Highly Transparent and Organosoluble Polyimides Derived from 2,2′-Disubstituted-4,4′-Oxydianilines

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ABSTRACT: To improve the optical transparency and organosolubility of aromatic polyimides derived from 4,4′-oxydianiline (4,4′-ODA), two new aromatic diamines, 2,2′-diiodo-4,4′-oxydianiline (DI-ODA) and 2,2′-bis[(p-tri-fluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA) were synthesized by using 4,4′-ODA as a starting material. Novel polyimides were prepared from these two diamines with various commercially available aromatic dianhydrides via a one-step high-temperature polycondensation procedure. Most of these polyimides showed enhanced solubility in common organic solvents compared with those corresponding polyimides derived from 4,4′-ODA. Especially, polyimide derived from BTFP-ODA and rigid pyromellitic dianhydride (PMDA) was also soluble in DMF, DMAc, DMSO, NMP, and m-cresol at room temperature. These polyimides had inherent viscosities from 0.41 to 1.26 dLg^{-1} in NMP or m-cresol at 30°C. Transparent, flexible, and tough films can be obtained by casting from their DMAc or m-cresol solutions. These films had the UV onset wavelengths in the range of 347–391 nm and the wavelengths at 80% transmission of 445–544 nm, indicating high optical transparency. They also exhibited good thermal stability with glass transition temperatures in the range of 260–327°C. The decomposition temperatures of these polyimides at 5% weight loss under nitrogen were 429–609°C. Because of the weak carbon-iodine bond, polyimides derived from DI-ODA decomposed at lower temperatures than polyimides derived from BTFP-ODA. The effects of the substituents at the 2 and 2′ positions of 4,4′-ODA on the properties of polyimides are also discussed. High optical transparency and good solubility combined with high thermal stability make these polyimides potential candidates for soft electronics applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3159–3170, 2011

Key words: polyimides; synthesis; solubility; optical transparency; thermal stability

INTRODUCTION

Aromatic polyimides are widely used in the aerospace and microelectronic industry in the forms of films and moldings because of their excellent thermal stability, chemical resistance, and electric properties. Other applications such as adhesives, gas separation membranes, composite matrices, coatings, and foams have also been extensively investigated.[1–4] Despite the versatile applications, most polyimides have high melting temperatures or softening temperatures and limited solubility in most organic solvents. Therefore, the processing of the polyimides is generally carried out via their soluble poly(amic acid) precursors, which are cast onto various substrates and then converted into polyimide films by thermal imidization. This process has severe inherent limitations such as the emission of volatile by-product during curing and poor stability of the poly(amic acid) precursors during storage. Besides, the high temperature (>300°C) and sophisticated heating cycle required during thermal imidization would also hinder their applications. Polyimides that are soluble in organic solvents may be prepared by the so called one-step method. This method involves mixing an equal molar amount of the dianhydride and diamine in a high boiling-point organic solvent at a temperature around 200°C. Under these conditions, chain growth and imidization essentially occur spontaneously.[5] Meanwhile, wholly aromatic polyimides often have strong absorption in the visible light region observed from their UV-Visible spectra and exhibit yellow to orange colors. This is resulted from their high aromaticity and the formation of the intermolecular charge transfer complex (CTC).[6–8] These effects are also responsible for the poor solubility of polyimides. However, high optical transparency together with good solubility in common organic solvents is also one of the most attractive properties of polyimides for optical applications. To overcome these problems, many attempts have been focused on the synthesis of soluble and optically transparent polyimides without sacrificing their excellent thermal stability. The main concept behind these approaches is to reduce the

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intermolecular interactions (i.e., CTC formation) by disrupting the chain packing. The strategies include the incorporation of the flexible linkages, bulky side groups and asymmetrical or noncoplanar structures into polyimides.[9–17] For example, one successful approach to enhance solubility without sacrificing backbone rigidity and linearity has involved the polymerization of 4,4′-diamino-2,2′-disubstituted biphenyls with aromatic dianhydrides.[18,19] The steric repulsion of the substitutents at the 2 and 2′ positions of the biphenyl moieties twists the rings dramatically out-of-plane.[20] The resulted twisted, noncoplanar conformation inhibits chain packing and thus hinders the formation of intermolecular charge-transfer complexes. The severe twist also breaks up the conjugation along the polyimide backbone. These effects contribute to a dramatic reduction in color. In addition, the introduction of trifluoromethyl groups is also proved to be effective. It has been demonstrated that the introduction of bulky trifluoromethyl group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lower dielectric constant, which was attributed to the low polarizability of the C—F bond and the increase in free volume.[21–28]

Among those commercially available aromatic diamines, 4,4′-ODA is widely used to prepare polyimides such as Kapton films. However, most polyimides derived from 4,4′-ODA and aromatic dianhydrides are insoluble in common organic solvents and exhibit deep yellow colors. Apparently, ether linkage alone is not sufficient to improve the solubility of polyimides. In this study, two new aromatic diamines, 2,2′-diiodo-4,4′-oxydianiline (DI-ODA 4) and 2,2′-bis[p-(trifluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA 5), were synthesized by using 4,4′-ODA as a starting material. These diamines contain ether linkages and bulky iodide or p-trifluoromethylphenyl substituents. Novel polyimides (6a ∼ f and 7a ∼ f) were prepared by one-step polycondensation with various aromatic dianhydrides. The effects of iodide and p-trifluoromethylphenyl groups on solubility, thermal properties, mechanical properties and optical transparency of the polyimides were investigated in details.

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 purchased from Kriskev Co., dried

at 150°C and sublimated under reduced pressure prior to use. 4,4′-Oxydianiline (4,4′-ODA) was obtained from Kriskev Co. and used as received. m-Cresol (Lancaster Synthesis) was dried with P_2O_5 and distilled under reduced pressure. Other chemicals and solvents were used as received.

Monomers synthesis

Synthesis of p-(trifluoromethyl)phenylboronic acid (1)

To a cold (−78°C) solution containing 4-bromobenzotrifluoride (10.00 g 52.7 mmol) and dry diethyl ether (134 mL), n-butyllithium (30 mL, 1.6M in hexane) was added slowly by syringe under nitrogen. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was then cooled to −40°C and trimethylborate (16 mL) was added. The reaction mixture was warmed to room temperature and stirred for 8 h. The reaction mixture was poured into 2N hydrochloric acid (215 mL) and stirred at room temperature for 30 min. The aqueous phase was separated from organic phase and extracted with dry diethyl ether (50 mL) three times. The combined organic phase was collected and evaporated to dryness. Petroleum ether (45 mL) and water (4.5 mL) were added. The solution was stirred for 1 h during which time a white crystalline precipitate was formed, which was collected by filtration and air-dried at room temperature for 24 h to afford 6.80 g (80% yield) of white needle-like crystals, mp: 233 ∼ 237°C. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.69 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 8.36 (broad, 2H, -B (OH)$_2$).

