Synthesis of Highly Refractive and Transparent Polyimides Derived from 4,4′-Thiobis[2″,6″-dimethyl-4″-(*p*-phenylenesulfanyl)aniline]

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ABSTRACT: New sulfur-containing aromatic diamines with methyl groups at the *ortho* position of amino groups have been developed to prepare highly refractive and transparent aromatic polyimides (PIs) in the visible region. All aromatic PIs derived from 4,4′-thiobis[2″-methyl-4″-(*p*-phenylenesulfanyl)aniline (**2**), 4,4′-thiobis[2,″6″-dimethyl-4″-(*p*-phenylenesulfanyl)aniline (**5**), and aromatic dianhydride, 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (**6**) were prepared via a two-step polycondensation. All PIs showed good thermal properties, such as 10% weight loss temperature in the range of 497–500 °C and glass transition temperatures above 196 °C. In addition, the PIs showed good optical properties, such as optical transparency above 75% at 450 nm with a 10-μm film thickness, high refractive indices ranging from 1.7135 to 1.7301, and small in-plane/out-of-plane birefringences between 0.0066 and 0.0076. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 656–662, 2010

KEYWORDS: high-performance polymers; highly refractive index; high transparency; low birefringence; polyimides; step-growth polymerization; transparency

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INTRODUCTION In recent years, much attention has been paid to high-refractive index polymers for their practical application in advanced optoelectronic fabrications,[1–3] such as encapsulants for organic light-emitting diode devices,[4] charge-coupled devices, and complementary metal oxide semiconductor image sensors.[5] According to the Lorentz-Lorenz equation, the refractive index of polymers depends on several factors such as the molar refraction, molar volume, or density.[6,7] Thus, the introduction of heavy halogen atoms, sulfur atoms, and metal atoms with high molar refractions is effective to increase the refractive indices of polymers.[8,9] Aromatic polyimides (PIs) are one of the most important classes of advanced polymers, which possess various outstanding properties, such as excellent thermal and chemical resistance, low dielectric constants, high mechanical properties, and inherently high refractive indices. Therefore, much attention has been devoted to optical device applications of PIs.

Recently, we have developed highly refractive and transparent PIs derived from aromatic dianhydrides and aromatic diamines containing sulfur atoms with thioether linkages.[10–15] All PIs showed high refractive indices, high transparency, and low birefringence. Although the refractive index of polymers can be effectively improved by using the aforementioned methods, optical polymers require several other functions, such as low in-plane/out-of-plane birefringence (Δn) and high transparency in the visible light region for optical device applications. The considerable coloration of aromatic PIs originates from the formation of intermolecular or intramolecular charge-transfer complexes (CTCs) between the electron-donating diamine moiety and the electron-accepting dianhydride moiety.[16] To decrease the coloration of conventional PIs, several approaches, such as the introduction of bulky substituents with methyl groups at *ortho* position of diamine, fluoro-containing substituents, alicyclic moieties, and noncoplanar or unsymmetrical structures in the polymer main chains, have been developed for electrooptic device, semiconductor, and optical device applications.[17–26] However, the aforementioned procedures generally result in decrease in the refractive indices.[27] Thus, the breakthrough for a trade-off between the refractive index and transparency is a challenging subject. Quite recently, we have developed a new aromatic PI from 4,4′-thiobis[(*p*-phenylenesulfanyl)aniline] (3SDA) and 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride containing thioether linkages.[28] Although this PI is one of the highest refractive index aromatic PIs, the optical transparency in the visible light region is not enough for optical device application. Therefore, we have focused on the synthesis of highly transparent aromatic PIs while maintaining high refractive indices.

