineering, National Taiwan University of Science and Technology, No. 43 Sec. 4 Keelung Road, Taipei 106, Taiwan*
[2]*Material and Chemical Laboratories, Industrial Technology Research Institute, 195 Chung Hsing Road, Sec.4 Chu Tung 310, Taiwan*

ABSTRACT: Two new aromatic diamines, 2,2′-dibromo-4,4′-oxydianiline (DB-ODA **4**) and 2,2′,6,6′-tetrabromo-4,4′-oxydianiline (TB-ODA **5**), have been synthesized by oxidation, bromination, and reduction of 4,4′-oxydianiline (4,4′-ODA). Novel polyimides **6a–f** and **7a–f** were prepared by reacting DB-ODA (**4**) and TB-ODA (**5**) with several dianhydrides by one-step method, respectively. The inherent viscosities of these polyimides ranged from 0.31 to 0.99 dL/g (0.5 g/dL, in NMP at 30°C). These polyimides showed enhanced solubilities compared to those derived from 4,4′-oxydianiline and corresponding dianhydrides. Especially, polyimides **7a**, derived from rigid PMDA and TB-ODA (**5**) can also be soluble in THF, DMF, DMAc, DMSO, and NMP. These polyimides also exhibited good thermal stability. Their glass transition temperatures measured by thermal mechanical analysis (TMA) ranged from 251 to 328°C. When the same dianhydrides were used, polyimides **7** containing four bromide substituents had higher glass transition temperatures than polyimides **6** containing two bromide substituents. The effects of incorporating more polarizable bromides on the refractive indices of polyimides were also investigated. The average refractive indices (n_{av}) measured at 633 nm were from 1.6088 to 1.7072, and the in-plane/out-of-plane birefringences (Δn) were from 0.0098 to 0.0445. It was found that the refractive indices are slightly higher when polyimides contain more bromides. However, this effect is not very obvious. It might be due to loose chain packing resulted from bromide substituents at the 2,2′ and 2,2′,6,6′ positions of the oxydiphenylene moieties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1144–1155, 2010

Key words: birefringence; polyimides; refractive index; solubility; synthesis

INTRODUCTION

Aromatic polyimides are well known for their excellent mechanical properties and outstanding thermal stability. They also exhibit superior solvent resistance. This is resulted from high aromaticity and heterocyclic imide linkage of their chemical structures. The strong inter- and intramolecular interactions resulted from the formation of charge transfer complex are also responsible.[1] Polyimides are generally processed in the form of their polyamic acid precursors, which are prepared by reacting dianhydrides with diamines in polar aprotic solvent. Polyamic acids are then thermally or chemically imidized. If thermal imidization is applied, sophisticated heating sequence is required to remove the solvent and water. Sometimes, the imidization temperature could be as high as 350°C to assure the complete imidization. On the other hand, soluble polyimides prepared by one-step method exist in the pre-imidized forms. Heating process only involves the removal of solvents. Therefore, polyimide films can be prepared at lower temperature. This advantage could facilitate the applications of polyimides in semiconductors, electronic packaging, and special optical films. Many attempts have been reported to enhance the solubility. These approaches include the introduction of bulky side groups,[2–8] flexible or asymmetrical linkages,[9–11] and noncoplanar structures.[12–15] In recent years, even the solubilities of the most intractable polyimides derived from pyromellitic dianhydride (PMDA) have been improved to be soluble in common organic solvents.[9,16–18]

When polyamic acid solutions were spin-coated into films and converted to polyimides by thermal imidization, Ikeda pointed out that the molecular chains of polyimides would align themselves parallel to the film surface.[19] Russell et al.[20] further measured the in-plane (n_{TE}) and out-of-plane (n_{TM})

refractive indices by a prism coupler. They found that the in-plane refractive indices were isotropic and larger than the out-of-plane ones. This phenomenon, called in-plane orientation, is resulted from the fact that polyimide chains would align themselves preferentially and randomly on the film surface. The magnitude of the birefringence is also related to the processing conditions and the chemical structures of polymer chains as well.[21] The more rigid chains exhibit larger birefringence.[22] Because of this birefringence characteristics, these polyimides can be used as compensator or retardation film in LCD display to improve the viewing angle.[23,24] On the contrary, zero birefringence is required if the polyimide films are targeted for the applications such as the flexible and transparent substrates for flat panel display, optical adhesives, lens, and thin-film waveguide. To reach zero birefringence, many methods have been proposed such as the copolymerization of monomers with different birefringence ($\Delta n < 0$ or $\Delta n > 0$) or the addition of small birefringent crystals.[25–27] In addition to birefringence, refractive indices are also an important optical property. The refractive indices of most polymers range from 1.45 to 1.55. Polymers with either very high or very low refractive indices have their specific applications. For example, polymers with low refractive indices can be used as the cladding layer for optical fibers. Most of these polymers contain fluorine or SiO_2 nanoparticles.[28,29] Polymers with high refractive indices can be exploited as optical adhesives, antireflective coatings, or micro lens for charge-coupled device (CCD) and complementary metal oxide semiconductor (CMOS).[29–31] It has been reported that the addition of metal oxide nanoparticles such as titanium oxide (TiO_2) and cesium oxide (Cs_2O) are effective to increase the refractive indices. The refractive indices can be as high as 1.95 when the weight percents of these metal oxide nanoparticles reach 90%.[29,32] Recently, the incorporations of thioether groups into the polyimide backbones have also been reported.[33–38] These sulfur-containing polyimides exhibited high refractive indices and low birefringence. The highest refractive index of polyimide, 1.769, was reported.[33]

It is well known from Lorentz-Lorenz equation that high polarizability and small molar volume of the polymer chains will lead to high refractive indices.[39] In addition to sulfur, highly polarizable halogens such as bromine and iodine should have the similar effect on increasing refractive indices. For example, polymethylacrylate containing brominated or iodinated carbazole had the refractive indices from 1.67 to 1.77.[40] To our knowledge, the effect of incorporating bromine on the refractive indices of polyimides has not been explored. In this study, we report the synthesis of two new brominated dia-

mines, 2,2′-dibromo-4,4′-oxydianiline (DB-ODA **4**) and 2,2′,6,6′-tetrabromo-4,4′-oxydianiline (TB-ODA **5**) by oxidation, bromination and reduction of 4,4′-oxydianiline (4,4′-ODA). Novel polyimides derived from these two brominated diamines with commercially available dianhydrides were prepared by one-step method in *m*-cresol. In addition to the solubility and thermal properties, the effects of incorporating bromine on the refractive indices of polyimides were investigated.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-oxydiphthalic anhydride (ODPA), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were all purchased from Kriskev Co., dried under reduced pressure at 150°C and sublimated before use. 4,4′-Oxydianiline (4,4′-ODA) was also obtained from Kriskev Co. and used as received. *m*-Cresol (Lancaster Synthesis) was dried with phosphorous pentoxide and distilled under reduced pressure. Other chemicals and solvents were used as received.