Synthesis of 4,4′-dinitrodiphenylether (2)

To a 500-mL, three-necked round-bottomed flask, 4,4′-ODA (6.00 g, 30.0 mmol), glacial acetic acid (180 mL), 30% hydrogen peroxide (54 mL) and concentrated sulfuric acid (2.4 mL) were added and heated at 85°C overnight. The reaction mixture was cooled to room temperature and poured into ice water (500 mL). The precipitate was collected, washed with water several times and dried at 90°C under reduced pressure overnight to afford 3.85 g (49% yield) of yellow powders, mp: 144 ∼ 146°C. The 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 (125 MHz, DMSO-d_6, δ, ppm): 119.6, 126.2, 143.7, 160.4.

Synthesis of 2,2′-diiodo-4,4′-dinitrodiphenylether (3)

To a 250-mL, three-necked round-bottomed flask, concentrated sulfuric acid (100 mL), water (10 mL), 4,4′-dinitrodiphenylether 2 (2.00 g, 7.69 mmol) and

N-iodosuccinimide (NIS) (3.63 g 16.13 mmol) 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 3.38 g of product (93% yield). The product was used without further purification for the next step. The product can be recrystallized from acetone/water to afford 2.70 g (64% yield) of off-white crystals, mp: 175 ~ 177°C. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 6.92 (d, J = 8.9 Hz, 2H), 8.25 (dd, J$_1$ = 2.7 Hz, J$_2$ = 8.9 Hz, 2H), 8.82 (d, J = 2.7 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$, δ, ppm): 89.5, 118.8, 125.8, 135.0, 144.4, 159.6. EIMS(m/z): calcd for C$_{12}$H$_6$I$_2$N$_2$O$_5$, 511.8; found, 511.9 [M]$^+$. Anal. calcd for C$_{12}$H$_6$I$_2$N$_2$O$_5$: C, 28.13; H, 1.18; N, 5.47. Found: C, 28.87; H, 1.52; N, 5.42.

Synthesis of 2,2′-diiodo-4,4′-oxydianiline (DI-ODA 4)

To a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer were added 2,2′-diiodo-4,4′-dinitrodiphenylether 3 (2.00 g, 3.91 mmol), concentrated hydrogen chloride (9.8 mL) and ethanol (40 mL). Tin powder (1.92 g) was slowly added and the reaction mixture was heated at reflux for 3 h. The reaction mixture was then poured into ice water and neutralized with aqueous NaOH solution to pH = 12. Diethyl ether was 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 ethanol to afford 0.78 g (60% yield) of off-white needle-like crystals, mp: 193 ~ 195°C. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 5.02 (s, 4H), 6.43 (d, J = 8.7 Hz, 2H), 6.51 (dd, J$_1$ = 2.6 Hz, J$_2$ = 8.7 Hz, 2H), 7.06 (d, J = 2.6 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$, δ, ppm): 88.8, 114.8, 118.6, 123.4, 146.0, 146.8. EIMS(m/z): calcd for C$_{12}$H$_{10}$I$_2$N$_2$O, 451.9; found, 451.7 [M]$^+$. Anal. calcd for C$_{12}$H$_{10}$I$_2$N$_2$O: C, 31.88; H, 2.23; N, 6.20. Found: C, 31.83; H, 2.62; N, 6.12.

Synthesis of 2,2′-bis[*p*-(trifluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA 5)

To a 250 mL, three-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer and a condenser were added 2,2′-diiodo-4,4′-oxydianiline (DI-ODA 4) (3.00 g, 6.64 mmol) and toluene (75 mL). The reaction mixture was heated to 60°C under nitrogen to become a homogeneous solution. A sodium carbonate aqueous solution (3.10 g, 29.25 mmol, in 15 mL of water) and Pd(PPh$_3$)$_4$ (0.47 g, 0.41 mmol) were added. The solution was vigorously stirred for 30 min under nitrogen. A solution
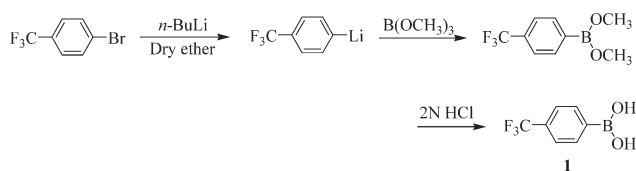
of *p*-(trifluoromethyl)phenylboronic acid 1 (3.03 g, 15.95 mmol) in ethanol (13 mL) was added. The mixture was heated at reflux for 24 h under nitrogen. It was then filtered to remove the insoluble components at room temperature. The filtrate was washed several times with a saturated NaCl aqueous solution and dried with anhydrous magnesium sulfate. The solvents of combined organic phase were removed under reduced pressure. The residue was dissolved in ethanol (60 mL). Concentrated hydrochloric acid (60 mL) was added slowly and the solution was heated to 70°C for 1 h. The precipitate that formed was collected then dissolved in 500 mL of water. The solution was heated to 90°C and filtered to remove the insoluble components. The clear filtrate was neutralized with ammonium hydroxide. The precipitate that formed was collected by filtration, washed with water and recrystallized from a mixture of water and ethanol to afford 1.82 g (56% yield) of off-white crystals, mp: 166 ~ 167°C. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 4.96 (s, 4H), 6.55 (dd, J$_1$ = 8.8 Hz, J$_2$ = 2.5 Hz, 2H), 6.61 (m, 4H), 7.54 (d, J = 8.2 Hz, 4H), 7.69 (d, J = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, DMSO-d$_6$, δ, ppm): 127.8, 127.4, 127.2, 126.9 (Quartet, Ar-CF$_3$), 127.5, 125.4, 123.2, 121.1 (Quartet, CF$_3$), 115.0, 115.4, 119.4, 124.7, 129.4, 130.7, 142.4, 144.5, 144.7. EIMS(m/z): calcd for C$_{26}$H$_{18}$F$_6$N$_2$O, 488.13; found, 488.00 [M]$^+$. Anal. Calcd for C$_{26}$H$_{18}$F$_6$N$_2$O: C, 63.92; H, 3.72; N, 5.74. Found: C, 63.79; H, 4.20; N, 5.56.