In this study, new aromatic diamines with methyl groups at the *ortho* position of amino groups were prepared to develop high-transparent aromatic PIs in the visible region. Figure 1 shows the calculated absorption spectra of *N*-phenylphthalimide

Additional Supporting Information may be found in the online version of this article. Correspondence to: M. Ueda (E-mail: ueda.m.ad@m.titech.ac.jp)
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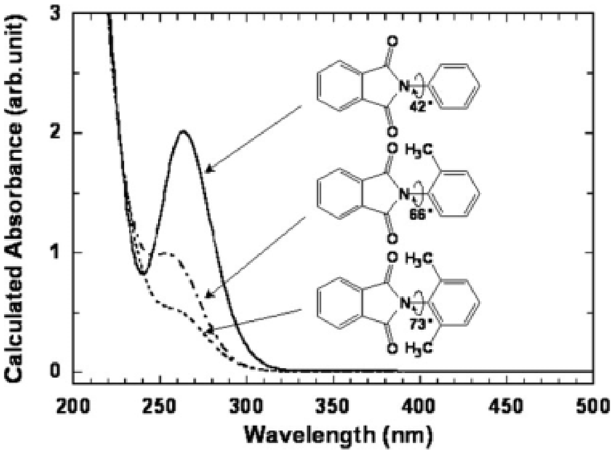


FIGURE 1 Calculated absorption spectra of *N*-phenylphthalimide and its derivatives having methyl groups at the *ortho* positions of C—N imide bond.

and its derivatives having methyl groups at the *ortho* position. As clearly indicated by the optimized torsion angles (ω), the introduction of methyl groups induces highly twisted conformations ($\omega = 42^\circ \rightarrow 66^\circ \rightarrow 73^\circ$) in the phenylimides, which should prevent intermolecular CTC formation. As seen in the figure, the calculated absorption peaks originating from π–π* transitions from the occupied molecular orbitals (MOs) located at the amine moiety to the unoccupied MOs at the anhydride moiety (263–279 nm) are significantly reduced, and thus the optical transmission near the absorption edges ($\sim$300 nm) should be improved. Based on these results, this article presents the synthesis and properties of optically transparent PIs by the polymerization of 4,4′-thiobis[2″-methyl-4″-(*p*-phenylenesulfanyl)aniline (**2**) and 4,4′-thiobis[2,″6″-dimethyl-4″-(*p*-phenylenesulfanyl)aniline (**5**) with aromatic dianhydrides such as 4,4′-[*p*-thiobis(phenylsulfanyl)]diphthalic anhydride (**6**). The PIs exhibited relatively high refractive indices in the range of 1.7135–1.7301 at 633 nm, high thermal stability (10% weight loss temperatures > 450 °C), low birefringences in the range of 0.0066–0.0076, and good transmittance higher than 75% at 450 nm. The structural effects of the PIs on the thermal properties, optical transparency, and refractive indices are discussed.

EXPERIMENTAL

Materials

4,4′-Thiobisbenzenethiol, 1-bromo-3,5-dimethylbenzene, and 5-chloro-2-nitrotoluene were purchased from TCI, Japan. Nitric acid (fuming, 96%) and cesium carbonate were purchased from Wako, Japan. *N*,*N*-Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone dehydrated (NMP) were used as received. All other chemicals were purchased from TCI and Wako, Japan. Compound **6** was synthesized according to our previous works.[28]

Synthesis of 4,4′-Bis(3″-methyl-4″-nitrophenylsulfanyl) diphenyl Sulfide (1)

To a three-necked 100-mL flask was added a mixture of *p*-chloronitrobenzene (7.55 g, 0.044 mol), 4,4′-thiobisbenzenethiol (5.01 g, 0.02 mol), anhydrous K_2CO_3 (6.91 g, 0.050 mol), and DMF (50 mL). The mixture was heated with stirring at 130 °C for 12 h. The solvent was removed by vacuum distillation. The mixture was poured into water. The precipitate was collected by filtration, washed with water, and dried in vacuum at room temperature for 24 h. The crude product was recrystallized from 2-methoxyethanol to afford pale yellow crystals, **1**. Yield: 7.8 g (75.0%); m.p. 115 °C (DSC peak temperature).