Monomer synthesis

Synthesis of 4,4′-dinitrodiphenylether(1)

To a 500-mL, three-necked round-bottomed flask, 6.00 g (30.0 mmol) of 4,4′-oxydianiline (4,4′-ODA), 180 mL of glacial acetic acid, 54 mL of 30% hydrogen peroxide, and 2.4 mL of concentrated sulfuric acid were added and heated at 85°C overnight. After cooled to room temperature, the reaction mixture was poured into 500 mL of ice water. The precipitate was collected and washed with water several times. After dried at 90°C under reduced pressure overnight, 3.85 g (49% yield) of yellow powder was obtained: mp 144–146°C. The crude product was used directly for the next step without further purification. ^{1}H-NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.37 (d, $J = 9.2$ Hz, 4H), 8.33 (d, $J = 9.2$ Hz, 4H). ^{13}C-NMR (500 MHz, DMSO-d_6): δ (ppm) = 119.6, 126.2, 143.7, 160.4. EIMS(*m/z*): Calcd. for $C_{12}H_8N_2O_5$, 260.0; Found, 260.0 [M]$^{+}$. $C_{12}H_8N_2O_5$: Calcd. C 55.39, H 3.10, N 10.77; Found: C 55.47, H 3.24, N 11.03.

Synthesis of 2,2′-dibromo-4,4′-dinitrodiphenylether (2)

To a 250-mL, three-necked round-bottomed flask, 100 mL of concentrated sulfuric acid, 10 mL of

water, 4.00 g (15.37 mmol) of 4,4′-dinitrodiphenylether (**1**), and 5.74 g (32.25 mmol) of N-bromosuccinimide (NBS) were added and heated at 85°C for 6 h. After the reaction mixture was allowed to cool to room temperature, it was poured into ice water. The precipitate was collected, washed several times with water and dried at 90°C under reduced pressure overnight to afford 6.00 g of crude product (93% yield). The crude product was used without further purification for the next step. The crude product can be recrystallized from acetone/water to afford 4.11 g (64% yield) of off-white powder: mp 155–158°C. ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 7.33 (d, J = 9.0 Hz, 2H), 8.29 (dd, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 2H), 8.65 (d, J = 2.6 Hz, 2H). ^{13}C-NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 113.8, 120.0, 125.3, 129.3, 144.4, 156.6. EIMS(m/z): Calcd. for C$_{12}$H$_6$Br$_2$N$_2$O$_5$, 415.9; Found, 415.8 [M]$^+$. C$_{12}$H$_6$Br$_2$N$_2$O$_5$: Calcd. C 34.48, H 1.45, N 6.70; Found: C 34.54, H 1.47, N 6.72.

Synthesis of 2,2′,6,6′-tetrabromo-4,4′-dinitrodiphenylether (3)

To a 250-mL, three-necked round-bottomed flask, 100 mL of concentrated sulfuric acid, 10 mL of water, 2.00 g (7.69 mmol) of 4,4′-dinitrodiphenylether (**1**) and 6.84 g (38.43 mmol) of N-bromosuccinimide (NBS) were added and heated at 85°C for 6 h. After the reaction mixture was allowed to cool to room temperature, it was poured into ice water. The yellow precipitate was collected and dried at 90°C under reduced pressure overnight to afford 4.37 g of raw product. After recrystallization from acetone, 1.60 g (36% yield) of yellow crystals was obtained: mp 232–234°C. ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 8.60 (s, 4H). ^{13}C-NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 114.5, 128.6, 144.4, 153.0. EIMS(m/z): Calcd. for C$_{12}$H$_4$Br$_4$N$_2$O$_5$, 571.7; Found, 571.7 [M]$^+$. C$_{12}$H$_4$Br$_4$N$_2$O$_5$: Calcd. C 25.03, H 0.70, N 4.87; Found: C 25.02, H 0.76, N 4.76.

Synthesis of 2,2′-dibromo-4,4′-oxydianiline (4)

To a 250-mL, three-necked round-bottomed flask equipped with a mechanical stirrer were added 4.00 g (9.57 mmol) of 2,2′-dibromo-4,4′-dinitrodiphenylether (**2**), 20 mL of concentrated hydrogen chloride and 60 mL of ethanol. After 4.69 g of tin powder was slowly added, the reaction mixture was heated at reflux for 3 hours. After cooled to room temperature, the reaction mixture was poured into ice water and neutralized with aqueous NaOH solution to pH = 12. Ethyl ether was then added to extract the product several times. The combined organic solution was collected and dried with anhydrous magnesium sulfate. After ethyl ether was evaporated, the solid powder was collected and recrystallized in

ethanol/water to afford 1.90 g (55%) of off-white needle-like crystals: mp 147–149 °C. ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ (ppm) = 5.12 (s, 4H), 6.49 (dd, J_1 = 8.7 Hz, J_2 = 2.5 Hz, 2H), 6.54 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 2.5 Hz, 2H). ^{13}C-NMR (500 MHz, DMSO-d$_6$) δ (ppm) = 113.2, 114.1, 117.5, 119.8, 143.7, 145.9. EIMS(m/z): Calcd. for C$_{12}$H$_{10}$Br$_2$N$_2$O, 355.9; Found, 355.9 [M]$^+$. C$_{12}$H$_{10}$Br$_2$N$_2$O: Calcd. C 40.26, H 2.82, N 7.82; Found: C 40.09, H 2.57, N 7.74. Crystal data: C$_{12}$H$_{10}$Br$_2$N$_2$O, colorless crystal, 0.28 × 0.13 × 0.08 mm^3, monoclinic with a = 12.0665 (7) Å, b = 8.4877 (5) Å, c = 13.4175 (8) Å, α = 90°, β = 117.198 (3)°, γ = 90° with Dc = 1.946 Mg/m^3 for Z = 4, V = 1222.24 (12) Å^3, T = 200(2) K, λ = 0.71073 Å, F(000) = 696, final R indices: R1 = 0.0457, WR2 = 0.1018.

Synthesis of 2,2′,6,6′-tertabromo-4,4′-oxydianiline (5)

To a 250-mL, three-necked round-bottomed flask equipped with a mechanical stirrer were added 4.00 g (6.95 mmol) of 2,2′,6,6′-tetrabromo-4,4′-dinitrodiphenylether (**3**), 40 mL of concentrated hydrochloric acid, and 120 mL of ethanol. After 3.40 g of tin powder was slowly added, the reaction mixture was heated at reflux for 3 hours. After cooled to room temperature, the reaction mixture was poured into ice water and neutralized with aqueous NaOH solution to pH = 12. Ethyl acetate was then added to extract the product several times. The combined organic solution was collected and dried with anhydrous magnesium sulfate. After solvent was evaporated, the solid powder was collected and recrystallized in acetone/water to afford 1.09 g (30% yield) of off-white crystals: mp > 300 °C. ^{1}H-NMR (500 MHz, DMSO-d$_6$) δ (ppm) = 5.34 (s, 4H), 6.78 (s, 4H). ^{13}C-NMR (500 MHz, DMSO-d$_6$) δ (ppm) = 14.5, 117.4, 139.6, 146.6. EIMS(m/z): Calcd. for C$_{12}$H$_8$Br$_4$N$_2$O, 511.7; Found, 511.7 [M]$^+$. C$_{12}$H$_8$Br$_4$N$_2$O: Calcd. C 27.94, H 1.56, N 5.43; Found: C 28.06, H 1.87, N 5.74. Crystal data: C$_{12}$H$_8$Br$_4$N$_2$O, colorless crystal, 0.13 × 0.10 × 0.02 mm^3, triclinic with a = 9.725(7) Å, b = 11.969(8) Å, c = 12.997(9) Å, α = 88.129(8)°, β = 68.03°, γ = 84.995(11)° with Dc = 2.452 Mg/m^3 for Z = 4, V = 1397.6 (17) Å, ^3T = 200(2) K, λ = 0.71073 Å, F(000) = 968, final R indices: R1 = 0.1171, WR2 = 0.2815.