Polyimide synthesis

Polyimides 6a ~ f and 7a ~ f were synthesized according to the following procedures. The dianhydride was added to a stirred solution of an equal molar amount of the diamine in the appropriate amount of *m*-cresol (10 w/v %) containing a catalytic amount of isoquinoline under nitrogen at room temperature. The reaction mixture was heated at 200°C for 12 h. During this period of time, 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 120°C for 24 h.

Preparation of polyimide films

Except 6a, the well-dried polyimides were dissolved in DMAc or *m*-cresol (polyimides 6b and 7b) with a solid content of 8% (w/v). The formed clear polyimide solution was filtered through a 0.45-μm Teflon syringe filter to remove any contaminates that might

Scheme 1 Synthesis of *p*-(trifluoromethyl)phenylboronic acid (**1**).

affect the quality of the film. The solution was then cast onto a clean glass. Polyimide films of 30 ∼ 60 µm in thickness were obtained by removing the solvent in an air-circulated oven with the following heating cycle: 50°C/1 h, 80°C/1 h, 120°C/1 h, 170°C/ 1 h, and 220°C/2 h.

Measurements

All melting points were determined on a Melt-Temp capillary melting point apparatus and uncorrected. FT-IR spectra were obtained with a Digilab-FTS1000 FTIR. ^{1}H and ^{13}C NMR were performed on a Bruker Avance-500 spectrometer operating at 500 and 125 MHz, respectively. Mass spectrometry was conducted on a Finnigan TSQ 700 mass spectrometer. Elemental analyses were performed on a Heraeus Vario analyzer. Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g dL^{-1} NMP solution at 30°C. High performance liquid chromatography was performed on a JASCO HPLC system equipped with a UV (254 nm) detector using a Thermo Hypersil column (250 mm × 4.6 mm, particle size 5 µm) with an 80/20 (v/v) acetonitrile/ water mixture as the eluent. 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), using dimethylacetamide (DMAc) as the eluent and calibrated with polystyrene standards. Thermal gravimetric analyses (TGA) were performed in nitrogen with TA TGA Q 500 thermal gravimetric analyzer using a heating rate of 10°C/min. Glass transition temperatures (T_gs) and coefficients of thermal expansion (CTEs) were determined by thermal mechanical analysis (TMA) using 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 a film dimension change versus temperature occurred. The CTE value was taken as the mean of the dimension change between 50 to 150°C. UV-Visible spectra were recorded on a Cary-100 UV-Visible spectrometer at room temperature. The wide-angle X-ray diffraction (WAXD) measurements were carried out on a PANalytical X′ Pert PRO X-ray diffractometer. The tensile properties of the films were measured on a mechanical tester CHUN YEN at a cross-head speed of 5 mm/min at 25°C.

RESULTS AND DISCUSSION

Monomer synthesis

Two new aromatic diamines were synthesized by the reaction routes shown in Schemes 1 and 2. *p*-(Trifluoromethyl)phenylboronic acid **1** was prepared by adding *n*-butyllithium to 4-bromobenzotrifluoride in dry diethyl ether to give aryllithium
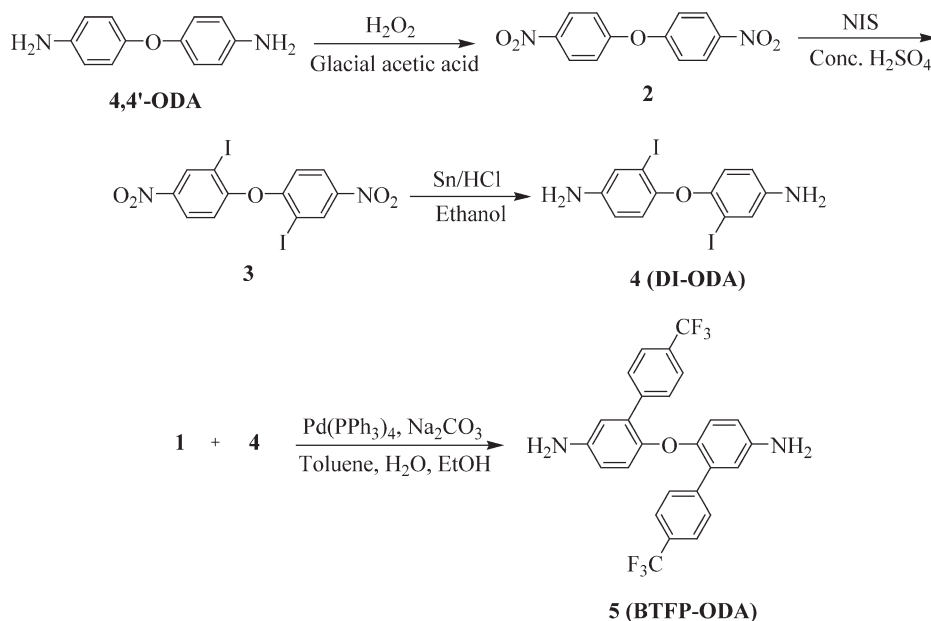
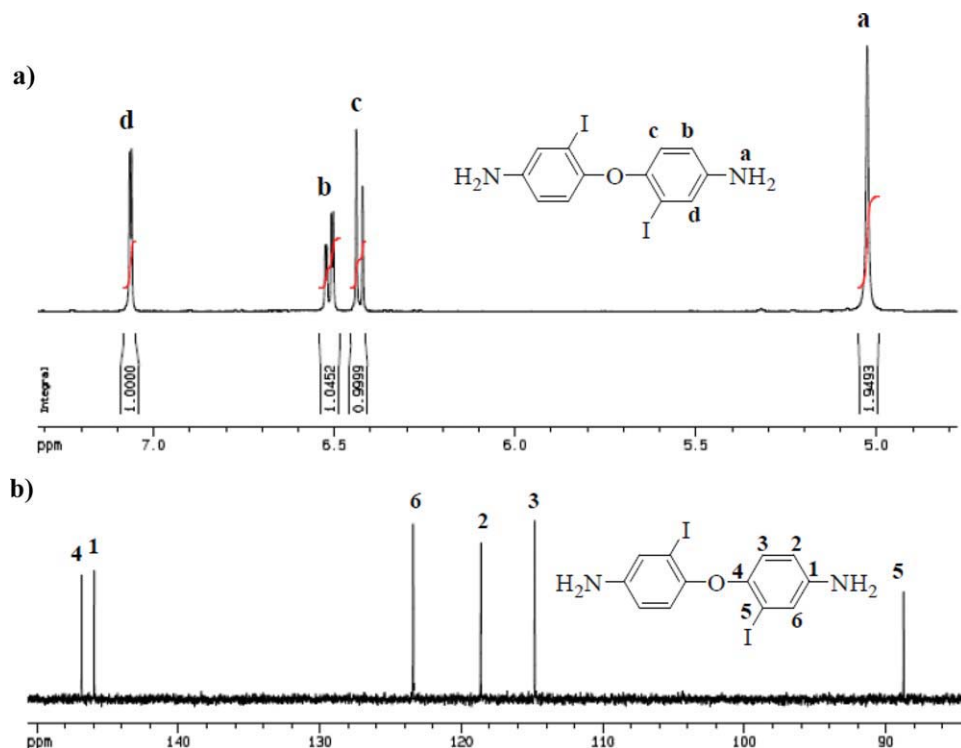**Scheme 2** Synthetic route of DI-ODA (**4**) and BTFP-ODA (**5**).