^{1}H NMR (300 MHz, $CDCl_3$-d_6/TMS, ppm): 7.86–7.88 (d,2H), 7.40–7.43 (d, 4H), 7.35–7.38 (d, 4H), 7.13 (s, 2H), 7.06–7.10 (d, 2H), 2.54 (S, 6H). ^{13}C NMR (300 MHz, $CDCl_3$-d_6/TMS, ppm): 136.93, 134.72, 134.57, 132.41, 132.00, 131.97, 131.83, 126.50, 126.47, 125.87, 20.85. Anal. Calcd. for $C_{26}H_{20}N_2O_4S_3$ (520.64): C, 59.98; H, 3.87. Found: C, 60.47; H, 4.09.

Synthesis of 4,4′-Thiobis[2″-methyl-4″-(*p*-phenylenesulfanyl) aniline] (2)

A 100-mL three-necked flask was charged with a mixture of **1** (5.21 g, 0.01 mol), ethanol (50 mL), and a catalytic amount of 10% palladium on activated carbon (0.60 g). The reaction mixture was refluxed and then hydrazine monohydrate (25 mL) was added. The reaction mixture was refluxed for 12 h. Then, the hot mixture was filtered to remove the catalyst and the filtrate was cooled to room temperature. The precipitated white crystals were filtered out, washed with cold ethanol, and dried under vacuum at room temperature for 6 h to afford **2**. Yield: 3.43 g (74.5%); m.p. 117 °C (DSC peak temperature).

^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.05 (s, 6H), 5.32 (s, 4H), 6.66–6.68 (d, 2H), 6.67–6.95 (d, 4H), 7.05–7.06 (d, 2H), 7.08–7.10 (d, 2H), and 7.13–7.16 (d, 4H). ^{13}C NMR (300 MHz, DMSO-d_6/TMS, ppm): 148.6, 140.5, 137.3, 134.4, 131.7, 131.3, 127.0, 122.7, 115.1, 114.4, and 117.6. Anal. Calcd. for $C_{26}H_{24}N_2S_3$ (460.68): C, 67.95; H, 5.25. Found: C, 67.95; H, 5.24.

Synthesis of 4-Bromo-2,6-dimethyl-1-nitrobenzene (3)

To a neat 1-bromo-3,5-dimethylbenzene (20 g, 0.108 mol) was added dropwise fuming HNO_3 (96%, 4.48 mL, 6.8 g, 1 equiv) at −15 °C, and the mixture was stirred for 6 h at room temperature. After the reaction, the obtained solution was poured into water and extracted with methylene chloride. The solvents were evaporated to give a mixture of 4-bromo-2,6-dimethyl-1-nitrobenzene and 6-bromo-2,4-dimethyl-1-nitrobenzene. The two isomers were separated by column chromatography (ethyl acetate/hexane, vol % 1:15) and recrystallized from ethanol to give **3** as white crystals. Yield: 3.73 g (15%); m.p. 67 °C (DSC peak temperature).

^{1}H NMR (300 MHz, DMSO-d_6, ppm): $\delta = 7.28$ (s, 2H), 2.28 (s, 6H).

Synthesis of 4,4′-Bis(3″,5″-dimethyl-4″-nitrophenylsulfanyl)diphenyl Sulfide (4)

To a 50-mL round flask was charged with **3** (3.5 g, 15.2 mmol), 4,4′-thiobisbenzenethiol (1.73 g, 6.92 mmol), cesium carbonate (2.27 g, 15.23 mmol), and DMSO (30 mL). The mixture was heated with stirring at 140 °C for 12 h under a nitrogen atmosphere. Then, the reaction mixture was filtered. The solvent was evaporated, and the crude solids were purified by column chromatography using methylene chloride and recrystallized from 2-methoxyethanol to give **4** as pale green crystals. Yield: 2.32 g (61.4%); m.p. 120 °C (DSC peak temperature).