Polyimide synthesis

Polyimides **6** and **7** were prepared according to the following procedure. The dianhydride was added to a stirred solution of an equal molar amount of the diamine in the appropriate amount of m-cresol (total solid content 10 w/v%) containing a catalytic amount of isoquinoline under nitrogen at room temperature. The reaction mixture was heated to 200°C and maintained at that temperature for 12 h. During

this period, the water of imidization was allowed to distil from the reaction mixture along with 1 or 2 mL of solvent. After the solution was allowed to cool to ambient temperature, it was diluted with *m*-cresol and then slowly added to 1 L of vigorously stirred methanol. The polymer that precipitated was collected by filtration, extracted with hot ethanol, and dried under reduced pressure at 150°C for 24 h.

Preparation of polyimide films

Polyimide films were mostly prepared by their DMAc solutions (solid content around 8% w/v) except polyimides **6b** and **7b**, which were prepared by using *m*-cresol as solvent. The polyimide solutions were first filtered through a 0.45 µm Teflon syringe filter before use. For TMA measurements, polyimide films of 20 to 30 µm in thickness were prepared by casting the polyimide solution on glass plate. For UV-Visible transparency test and refractive index measurements, the thickness of the polyimide films was controlled around 5 to 10 µm. The polyimide films were dried in an air-circulated oven at 50°C for 1 h, 80°C for 1 h, 150°C for 1 h and 220°C for 1 h.

Instrumentation

All melting points were determined on a Mel-Temp capillary melting point apparatus and uncorrected. Proton and carbon (^{1}H- and ^{13}C-NMR) nuclear magnetic resonance spectra were measured at 500 MHz on a Bruker Avance-500 spectrometer. Infrared spectra were obtained with a Digilab-FTS1000 FTIR. Mass spectroscopy was conducted on a Finnigan TSQ 700 mass spectrometer. Elemental analyses were performed on a Heraeus Vario analyzer. The X-ray crystallographic data were collected on a Bruker SMART APEX 2 diffractometer. High performance liquid chromatography was performed on a JASCO HPLC system equipped with a UV (254 µm) detector using a Thermo Hypersil column (250 mm × 4.6 mm, particle size 5 µm) with a 80/20 (v/v) acetonitrile/water mixture as the solvent. Intrinsic viscosities were determined with a Cannon-Ubbelohde No. 100 viscometer at 30.0 ± 0.1°C in *N*-methyl pyrrolidinone (NMP). Molecular weights were measured on a JASCO GPC system (PU-980) equipped with an RI detector (RI-930), a Jordi Gel DVB Mixed Bed column (250 mm × 10 mm) column, using dimethyl acetamide (DMAc) as the eluent and calibrated with polystyrene standards. Thermal gravimetric analyses (TGA) were performed in nitrogen with a TA TGA Q500 thermogravimetric analyzer using a heating rate of 10°C/min. Glass Transition temperatures (T_gs) and coefficients of thermal expansion (CTEs) were determined by ther-
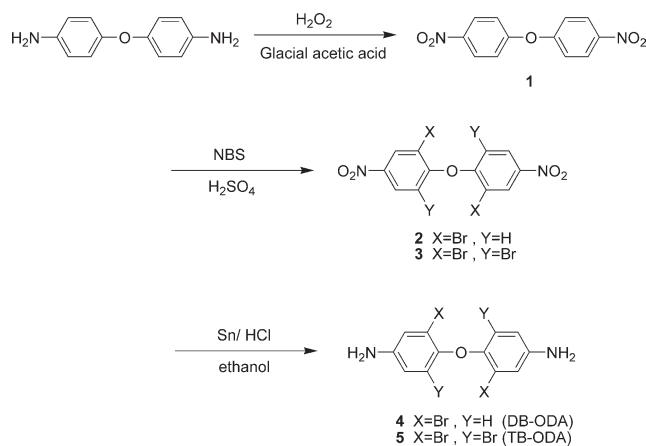
Scheme 1 Synthetic route for DB-ODA (**4**) and TB-ODA (**5**).

mal mechanical analysis (TMA) using a TA TMA 2940 thermal mechanical analyzer with a tension mode (0.05 *N*) at a heating rate of 10°C/min. The T_g was taken as the temperature at which a change in slope of a plot of film dimension change versus temperature occurred. The CTE value was taken as the average of the dimension change between 50 and 150°C. UV-Visible transparency measurements were carried out on a Cary-100 UV-Visible spectrometer. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the polyimide films were measured on a prism coupler (SAIRON SPA-4000) equipped with a He-Ne laser light source (wavelength 633 nm). The birefringence was calculated as the difference between n_{TE} and n_{TM}. The average refractive index (n_{av}) was calculated by the equation, $n_{av} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$.

RESULTS AND DISCUSSION

Monomer synthesis

Two aromatic diamines, 2,2′-dibromo-4,4′-oxydianiline (DB-ODA **4**) and 2,2′,6,6′-tetrabromo-4,4′-oxydianiline (TB-ODA **5**), were synthesized by oxidation, bromination and reduction of 4,4′-oxydianiline (4,4′-ODA) as shown in Scheme 1. First, 4,4′-ODA was oxidized by hydrogen peroxide. The purpose of the oxidation was to make sure that the following bromination could occur exclusively on the 2,2′ or 2,2′,6,6′ positions of the diphenylether structure, depending on the amount of *n*-bromosuccinimide used. It has been reported that the direct bromination of 4,4′-ODA would lead to a mixture containing different number of bromides at 3,3′5,5′ positions.[41] Figure 1 shows the HPLC chromatogram of the brominated nitro compounds obtained by using different equivalents of NBS. Nitro compounds containing from one to 7 bromides (1-Br to 7-Br) can be identified either by ^{1}H-NMR or mass spectra. For
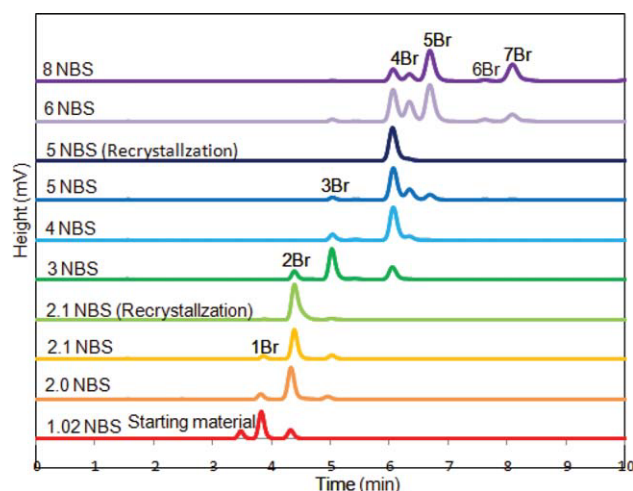
Figure 1 HPLC chromatograms of brominated products at different equivalents of NBS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 2 ^{1}H NMR spectrum of brominated products using three equivalents of NBS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