Figure 1 (a) ^{1}H and (b) ^{13}C NMR spectra of DI-ODA **4** (DMSO-d$_6$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compound, which reacted with trimethylborate then hydrolyzed with 2N HCl aqueous solution. From the ^{1}H NMR spectrum, the presence of one broad absorption peak at 8.33 ppm attributed to OH groups and two doublets at 7.69 and 7.98 ppm attributed to the aromatic protons confirmed the chemical structure.

New diamines, 2,2′-diiodo-4,4′-oxydianiline (DI-ODA **4**) and 2,2′-bis[p-(trifluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA **5**) were synthesized by using 4,4′-ODA as the starting material (Scheme 2). To control the iodination occurring precisely at the 2 and 2′ positions of the diphenylether moiety, 4,4′-ODA was first oxidized by hydrogen peroxide to give nitro compound **2**. It has been reported that the direct bromination of 4,4′-ODA would lead to a mixture containing bromides at 3, 3′, 5 and 5′ positions.[29] The iodination was carried out by using N-iodosuccinimide (NIS) in the presence of concentrated sulfuric acid to gives compound **3**. The iodination took place smoothly despite the presence of electron-withdrawing nitro groups. It indicates that the phenyl rings of this compound are not so electron-deficient as expected. In fact, from HPLC chromatograms and complicated ^{1}H NMR spectra, it can be assumed that up to seven iodides can be attached onto compound **2**, depending on the equivalents of NIS used.[30] It was reported that iodine/ silver sulfate in concentrated sulfuric acid can be used as the iodinating agent for the preparation of

compound **3**.[31] The formed 2,2′-diiodo-4,4′-dinitrodiphenylether **3** was further reduced by tin powder in acidic condition to form 2,2′-diiodo-4,4′-oxydianiline **4**. It is well known that aromatic halides can be easily converted to other functional groups. This new iodide-containing diamine **4** has thus the potential to be further functionalized by using the reactions involving aryl iodide either at dinitro (electron-deficient) or diamino (electron-rich) conditions. Some reactions such as trifluoromethylation, Suzuki cross-coupling, intramolecular Ullmann coupling, nucleophilic substitution and copper-catalyzed carbon-nitrogen coupling[32] are currently investigated in our lab. By doing so, substituents exhibiting opto-electronic functions such as carbazole, triphenylamine, benzimidazole and benzothiazole can be attached onto the 2 and 2′ positions of 4,4′-ODA.

The other new diamine, 2,2′-bis[p-(trifluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA **5**) was prepared from p-(trifluoromethyl)phenylboronic acid **1** and diamine **4** by Suzuki coupling reaction as shown in Scheme 2. Even though electron-donating nature of amino group of aryl iodide combined with the electron-withdrawing trifluoromethyl group in the phenylboronic acid are expected to have a deleterious effect on the coupling reaction according to the proposed reaction mechanism,[33] the reaction was carried out in the presence of 3 mol % of Pd(PPh$_3$)$_4$ and 2 equivalents of an aqueous sodium carbonate solution with 56% yield. It was reported that higher
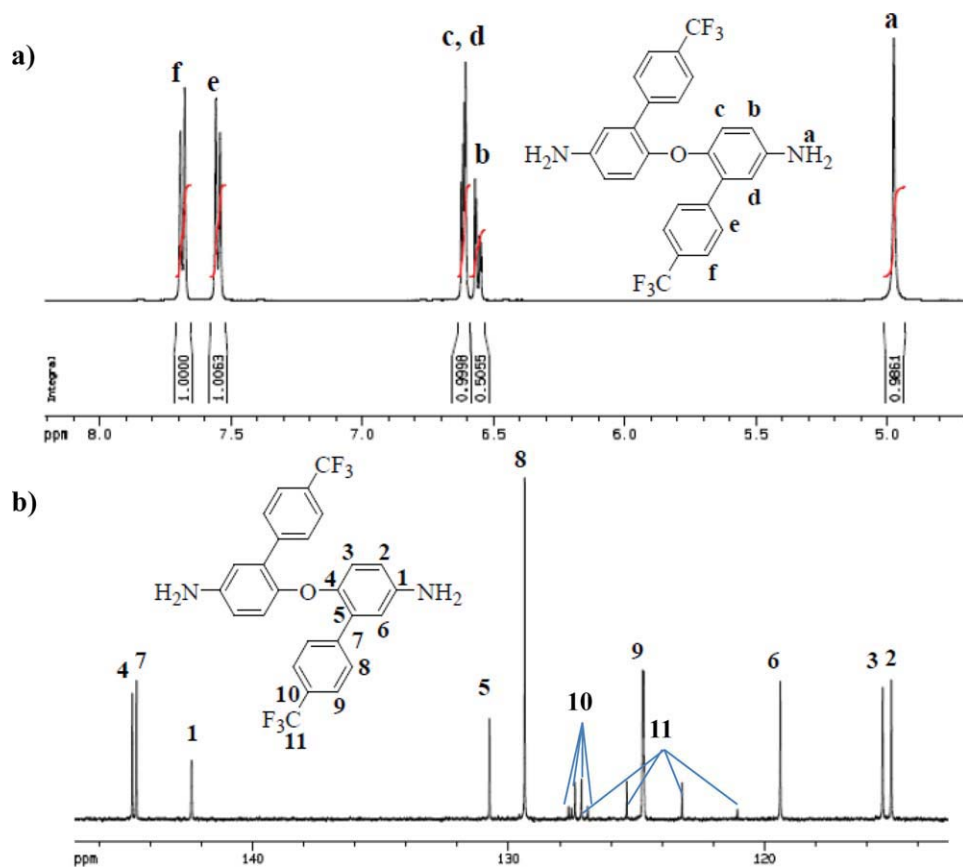
Figure 2 (a) ^{1}H and (b) ^{13}C NMR spectra of BTFP-ODA **5** (DMSO-d$_6$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yields from the cross-coupling reactions can be obtained when the amine was converted to an acetamide.[33] The acetamide derivative of DI-ODA **4** was not very soluble in toluene, the cross-coupling reaction solvent. Therefore, the coupling reaction was carried out without protecting the amino groups.

Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra of diamines **4** and **5**, respectively. Combined with their HMQC spectra as shown in Figure 3, the corresponding peaks were assigned accordingly. The assignments in the NMR spectra and the results from element analysis confirmed the formation of these two diamines.

Polyimides synthesis

Polyimides **6a** ∼ **f** and **7a** ∼ **f** were prepared from diamines **4** and **5** with six commercially available dianhydrides by a one-step polycondensation method as shown in Scheme 3. In this procedure, the diamines and dianhydrides were polymerized in m-cresol at 200°C in the presence of isoquinoline as a catalyst. Throughout the polymerization, except **6a** with rigid PMDA structure, all of the polyimides remained in m-cresol without any premature precipitation. In addition, polyimide **7b** exhibited thermally

reversible gel formation. During polymerization, polyimide **7b** remained in m-cresol. When the reaction mixture was slowly cooled to the room temperature, it became gel at temperature lower than 150°C. The gel became a clear solution when it was heated up to 200°C again. All the polyimides were obtained in quantitative yields after being collected by precipitating in methanol, washing by hot ethanol and drying under reduced pressure. All the polymers exhibited characteristic IR absorption bands at 1780 and 1720 cm^{-1} due to the asymmetric and symmetric stretching of carbonyl groups. The absorption band at 1380 cm^{-1} confirmed the C-N stretching of the imide structure. The representative ^{1}H NMR (DMSO-d$_6$) spectra of polyimides **6e** and **7e** are shown in Figure 4. Because of the formation of electron-withdrawing imide rings, all the peaks of aromatic protons shifted to the downfield region. The aromatic protons in the dianhydride moieties appeared at the farthest downfield region ($>$8.20 ppm) in the spectra. The aromatic protons in diamine moieties appeared in higher field region (between 7.0 and 8.0 ppm) because of the electron-donating aromatic ether linkages. The ^{1}H NMR results combined with the characteristic peaks from their IR spectra confirmed the chemical structures of the polyimides.
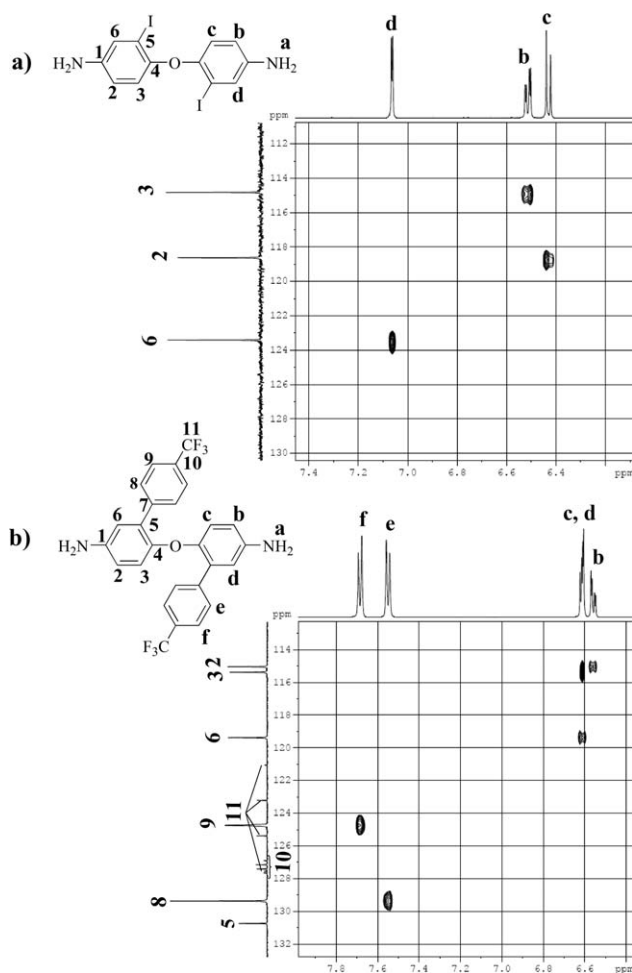
Figure 3 (a) HMQC spectra of DI-ODA **4** and (b) BTFP-ODA **5** (DMSO-d_6).

Properties of polyimides

Molecular weights and solubilities of polyimides 6 and 7

Except **6a, 6b**, and **7b**, the inherent viscosities of all the polyimides were determined in N-methyl-2-pyrrolidone (NMP) with a concentration of 0.5 gdL^{-1} at 30°C, while those of polyimides **6b** and **7b** were measured in m-cresol with the same concentration. The inherent viscosity of polyimide **6a** cannot be obtained because of its poor solubility. These values together with GPC molecular weights of polyimides **6** and **7** are shown in Table I. The inherent viscosities of polyimides **6b** ∼ **f** and polyimides **7a** ∼ **f** were in the range of 0.41–0.90 and 0.53–1.26 dLg^{-1}, respectively. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of polyimides **6** and **7** were 15,000-67,000 and 34,000-97,000 g/mol relative to polystyrene standards, respectively. The polydispersity indices of these polyimides were in the range of 1.34–2.24. Except **6a**, these polyimides can be cast or spin-coated to prepare transparent and flexible films in appropriate solvents.