^{1}H NMR (300 MHz, $CDCl_3$-d_6, ppm): $\delta = 2.26$ (s, 12H), 7.00 (s, 4H), 7.33 (s, 8H). ^{13}C NMR ($CDCl_3$-d_6, ppm): $\delta = 139.4$, 135.8, 133.4, 133.2, 132.2, 131.3, 129.9, and 18.0. Anal. Calcd. for $C_{28}H_{24}N_2O_4S_3$; (548.70): C, 61.29; H, 4.41. Found: C, 61.28; H, 4.48.

Synthesis of 4,4′-Thiobis[2,″6″-dimethyl-4″-(*p*-phenylenesulfanyl)aniline] (5)

A 250-mL three-necked flask fitted with a magnetic stirrer, a thermometer, and a dropping funnel was charged with a mixture of 4 (2 g, 36.4 mmol), ethanol (15 mL), and a catalytic amount of 10% palladium on activated carbon (0.20 g). The reaction mixture was heated to reflux and then hydrazine monohydrate (6 mL) diluted with ethanol (15 mL) was added dropwise over a period of 1.5 h. After the addition was completed, the reaction system was refluxed for 24 h. Then, the hot mixture was filtered to remove the catalyst and the filtrate was cooled to room temperature. The precipitated white crystals were filtered out, washed with cold ethanol, and dried under vacuum at 80 °C overnight to afford **5**. Yield: 1.25 g (70.6%); m.p. 73.3 °C (DSC peak temperature).

FTIR (KBr, cm^{-1}): ^{1}H NMR (300 MHz, DMSO-d_6, ppm): $\delta =$ 2.10 (s, 12H), 4.99 (s, 4H), 6.93–6.96 (d, 4H), 7.00 (s, 4H), 7.10–7.14 (d, 4H). ^{13}C NMR (DMSO-d_6, ppm): $\delta = 146.3$, 140.5, 135.2, 131.7, 131.3, 127.0, 122.3, 114.2, and 18.0. Anal. Calcd. for $C_{28}H_{28}N_2S_3$; (488.73): C, 68.81; H, 5.77. Found: C, 68.47; H, 5.66.

Polyimide Synthesis

The PIs were prepared by the general polycondensation procedure via poly(amic acid) (PAA) precursors, followed by thermal imidization at elevated temperatures. A typical polymerization procedure can be illustrated by the synthesis of PI-1 as follows. To a solution of **5** (0.4607 g, 1.00 mmol) in dehydrated NMP (2.0 mL) was added **6** (0.5426 g, 1.00 mmol) under nitrogen atmosphere. An additional NMP (2.0 mL) was added into the reaction mixture and stirred at room temperature for 24 h to obtain a viscous PAA solution. The solid content of reaction system was adjusted to 20 wt % by weight. The PAA solution was spin-coated on a fused silica substrate or a silicon wafer, and the thickness of PIs films was controlled to be ~10 μm for UV–vis and FTIR measurements. The specimen was adjusted from 30 to 100 μm prepared by casting onto the glass substrate for thermal properties. The PI films were prepared by thermal imidization from PAA solutions in an oven for 1 h each step at 80, 120, 150, 200, 250 °C and 30 min at 300 °C, respectively, as shown in Scheme 2. The film of PI-2 was prepared by a similar process from PAA solutions.

PI-1

$[\eta]_{inh}$: 0.68 g dL^{-1} (from PAA-1), FTIR (film, cm^{-1}): 1778, 1720 (C=O imide), 1095 (C—S—C). Elem. Anal. Calcd. for [$C_{54}H_{36}N_2O_4S_6$]: C, 66.91%; H, 3.74%; N, 2.89%. Found: C, 66.90%; H, 3.65%; N, 2.58%.

PI-2

$[\eta]_{inh}$: 0.32 g dL^{-1} (from PAA-2), FTIR (film, cm^{-1}): 1774, 1724 (C=O imide), 1099 (C—S—C). Elem. Anal. Calcd. for [$C_{56}H_{40}N_2O_4S_6$]: C, 67.44%; H, 4.04%; N, 2.81%. Found: C, 67.04%; H, 3.88%; N, 2.30%.