example, when three equivalents of NBS were used, the HPLC chromatogram showed three peaks (Fig. 1). The brominated mixtures were identified by ^{1}H-NMR spectrum (Fig. 2) as 2-Br, 3-Br, and 4-Br compounds. The presence of the molecular ion peaks in the mass spectra combined with the characteristic isotope peaks of nitro compounds containing different number of bromine atoms provided further evidence. For example, the mass spectrum of the brominated nitro compound obtained by using three equivalents of NBS shows the molecular ion peaks at m/z 415.8, 493.6, and 571.7, corresponding to 2-Br, 3-Br, and 4-Br nitro compounds, respectively. Furthermore, the ratio of intensities of the isotope peaks of 2-Br is 100 : 200 : 154(M : M+2 : M+4), that of 3-Br is 100 : 213 : 273 : 83 (M : M+2 : M+4 : M+6) and that of 4-Br is 100 : 400 : 650 : 450 : 125 (M : M+2 : M+4 : M+6 : M+8). The fact that the 4-Br compound can also be formed even only three equivalents of NBS were used indicates that the electron density of the starting nitro compound is not as deficient as expected. Thus, when NBS amount was increased to eight equivalents, the existence of 4-Br to 7-Br nitro compounds can be confirmed by the molecular ion peaks in the mass spectrum. It was found that pure 2-Br (**2**) and 4-Br (**3**) nitro compounds can be obtained by using 2.1 and 5 equivalents of NBS followed by recrystallization, respectively.

The formed nitro compounds were then reduced by Sn/HCl to form DB-DDA (**4**) and TB-ODA (**5**). The proper reduction conditions are required in order to get the clean products. We have tried reduction methods other than Sn/HCl in ethanol. From ^{1}H-NMR spectra, it suggests that debromination could occur to some extent which complicates
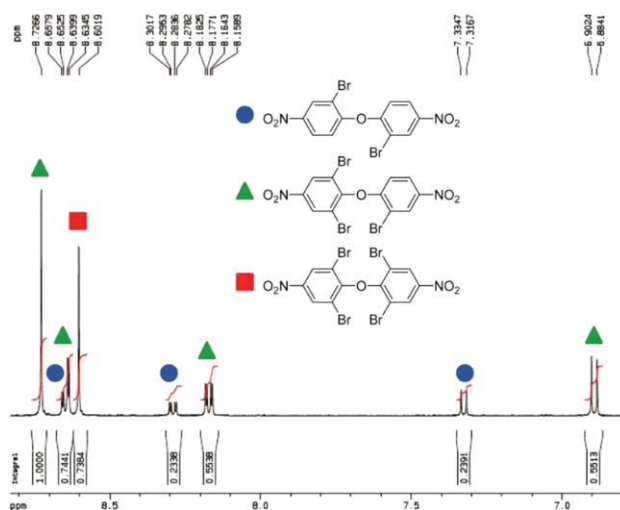
the workup process. Figure 3 shows the ^{1}H- and ^{13}C-NMR spectra of DB-ODA (**4**). One doublet–doublet peak at 6.49 ppm and two doublet peaks at 6.54 and 6.84 ppm suggest the correct chemical structure. The ^{1}H- and ^{13}C-NMR spectra of TB-ODA (**5**) are shown in Figure 4. Two singlet peaks (5.34, 6.78 ppm) shown in ^{1}H-NMR spectrum [Fig. 4(a)] and four peaks shown in ^{13}C-NMR spectrum [Fig. 4(b)] assure the chemical structure of TB-ODA (**5**).

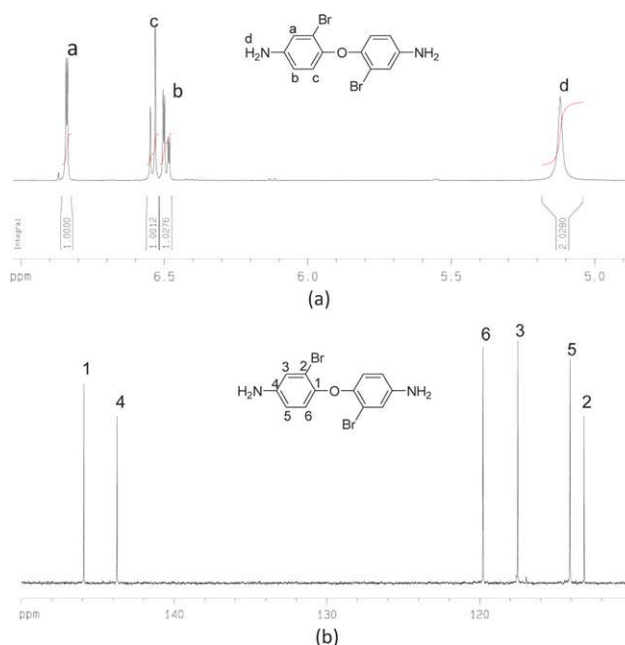In addition, X-ray diffraction analysis also confirmed the chemical structures of DB-ODA (**4**) and

Figure 3 (a) ^{1}H- and (b) ^{13}C-NMR spectra of DB-ODA (**4**). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 (a) ^{1}H- and (b) ^{13}C-NMR spectra of TB-ODA (**5**). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