The solubilities of the polyimides were determined in various organic solvents with the concentration of 20 mg/mL at room temperature. The results are summarized in Table II. Polyimide **6a** derived from PMDA was insoluble in all tested solvents due to its rigid chain structure. Polyimides **6b** and **7b** derived from BPDA were only soluble in m-cresol. The remaining polyimides were soluble in polar organic solvents such as DMAc, DMSO (dimethylsulfoxide), NMP and m-cresol. Polyimides **6f, 7e** and **7f** containing DSDA or 6FDA moieties were even soluble in acetone at room temperature. In general, polyimides derived from rigid PMDA are insoluble in common organic solvents. It is surprising that polyimide **7a** derived from PMDA could exhibit good solubility in polar solvents such as DMF, DMAc, DMSO, NMP, and m-cresol at room temperature and was also soluble in THF upon heating. Compared with polyimides prepared from 4,4′-ODA with the same dianhydrides by a two-step method, polyimides **6** and **7** exhibited excellent solubility as shown in Table II.[34] For example, polyimides prepared from 4,4′-ODA with PMDA, BPDA and BTDA were insoluble in all tested solvents. When ODPA and DSDA was used, 4,4′-ODA-polyimides can be soluble only in hot NMP and m-cresol. The improvement in solubility demonstrated by polyimides **6** and **7** could be resulted from effects of bulky iodide and p-trifluoromethylphenyl substituents. Polymer chain packing is hindered by the presence of these bulky substituents. The increased free volume facilitates the penetration of small solvent molecules into polyimide chains, leading to the excellent solubility. From Table II, it also indicates that polyimides **7** exhibited better solubility than polyimides **6**. For example, when ODPA was used, polyimide **7d** can be dissolved in all tested solvents except acetone at room temperature, while polyimide **6d** was only soluble in high boiling-point, polar solvents such as DMAc, DMSO, NMP and m-cresol. The better solubility of polyimides **7** compared to that of polyimides **6** could be resulted from the more bulky p-trifluoromethylphenyl substituent. This result also confirms the positive effect of bulky substituents on improving the solubility of polyimides.

Morphological structures

The morphological structures of polyimides **6** and **7** were analyzed by Wide-Angle X-ray Diffraction (WAXD). The diffraction patterns of polyimides **6** and **7** were broad without obvious crystalline peaks. It suggests that polyimides **6** and **7** are amorphous in nature. This is possibly attributed to the loose chain packing resulted from the combined effects of ether linkages and bulky iodide and p-trifluoromethylphenyl substituents.
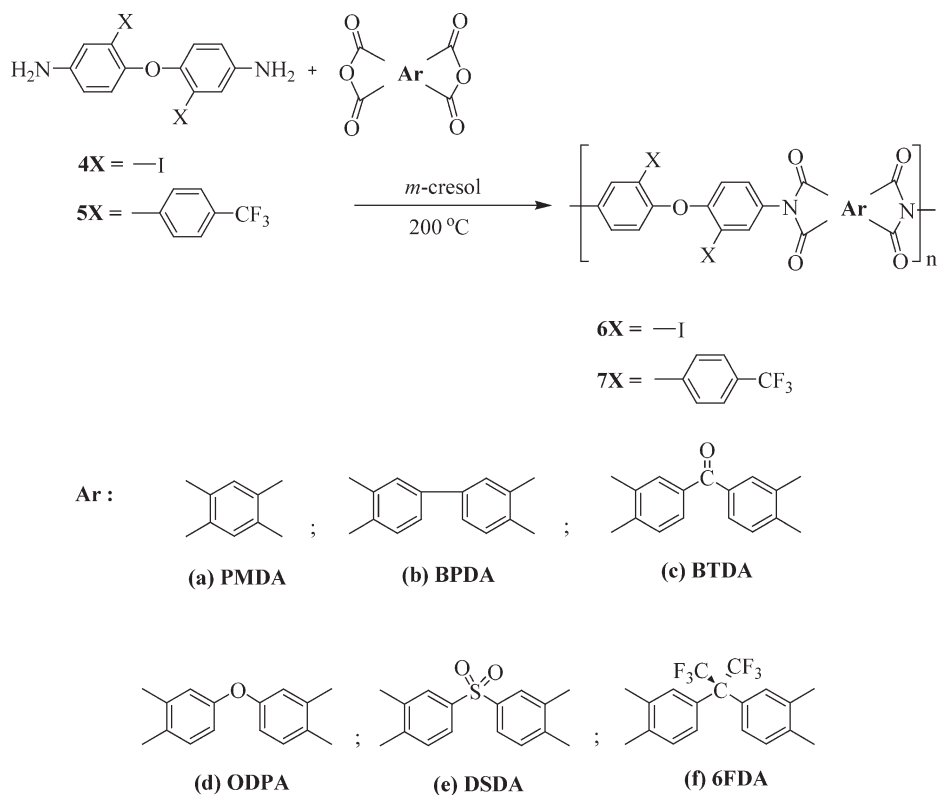
Scheme 3 Synthesis of polyimides **6** and **7** by one-step method.
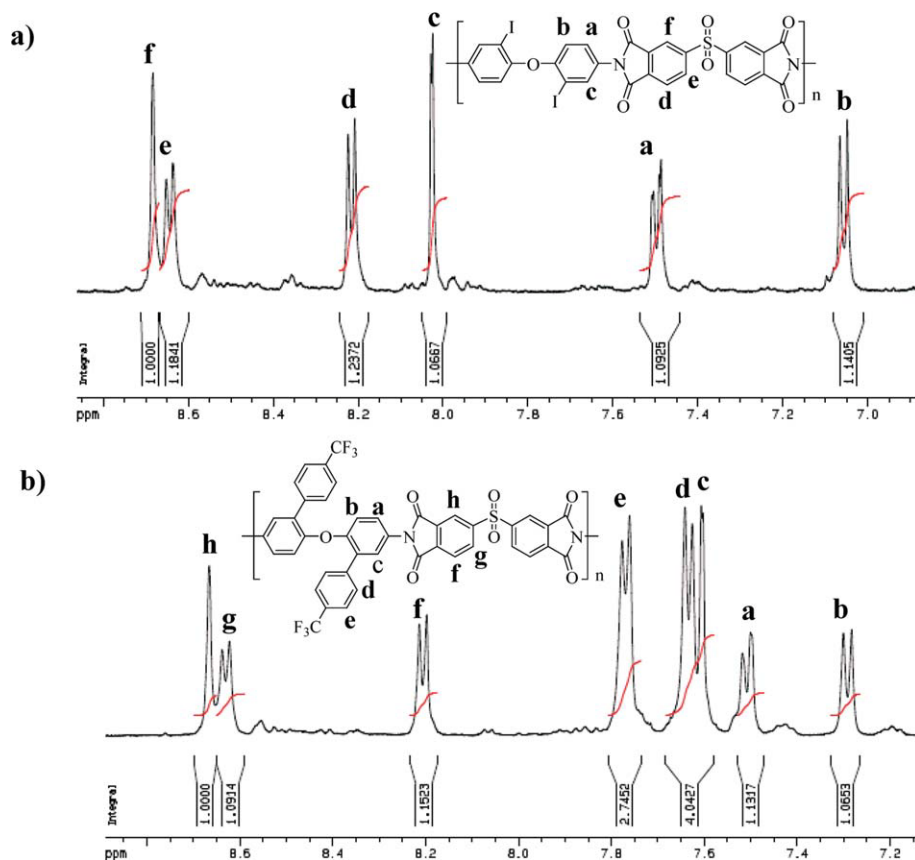