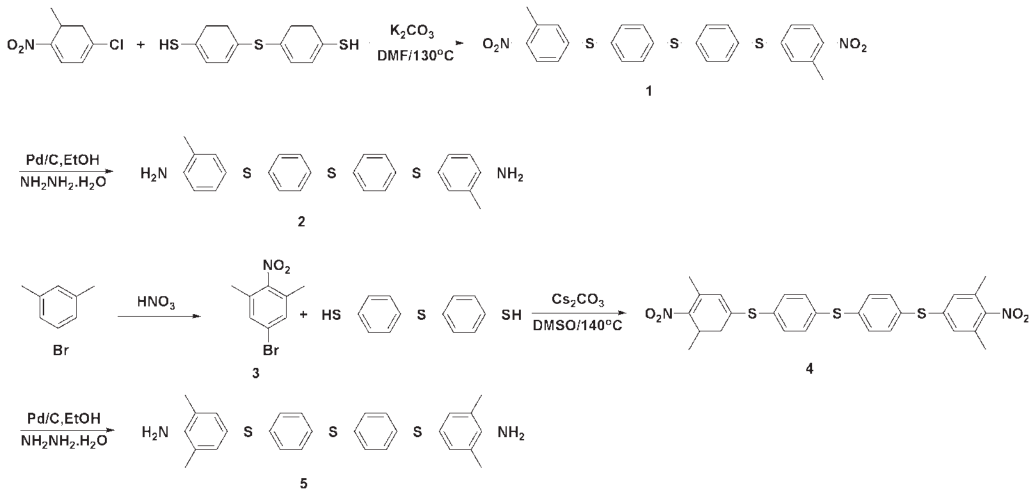
Measurements

The NMR spectra were recorded on a BRUKER DPX-300S spectrometer at the resonant frequencies at 300 MHz for ^{1}H and at 75 MHz for ^{13}C nuclei using $CDCl_3$ and DMSO-d_6 as the solvents. The ^{13}C DEPT (distortionless enhancement by polarization transfer) experiment was carried out using DMSO-d_6 as solvent. The FTIR spectra were obtained by a Horiba FT-120 Fourier transform spectrophotometer. Inherent viscosity was measured with an Ubbelohde-viscometer with a 0.5 g dL^{-1} NMP solution at 30 °C. The ultraviolet–visible (UV–vis) spectra were performed on a Hitachi U-3210 spectrophotometer. The transmittance of PI films was evaluated in the wavelengths range of 250–800 nm at 10-μm film thickness. Elemental analyses were carried out on a Yanaco MT-6 CHN recorder elemental analysis instrument. Thermogravimetric analysis (TGA) was estimated by a Seiko TG/DTA 6300 under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was estimated by using a Seiko DSC 6300 at a heating rate of 10 °C min^{-1}. Dynamic mechanical thermal analyses (DMA) were performed on PI film specimens (length: 30 mm, width: 10 mm, and thickness: 30–60 μm) by using a Seiko DMS 6300 instrument at a heating rate of 2 °C min^{-1} with a load frequency of 1 Hz in air. The glass transition temperature values (T_g) of the PIs were obtained as the peak temperature of the loss modulus (E'') plot. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PI films were carried out using a prism coupler (Metricon, model PC-2000) equipped with a He–Ne laser (wavelength: 633 nm) and a half-waveplate in the light path. The in-plane/out-of-plane birefringences (Δn) were estimated as a difference between n_{TE} and n_{TM}, and the average refractive indices were calculated according to the equation: $n_{AV} = [(2n_{TE}{}^2 + n_{TM}{}^2)/3]^{1/2}$.