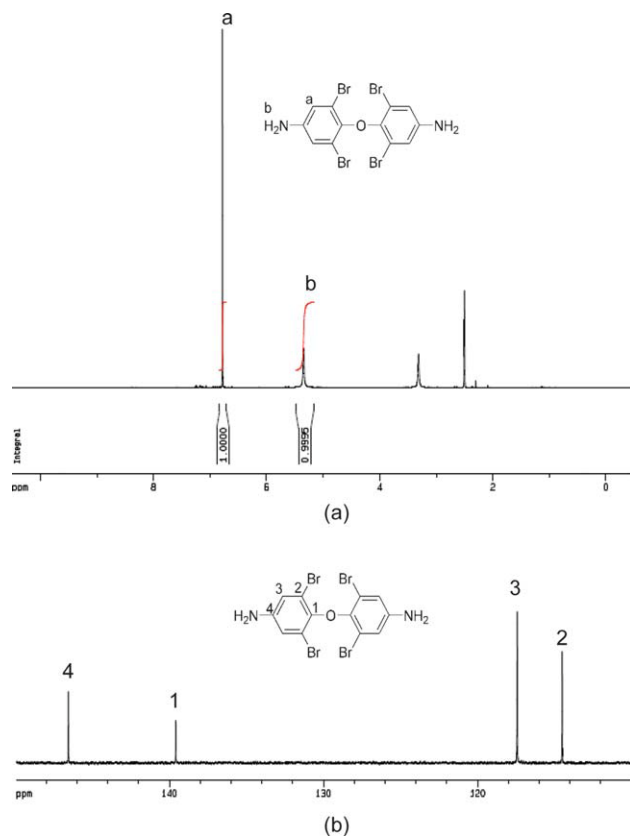TB-ODA (**5**) as shown in Figures 5 and 6, respectively. X-ray crystal data for DB-ODA (**4**) and TB-ODA (**5**) were acquired from single crystals, obtained by slowly crystallizing from EtOH/H$_2$O and acetone, respectively. In X-ray structures of DB-ODA (**4**) and TB-ODA (**5**) (Figs. 5 and 6), the dihedral angles of between two phenyl rings were found to be 88.5° and 86.7°, respectively. It indicates that the two benzene rings are noncoplanar. The results of elemental analysis were also consistent with the proposed chemical structures. These two brominated diamines have the possibility to be further functionalized using the reactions involving aryl bromide either at dinitro or diamino conditions such as trifluoromethylation, palladium-catalyzed cross-cou-
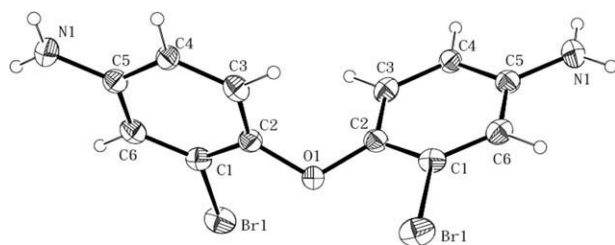

Figure 5 X-ray structure of DB-ODA (**4**).
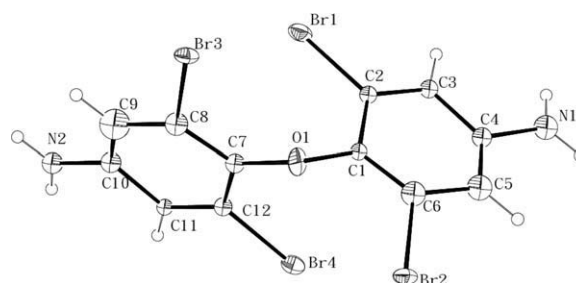

Figure 6 X-ray structure of TB-ODA (**5**).

pling, and intramolecular Ullmann coupling reactions.

Polyimide synthesis

Polyimides **6a–f** and **7a–f** were prepared in quantitative yield by reacting the new diamines DB-ODA (**4**) and TB-ODA (**5**) with six commercially available dianhydrides in *m*-cresol by one-step method as shown in Scheme 2. All of the polyimides, except **6a** and **7a**, remained in *m*-cresol throughout the polymerization without any premature precipitation. Figure 7 shows the IR spectra of the formed polyimides **6b–f** (except **6a**) and polyimides **7a–f**. The characteristic peaks appeared at 1780, 1720 (carbonyl asymmetrical and symmetrical stretching) and 1380 cm^{-1} (C—N stretching) confirm the formation of imide linkage. One of the representative ^{1}H-NMR spectrum of polyimide **7a**, derived from TB-ODA (**5**) and PMDA, is shown in Figure 8. The two singlet peaks appeared at 7.98 and 8.49 ppm are assigned to the hydrogen in TB-ODA (**5**) and PMDA moieties of the polyimide **7a**, respectively.
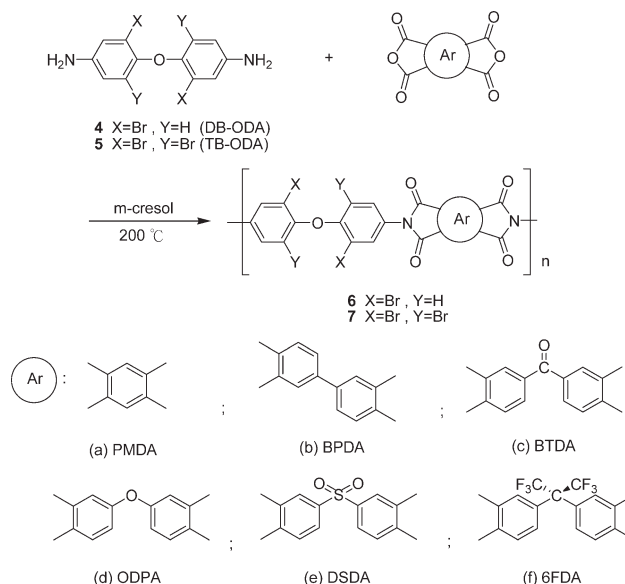
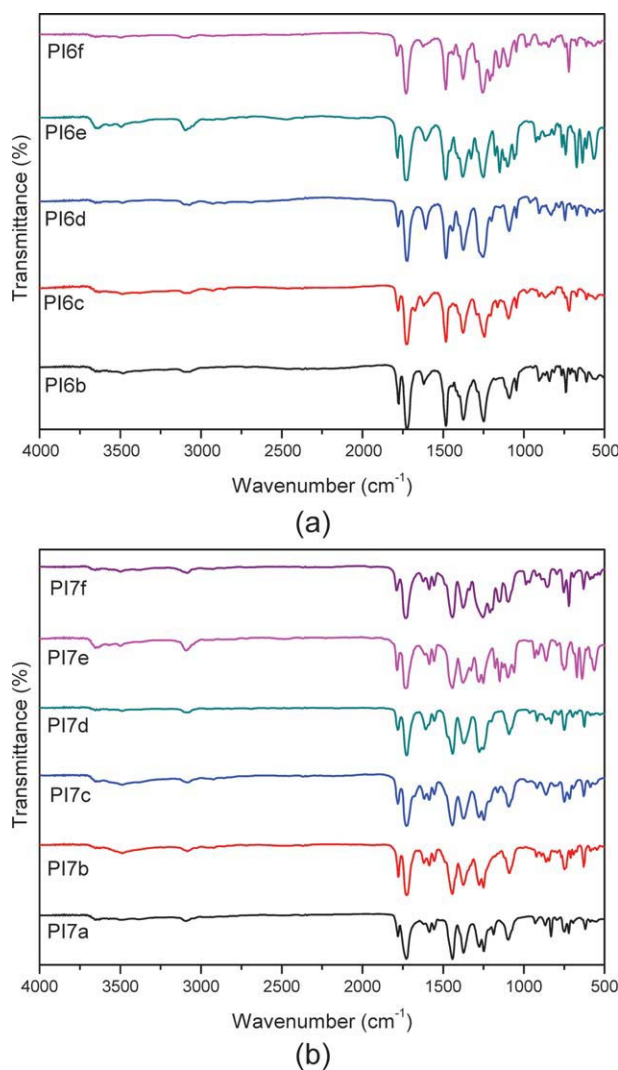**Scheme 2** Synthesis of polyimides **6** and **7** by one-step method.