Figure 4 (a) ^{1}H NMR spectra of polyimides **6e** and (b) **7e** (DMSO-d$_6$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

Polyimides	η_{inh}[a] (dL/g)	M_n[c]	M_w[c]	M_w/M_n[c]
6a	NA[d]	NA[d]	NA[d]	NA[d]
6b	0.90[b]	NA[d]	NA[d]	NA[d]
6c	0.69	46,000	70,000	1.53
6d	0.67	67,000	97,000	1.43
6e	0.41	15,000	34,000	2.24
6f	0.51	52,000	80,000	1.52
7a	0.53	23,000	34,000	1.48
7b	1.26[b]	NA[d]	NA[d]	NA[d]
7c	0.81	59,000	79,000	1.34
7d	0.59	47,000	82,000	1.74
7e	0.54	24,000	46,000	1.92
7f	0.74	59,000	96,000	1.63

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

Thermal properties

The thermal properties of polyimides **6** and **7** were evaluated by TMA and TGA. The results, including glass transition temperatures (T_g), 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 T_gs of polyimides **6b** $\sim$ **f** were in the range of 271–327°C and those of polyimides **7a** $\sim$ **f** were in the range of 260–306°C. The effect of different dianhydrides on the Tgs depends on their rigidity. In general, polyimides derived from ODPA with flexible ether linkage, such as **6d** and **7d**, show the lowest Tgs among these polyimides. The T_gs of polyimides **7b** $\sim$ **f** were 10 to 50° (°C) lower than those of polyimides **6b** $\sim$ **f** when the same dianhydrides were used. For example, the T_g of polyimide **6e** is about 51°C higher than that of polyimide **7e** as shown in Figure 5. This might be resulted from the more bulky p-trifluoromethylphenyl substituents of polyimides **7**, which hinder the chain packing and increase the free volume more than iodide substituents of polyimides **6**. The Tgs of polyimides **6** and **7** are comparable to those of polyimides derived from 4,4′-ODA. For example, the Tg of 6FDA-ODA polyimide is 296°C,[35–37] those of polyimides **6f** and **7f** are 295 and 271°C, respectively.

The coefficients of thermal expansion (CTEs) determined by TMA at temperature between 50 and 150°C are summarized in Table III. The CTEs of polyimides **6b** $\sim$ **f** ranged between 35 and 49 ppm/°C. Polyimides **7a** $\sim$ **f** exhibited the CTEs between 44 and 82 ppm/°C. Polyimides containing rigid PMDA and BPDA moieties, such as **6b**, **7a**, and **7b**, showed lower CTEs. The higher CTEs of polyimides **7** compared with those of polyimides **6** can be also attributed to the increased free volume resulted from more bulky p-trifluoromethylphenyl substituents.

TABLE II
Solubility of Polyimides 6 and 7

Polyimides	Solvents[b]						
	Acetone	THF	DMF	DMAc	DMSO	NMP	m-cresol
6a	−[a]	−	−	−	−	−	−
6b	−	−	−	−	−	−	++
6c	−	++	++	++	++	++	++
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 solvent. ++, soluble at room temperature; +, soluble on heating; +−, partially soluble on heating; −, 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. 34, the test concentration was 10 mg of sample in 1 mL of stirred solvent.
[d] Not available.

TABLE III
Thermal Properties of Polyimides 6 and 7

Polyimides	$T_g{}^a$ (°C)	CTE[b] (ppm/°C)	$T_{5\%}{}^c$ (°C)	$T_{10\%}{}^c$ (°C)	$R_{w800}{}^d$ (%)
6a	NA[e]	NA[e]	466	492	37
6b	303	35	462	485	52
6c	327	38	429	452	49
6d	271	47	448	471	39
6e	315	43	437	458	31
6f	295	49	458	485	46
7a	306	44	609	639	62
7b	286	49	603	621	58
7c	278	71	581	609	61
7d	260	73	589	610	57
7e	264	82	534	563	32
7f	271	67	565	582	64
6FDA-ODA	296[f]	—	510[g]	538[h]	45

[a] Measured by TMA (tension mode) at a heating rate of 10°C/min.
[b] Average values between 50 to 150°C.
[c] Measured by TGA at a heating rate of 10°C/min in nitrogen.
[d] Residual weight (%) when heated to 800°C.
[e] Insoluble in solvent.
[f] From Ref. 35, measured by DSC at a heating rate of 30°C/min.
[g] From Ref. 36, measured by TGA at a heating rate of 10°C/min.
[h] From Ref. 37, measured by TGA at heating rate of 20°C/min.

The thermal degradation temperatures ($T_{5\%}$ at 5% and $T_{10\%}$ at 10% weight loss) and residual weight percent at 800°C (R_{w800}) determined by TGA in a nitrogen atmosphere are also summarized in Table III. The decomposition temperatures, $T_{5\%}$ and $T_{10\%}$ of polyimides **6**, were in the range of 429–466°C and 452–492°C, respectively. Polyimides **7** had their $T_{5\%}$ and $T_{10\%}$ between 534–609°C and 563–639°C, respectively. The char yields of these polyimides were in the range of 31–64% in nitrogen at 800°C. The iodide substituted polyimides **6** began to decompose at 100°C lower than the corresponding *p*-trifluoromethylphenyl substituted polyimides **7**. For example, the $T_{5\%}$ of polyimide **6e** is at 437°C while that of polyimide **7e** is 534°C as shown in Figure 5. This is possibly attributed to the lower carbon-iodine bond energy. The chemical bond energies of carbon-iodine, carbon-bromine, carbon-hydrogen and carbon-fluorine are 240, 276, 413, and 441 KJ/mol, respectively.[38] It is concluded that the chemical bond energy of the carbon-halogen bond played an important role in the thermal degradation of polyimides **6** and **7**.

Mechanical and optical properties

Except **6a**, these polyimides can be cast to form transparent and flexible films from *m*-cresol (**6b** and **7b**) and DMAc solution. The tensile properties of these films are summarized in Table IV. The polyimide films had tensile strengths of 38–87 MPa, elongations at break of 4.5–7.9% and initial moduli of 0.9–2.2 GPa. These values are comparable to those of commercial polyimides.