RESULTS AND DISCUSSION

Synthesis of Diamines 2 and 5

Diamines **2** and **5** were prepared by a two- and three-step procedure, respectively, as shown in Scheme 1. Compound **3** was prepared by nitration of 3,5-dimethylbromobenzene with fuming nitric acid. Then, a mixture of *ortho*- and *para*-substituted nitro compounds was separated by column chromatography. Nucleophilic aromatic substitution of **3** with



SCHEME 1 Synthetic route for the preparation of diamine (**2**) and diamine (**5**).

4,4′-thiobisbenzenethiol in the presence of cesium carbonate produced **4**, which was converted to diamine **5** by catalytic reduction. On the other hand, diamine **2** was prepared by similar procedure according to the literature.[28] The structures of **2** and **5** were characterized by FTIR and NMR spectroscopy. The characteristic nitro absorptions of **1** and **4** at 1504, 1519, 1334, and 1361 cm^{-1} completely disappeared, and the absorptions of primary amino and thioether groups are distinctly observed at 3436–3385 and 1288 cm^{-1}, respectively (see Supporting Information).

The ^1H and ^{13}C NMR spectra of diamines **2** and **5** are shown in Figures 2 and 3 with assignments of all peaks, respectively. For example, the signals at 5.31 and 2.05 ppm in Figure 3(a) are assigned to the amino and methyl groups of **2**, respectively. On the other hand, aromatic protons containing an amino moiety are observed at 7.05–7.10 and 6.67 ppm. In the ^{13}C NMR spectrum [Fig. 2(b)], 11 carbon signals,

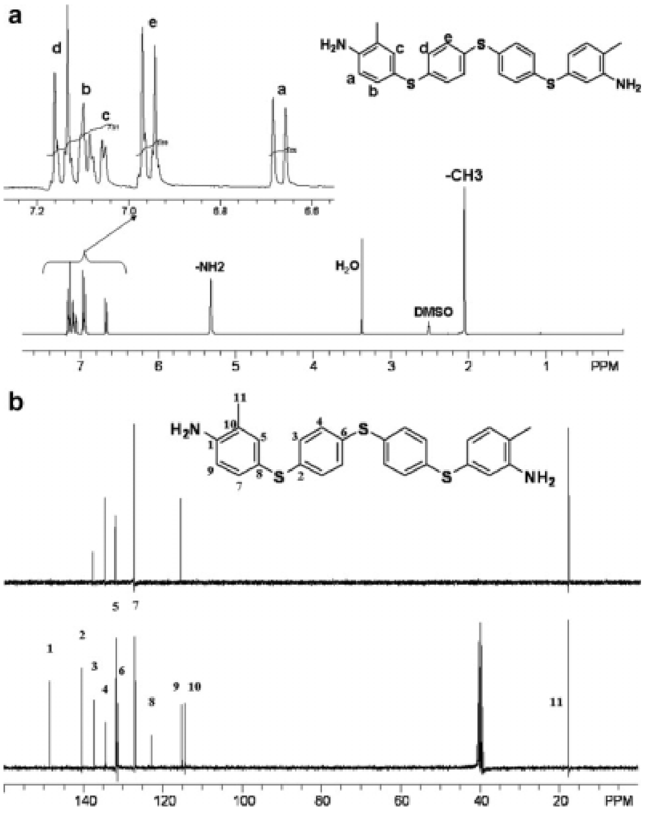


FIGURE 2 NMR spectra of diamine (**2**) (a) ^1H NMR; (b) ^{13}C NMR and DEPT-135.