Figure 7 (a) IR spectra of polyimides **6b–f** and (b) polyimides **7a–f**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Polymer molecular weights and solubilities

The inherent viscosities and molecular weights determined by GPC are reported in Table I. The inherent viscosities, except that of **6b**, were measured
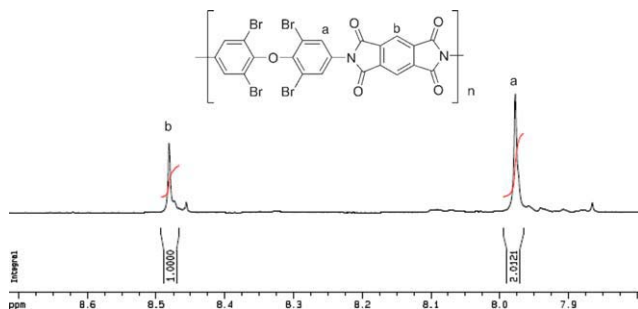

Figure 8 ^{1}H NMR Spectrum of polyimide **7a**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Inherent Viscosities and Molecular Weights of Polyimides 6 and 7

Polyimide	η_{inh} [a] (dL/g)	GPC data [b]		
		M_n [b]	M_w [b]	M_w/M_n [b]
6a	NA [c]	NA [c]	NA [c]	NA [c]
6b	0.98 [d]	NA [c]	NA [c]	NA [c]
6c	0.82	66000	98000	1.48
6d	0.85	100000	147000	1.46
6e	0.35	20000	40000	1.99
6f	0.37	26000	51000	1.97
7a	0.33	14000	23000	1.60
7b	0.99	NA [c]	NA [c]	NA [c]
7c	0.44	22000	45000	2.04
7d	0.49	31000	62000	2.01
7e	0.31	17000	34000	1.99
7f	0.39	29000	48000	1.64

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30°C.
[b] By GPC in DMAc (relative to polystyrene standards).
[c] Insoluble in solvent.
[d] Measured at a polymer concentration of 0.5 g/dL in *m*-cresol at 30°C.

at the polymer concentration of 0.5 g/dL in NMP at 30°C. The GPC measurements were conducted by using DMAc as the eluent and calibrated by polystyrene standards. The inherent viscosities of polyimides **6e** and **6f**, derived from DB-ODA (**4**) and DSDA and 6FDA, were 0.35 and 0.37 dL/g, respectively. These values are not high when compared with those of conventional soluble polyimides. Polyimides **6b**, **6c**, and **6d** exhibited high inherent viscosities ranging from 0.82 to 0.98 dL/g. The inherent viscosities of polyimides **7** showed similar results. Polyimides **7e** and **7f**, prepared from TB-ODA (**5**) and DSDA and 6FDA, had low inherent viscosities of 0.31 and 0.39 dL/g, respectively. The inherent viscosities of polyimides **7b**, **7c**, and **7d** ranged from 0.44 to 0.99 dL/g. These inherent viscosities correspond to the number-averaged molecular weights (Mn) of 14,000 to 100,000, determined by GPC with polystyrene standards. All of these polyimides, except **6a**, can be cast or spin-coated into free-standing film in adequate solvents.

Table II shows the solubilities of polyimides **6** and **7** in seven different solvents at the concentration of 20 mg/mL. Polyimide **6a**, precipitated during polymerization, was insoluble in all test solvents. Polyimide **6b** can be only dissolved in *m*-cresol. Polyimides **6c**, **6d**, and **6f** were soluble in DMAc, DMSO, NMP and *m*-cresol at room temperature. Similarly, polyimide **7b** can be only dissolved in NMP and *m*-cresol. Polyimides **7c**, **7d**, **7e**, and **7f** were soluble in THF, DMF, DMAc, DMSO, NMP, and *m*-cresol at room temperature. Polyimides **6f** and **7f** can be even dissolved in acetone at room temperature at the test

TABLE II
Solubility of Polyimides 6 and 7

Polyimide	Solvent[b]						
	Acetone	THF	DMF	DMAc	DMSO	NMP	m-cresol
6a	+−	+−	+−	+−	+−	+−	+−
6b	−[a]	−	−	S	−	+−	++
6c	s	+−	+	++	++	++	++
6d	−	+−	+−	++	++	++	++
6e	−	+−	++	++	++	++	+−
6f	++	++	++	++	++	++	++
7a	−	++	++	++	++	++	−
7b	−	+−	−	+−	−	++	++
7c	−	++	++	++	++	++	++
7d	−	++	++	++	++	++	++
7e	−	++	++	++	++	++	++
7f	++	++	++	++	++	++	++
PMDA-ODA[c]	NA[d]	−	−	−	−	−	−
BPDA-ODA[c]	NA[d]	−	−	−	−	−	−
BTDA-ODA[c]	NA[d]	−	−	−	−	−	−
ODPA-ODA[c]	NA[d]	−	−	−	−	+	+
DSDA-ODA[c]	NA[d]	−	−	−	−	+	+
6FDA-ODA[c]	NA[d]	−	++	+	+	++	+

[a] The solubility was determined by using 20 mg of sample in 1 mL of stirred solvent. ++ = soluble at room temperature; + = soluble on heating; +− = partially soluble on heating; S = swelling; − = insoluble even on heating.
[b] THF: tetrahydrofuran; DMF: N,N-dimethylformamide; DMAc: N,N-dimethylacetamide; DMSO: dimethyl sulfoxide; NMP: N-methyl-2-pyrrolidone.
[c] From ref. 42, the test concentration was 10 mg of sample in 1 mL of stirred solvent.
[d] Not available.

concentration. It is well known that aromatic polyimides, especially those derived from rigid dianhydride, such as pyromellitic dianhydride (PMDA), show very poor solubility in common organic solvents. Therefore, it is quite a challenge for any chemical structure modifications to tackle this problem. It is surprising that polyimide **7a**, prepared from TB-ODA (**5**) and PMDA, though precipitated during polymerization in m-cresol, exhibited very good solubility. It was soluble in THF, DMF, DMAc, DMSO, and NMP even at room temperature. Table II also indicates that polyimides **7** containing four bromide substituents showed even better solubilities than polyimides **6** containing two bromide substituents. For example, polyimide **6a** was insoluble in all test solvents, whereas polyimide **7a** was soluble in various solvents. In addition, polyimide **6b** can be only dissolved in m-cresol, while polyimide **7b**, with similar inherent viscosity, was soluble in five different solvents. Compared with polyimides derived from 4,4′-ODA and corresponding dianhydrides (Table II), 42 polyimides **6** and **7** showed enhanced solubilities in all test solvents. The improvement in solubility might be resulted from the flexible ether linkage on the polyimide backbone combined with the bulky bromide substituents. These effects would hinder intermolecular packing and increase the free volume, solubility is thus improved accordingly.