The optical transparency of all the polyimide films (thickness 5–10 μm) was measured using UV-Visible spectroscopy. Two quantities, the wavelengths of the transmission onset (λ_{onset}) and 80% transmission ($\lambda_{80\%}$), were used to evaluate the transparency of the films. The smaller wavelengths for the transmission onset and the 80% transmission indicate higher optical transparency of the polyimide films. Typical UV-Visible transmission spectra of polyimide films **6f, 7a**, and **7f** are shown in Figure 6. The wavelengths of onset and 80% transmission of polyimides **6** and **7** are listed in Table IV. The transmission onset and 80% transmission of polyimides **6b** ∼ **f** and **7a** ∼ **f** occurred at wavelengths of 347–391 and 445–544 nm, respectively. They exhibited colorless to yellow color. Conventional
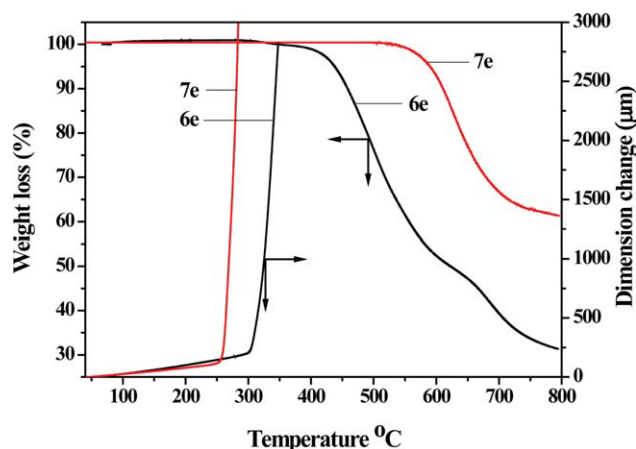

Figure 5 TMA and TGA curves of polyimides **6e** and **7e**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Mechanical and Optical Properties of Polyimides 6 and 7

Polyimides	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)	λ_{onset} (nm)[a]	$\lambda_{80\%}$ (nm)[a]
6a	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
6b	87	7.6	2.0	378	544
6c	67	7.3	1.6	373	543
6d	39	7.9	0.9	361	526
6e	54	7.9	1.1	381	532
6f	55	7.6	1.1	347	505
7a	61	5.7	1.8	391	523
7b	55	5.2	1.7	379	520
7c	42	5.6	1.3	374	519
7d	56	7.8	1.2	364	472
7e	38	4.8	2.2	390	480
7f	38	4.5	1.2	354	445
PMDA-ODA	—	—	—	444[c]	—
BPDA-ODA	—	—	—	421[c]	—
BTDA-ODA	—	—	—	424[c]	—
ODPA-ODA	—	—	—	386[c]	—
DSDA-ODA	—	—	—	416[c]	—
6FDA-ODA	—	—	—	387[c]	—

[a] Measured by UV-Visible spectroscopy with film thickness 5–10 μm.
[b] Insoluble in solvent.
[c] From Ref. 34, measured by UV-Visible spectroscopy with film thickness 31–52 μm.

polyimides are known for their yellow-orange color. The color has been postulated to be resulted from the formation of charge transfer complexes.[39,40] 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. Polyimides 6 and 7 containing iodide and p-trifluoromethylphenyl substituents at the 2 and 2′ positions of 4,4′-ODA revealed an significantly enhanced optical transparency in comparison with that of the corresponding polyimides derived from 4,4′-ODA (Table IV and Fig. 6).[34,41] Because of the loose packing resulted from the ether linkage and the bulky iodide and p-trifluoromethylphenyl substituents at the 2 and 2′ 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, while polyimides 6f and 7f derived from 6FDA showed the lightest color as expected. When the same dianhydride was used, polyimides 7 showed lighter color than polyimides 6. This might be resulted from the more bulky p-trifluoromethylphenyl substituents of polyimides 7. High optical transparency and good solubility combined with high thermal stability make these polyimides attractive for potential soft electronics applications.

CONCLUSIONS

In this study, we report the synthesis of two new aromatic diamines, 2,2′-diiodo-4,4′-oxydianiline

(DI-ODA 4) and 2,2′-bis[p-(trifluoromethyl)phenyl]-4,4′-oxydianiline (BTFP-ODA 5) by using 4,4′-ODA as the starting material. These new diamines contain ether linkage and bulky iodide or p-trifluoromethylphenyl substituents. To precisely control the substituents at the 2 and 2′ positions, the starting material, 4,4′-ODA, was oxidized first so that the following iodination can take place at these positions. Novel polyimides 6 and 7 were prepared from these two diamines with various commercially available aromatic dianhydrides via a one-step polycondensation procedure. These polyimides had high molecular weights and film-forming ability. Polyimides 6 and 7 exhibited enhanced solubilities
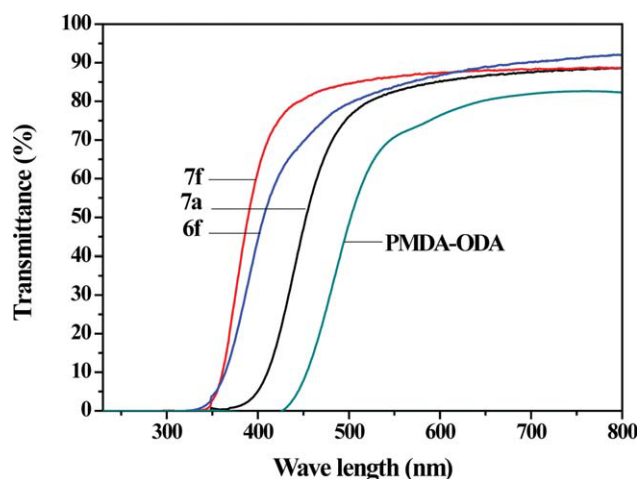

Figure 6 UV-Visible spectra of the polyimide films 6f, 7a, and 7f. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared with polyimides derived from 4,4′-ODA. Polyimides **7** had better solubilities, lower glass transition temperatures and showed lighter color than polyimides **6**. This might be due to the more bulky *p*-trifluoromethylphenyl substituents of polyimides **7** compared with iodide substituents of polyimides **6**. Polyimide **7a** derived from rigid PMDA and BTFP-ODA **5** was even soluble in DMF, DMAc, DMSO and NMP. These polyimides also exhibited good thermal stability. Because of the presence of weak carbon-iodine bond, polyimides **6** began to decompose at lower temperature than polyimides **7**.

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