Thermal properties

The thermal stability of polyimides **6** and **7** were evaluated by TMA and TGA. The results, including glass transition temperatures (Tg), coefficients of thermal expansion (CTE), decomposition temperatures at 5% ($T_{5\%}$) and 10% ($T_{10\%}$) weight loss, and residual weight percent (R_{w800}) at 800°C, are summarized in Table III. The glass transition temperature of polyimide **6a** cannot be measured because of the poor solubility in all test solvents. For polyimides **6b–f**, the Tgs ranged from 251 to 299°C. The glass transition of polyimide **7a** cannot be detected at the temperature lower than 350°C. For polyimides **7b–f**, the Tgs ranged from 283 to 328°C. The effect of different dianhydrides on the Tgs depends on the chain rigidity. As usual, polyimides derived from ODPA with flexible ether linkage, such as **6d** and **7d**, showed lower Tgs. The Tgs of polyimides **7b–f** were higher than those of polyimides **6b–f** when the same dianhydrides were used. This might be resulted from the fact that polyimides **7** containing 2,2′,6,6′ tetrabromo-substituted moiety have higher rotation energy than polyimides **6** containing 2,2′ dibromo-substituted moiety. For the same reason, polyimides **6** and **7** exhibited comparable or higher glass transition temperatures than polyimides derived from 4.4′-ODA and corresponding dianhydrides (Table III).[43,44] Therefore, the good solubilities of

TABLE III
Thermal Properties of Polyimides 6 and 7

Polyimide	T_g[a] (°C)	CTE[b] (µm/m°C)	$T_{5\%}$[c] (°C)	$T_{10\%}$[c] (°C)	R_{W800}[c] (%)
6a	NA[d]	NA[d]	522	553	45
6b	275	41	527	552	44
6c	296	47	442	500	36
6d	251	55	532	554	49
6e	281	60	483	523	57
6f	299	53	496	517	44
7a	ND[e]	42	501	539	29
7b	287	39	534	563	52
7c	323	58	455	484	39
7d	283	54	499	537	34
7e	328	46	508	531	44
7f	303	62	509	549	47
PMDA-ODA	362[f]	–	–	601[i]	54
BPDA-ODA	290[g]	–	567[h]	600[i]	63
BTDA-ODA	271[g]	–	492[h]	579[i]	56
ODPA-ODA	260[g]	–	493[h]	577[i]	57
DSDA-ODA	295[g]	–	–	542[i]	54
6FDA-ODA	296[g]	–	510[h]	538[i]	56

[a] Measured by TMA (tension mold) at a heating rate of 10°C/min.
[b] Average values between 50 and 150°C.
[c] Measured by TGA at a heating rate of 10°C/min in nitrogen.
[d] Insoluble in solvent.
[e] Not Detectable.
[f] From ref. 43 measured by DSC at a heating rate of 10°C/min.
[g] From ref. 44 measured by DSC at a heating rate of 30°C/min.
[h] From refs. 45 and 46, measured by TGA at heating rate of 10°C/min.
[i] From ref. 47, measured by TGA at heating rate of 20°C/min.

polyimides **6** and **7** were achieved without deteriorating their thermal stability. It is well known that the Tgs are closely related to the chain rigidity and free volume in the polymer system. Apparently, the bromide substituents stiffen the chain more than the unsubstituted counterparts. The more or larger substituents are expected to be more effective in hindering chain rotation. However, it is surprising that such rigid systems are more soluble in common organic solvents. This might be due to the fact that the free volume, generated by the loose packing of the bromide-substituted moieties, allows small solvent molecules to penetrate into the polymer chains, but it is not larger enough for the rigid segments to move. More experiments, such as an experimental determination of free volume, should be carried out to test this hypothesis.

The coefficients of thermal expansion (CTEs) determined by TMA at temperature between 50 and 150°C are summarized in Table III. The CTE of poly-

imide **6a** cannot be measured due to its poor solubility. The other polyimides exhibited CTEs between 39 and 62 µm/m°C. Polyimides containing rigid PMDA and BPDA moieties, such as **6b**, **7a**, and **7b**, showed lower CTEs.

The thermal degradation temperatures (at 5 and 10% weight loss) and residual weight percent at 800°C (R_{w800}) determined by TGA are summarized in Table III. Polyimides **6** and **7** had $T_{5\%}$ and $T_{10\%}$ in 442–534 and 484–563°C, respectively. Their R_{w800} ranged from 29 to 57%. Among them, polyimides containing BTDA moiety, such as **6c** and **7c**, showed lowest degradation temperatures both at 5 and 10% weight loss. The lower degradation temperatures compared with those of polyimides derived from 4,4'-ODA and corresponding dianhydrides might be resulted from the presence of weaker C—Br bond. However, these polyimides still exhibited good thermal stability without any significant weight loss up to 400°C.

Optical properties

The optical properties of polyimides **6** and **7** were characterized by their transparency, refractive indices, and birefringence. Table IV summaries the results. The transparency of polyimide films was investigated by UV-Visible spectroscopy as shown in Figure 9. Two quantities, the wavelengths of the transmission onset and 80% transmission, were used to evaluate the transparency of the films. The smaller wavelength for the transmission onset and the 80% transmission indicates the more transparent for the polyimide film. The transmission onset and 80% transmission of polyimides **6b–f** and **7a–f** occurred at wavelength of 312–446 and 404–682 nm, respectively. They exhibited colorless to yellow color. Conventional polyimides are known for their yellow-orange color. The color has been postulated to be resulted from the formation of charge transfer complexes.[1,48,49] The complexes are thought to form either by intermolecular charge transfer via donor-acceptor interaction or by intramolecular charge transfer from the upper filled π-orbital of the diamine component to the vacant π-orbital of the imide ring, which is facilitated by conjugation between the diamine and imide moieties. Due to the loose packing resulted from the ether linkage and the bromide substituents on the 2,2' or 2,2',6,6' positions of 4,4'-ODA, the intramolecular and intermolecular charge transfer interactions should also be hindered. Polyimide **7a** derived from rigid PMDA showed yellow color, whereas polyimides **6f** and **7f** derived from 6FDA showed the lightest color as expected.

The refractive indices of polyimides **6b–f** and **7a–f** are shown in Table IV. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices ranged from 1.6121

TABLE IV
Optical Properties of Polyimides 6 and 7

Polyimide	$\lambda_{onset}{}^a$ (nm)	$\lambda_{80\%}{}^a$ (nm)	d^b (µm)	Refractive indices and birefringence			
				$n_{TE}{}^c$	$n_{TM}{}^d$	$n_{av}{}^e$	Δn^f
6b	390	472	2.8	1.7070	1.6712	1.6952	0.0358
6c	373	564	11.8	1.6812	1.6616	1.6747	0.0196
6d	351	454	8.5	1.7002	1.6751	1.6919	0.0251
6e	379	632	12.0	1.6803	1.6651	1.6752	0.0152
6f	312	404	18.5	1.6121	1.6023	1.6088	0.0098
7a	446	682	5.0	1.7018	1.6691	1.6910	0.0327
7b	372	605	12.0	1.7219	1.6774	1.7072	0.0445
7c	379	581	12.0	1.6846	1.6636	1.6776	0.0210
7d	362	485	7.5	1.7020	1.6784	1.6942	0.0236
7e	394	609	13.0	1.6866	1.6697	1.6810	0.0169
7f	335	414	12.0	1.6181	1.6002	1.6122	0.0179
PMDA-ODA^g	-	-	9 ± 3	1.7163	1.6322	1.6883	0.0841
BPDA-ODA^g	-	-	9 ± 3	1.7209	1.6909	1.7109	0.0300
6FDA-ODA^g	-	-	9 ± 3	1.5942	1.5868	1.5917	0.0074

^{a} Measured by UV-Visible spectroscopy with film thickness 5–10 µm.
^{b} d: film thickness for refractive index measured.
^{c} n_{TE}: the in-plane refractive index.
^{d} n_{TM}: the out-of-plane refractive index.
^{e} n_{av}: average refractive index $[(2n_{TE}{}^2 + n_{TM}{}^2)/3]^{1/2}$.
^{f} Δn: n_{TE} - $n_{TM.}$
^{g} From ref. 51, measured using a prism coupler (Metricon,PC-2000) at a wavelength of 633 nm at room temperature.

to 1.7219 and 1.6002 to 1.6784, respectively. The average refractive indices, calculated based on the equation mentioned in the experimental section, were from 1.6088 to 1.7072. Refractive index was related to the polarizability, the van der Waals volume and the packing factor of the polymer chains as shown by the modified Lorentz-Lorenz equation proposed by Ando and coworker.[50] From this equation, refractive index increases as the ratio of the polarizability to van der Waals volume increases. In addition, the denser the polymer chains adapt to pack themselves (larger packing factor), the higher the refractive index is. When the same diamine was used, polyimides containing BPDA, such as **6b** and **7b**, had the highest refractive indices. For example, polyimide **7b** derived from TB-ODA (**5**) and BPDA had the highest refractive index 1.7072. Ando and coworkers pointed out that polyimides containing BPDA have looser chain packing than the corresponding polyimides containing PMDA. However, their ratio of polarizability to the van der Waals volume is significantly larger enough to compensate loose chain packing. Thus, polyimides derived from BPDA had higher refractive indices than polyimides derived from PMDA.[50] The result that the refractive index of **7b** is higher than that of **7a** is consistent with their proposal. On the contrary, polyimides **6f** and **7f** derived from 6FDA had the lowest values, 1.6088 and 1.6122, respectively. This is attributed to the less polarizable carbon-fluorine bond and the

large molar volume of the trifluoromethyl group. From Table IV, it also shows that, except BPDA-ODA polyimide, the refractive indices are slightly higher when polyimides contain more bromides. For example, the refractive indices of 6FDA-ODA polyimide, **6f** and **7f** were 1.5917, 1.6088, and 1.6122, respectively. However, the bromide effect on the refractive indices of polyimides was not conspicuous. As proposed by modified Lorentz-Lorenz equation, the refractive indices are a combined effect resulted not only from polarizability but from van der Waals volume and polymer chain packing as well.[50] Bromide substituents on the 2,2′ or 2,2′,6,6′ positions of 4,4′-ODA moieties in polyimides **6** and **7** might increase the polarizability, however, the chain packing is thus disrupted. Therefore, incorporating bromides alone is not sufficient to increase the refractive indices of polyimides significantly. The improved solubilities of polyimides **6** and **7** might be the indication of loose chain packing.

The values of birefringence for the polyimides **6b–f** and **7a–f**, taken as the difference between in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, ranged from 0.0445 to 0.0098. Due to the in-plane orientation of polyimide chains, the in-plane refractive indices were always larger than out-plane ones. In-plane orientation has been shown to be more pronounced for polyimides with higher chain rigidity.[22,52] Polyimides **6b** and **7b** derived from BPDA exhibited higher birefringence, while polyimides **6f**
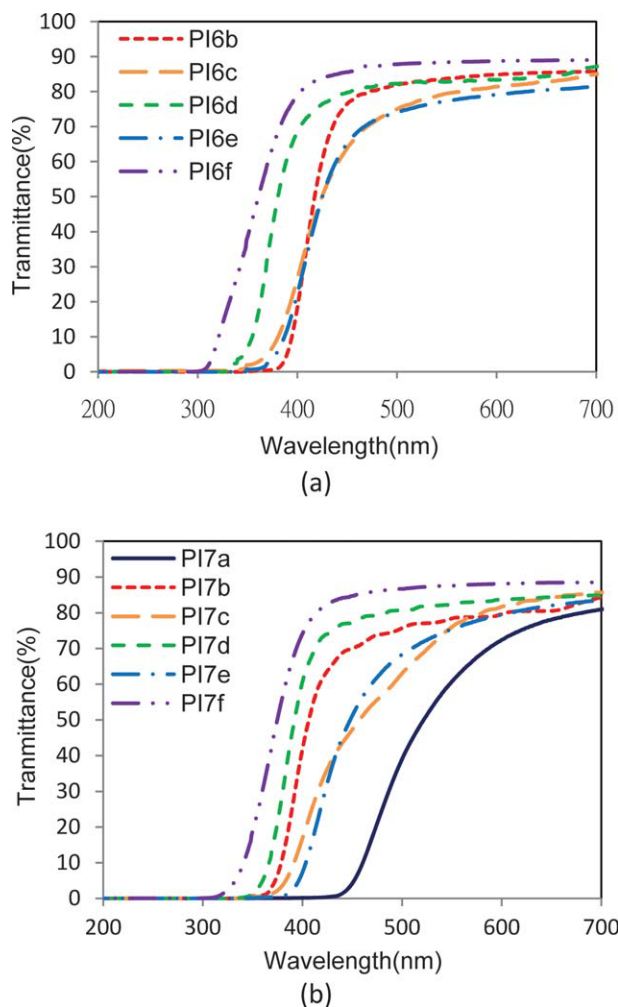
Figure 9 (a) UV-Visible spectra of polyimides **6b–f** and (b) polyimides **7a–f**. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

and **7f** derived from 6FDA showed lower birefringence.

CONCLUSIONS

Two new aromatic diamines DB-ODA (**4**) and TB-ODA (**5**) were prepared by oxidation, bromination and reduction of 4,4′-oxydianiline (4,4′-ODA). Oxidation would assure the following bromination occurring at the 2,2′ and 2,2′,6,6′ positions. Pure DB-ODA (**4**) and TB-ODA (**5**) were obtained by using 2.1 and 5 equivalents of NBS, respectively. Polyimides derived from these new diamines exhibited enhanced solubilities compared with polyimides derived from 4,4′-ODA. Polyimides **7** showed better solubilities than polyimides **6**. This might be due to the loose chain packing resulted from more bromide substituents. Polyimide **7a** derived from rigid PMDA and TB-ODA (**5**) was even soluble in THF,

DMF, DMAc, DMSO, and NMP. These polyimides also exhibited good thermal stability. Their glass transition temperatures were comparable or higher than those of polyimides derived from 4,4′-ODA. Polyimides **7** containing tetrabromo moieties had higher Tgs than polyimides **6** containing dibromo moieties. Polyimides **7** containing more bromides showed slightly higher refractive indices than polyimides **6**. The effect of incorporating more polarizable bromide substituents on increasing the refractive indices might be suppressed by the loose chain packing resulted from the bromide substituents.

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