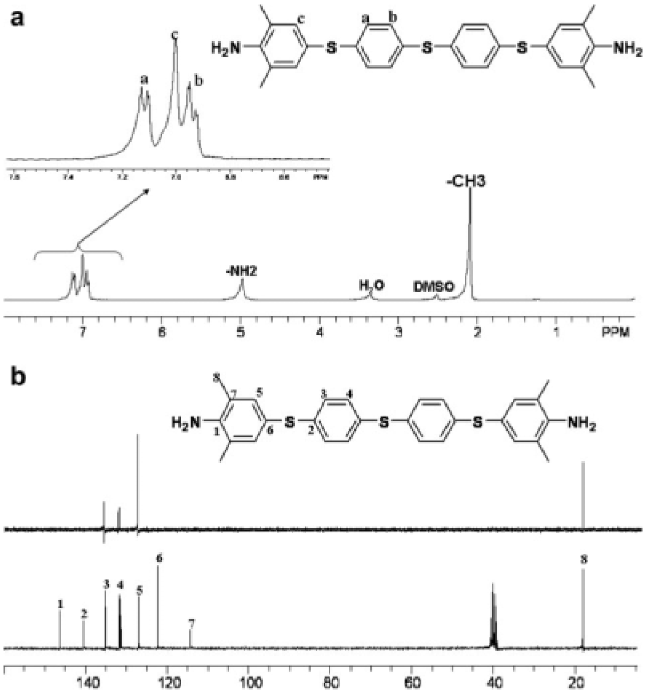
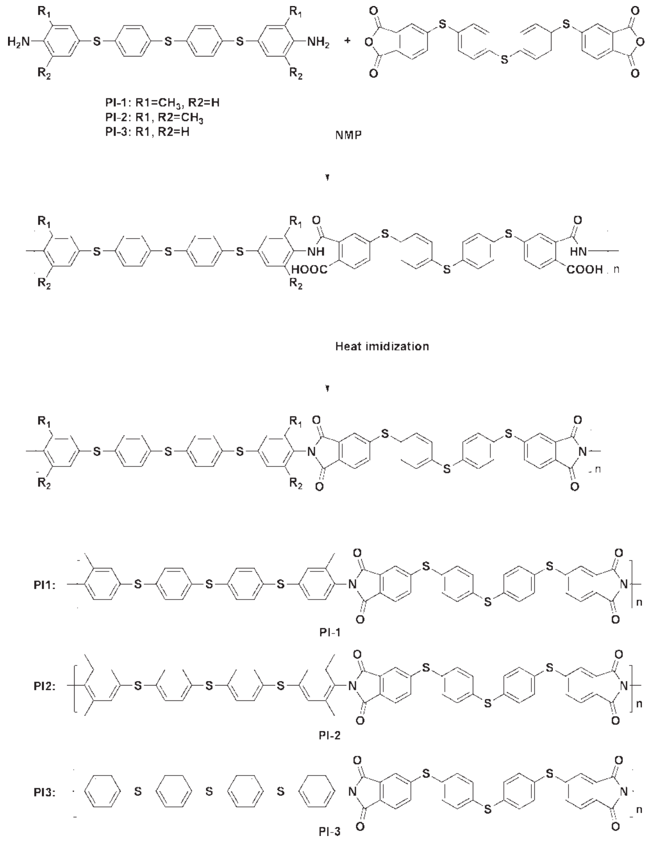


FIGURE 3 NMR spectra of diamine (**5**) (a) ^1H NMR; (b) ^{13}C NMR and DEPT-135.



SCHEME 2 Synthesis of polyimides.

which accord well with the expected structure, are observed. Among these peaks, six quaternary carbon signals are assigned by DEPT-135 measurement. In addition, the structures of TBPSA (**2**) and DTBPSA (**5**) were characterized by elemental analysis.

Synthesis and Characterization of Polyimides

All PIs were synthesized by a two-step polycondensation of diamines such as **2** and **5** with **6** via soluble PAA precursors, followed by thermal imidization at elevated temperatures (Scheme 2). The inherent viscosities of the PAA solutions are in the range of 0.32–0.68 g dL^{-1}, as shown in Table 1. Flexible PI films were prepared by thermal imidization of the corresponding PAA films cast onto glass substrates and fused silica under nitrogen. After thermal conversion from PAAs to PIs, the characteristic IR absorption peaks of the imide moiety, such as 1774 (as, C=O), 1727 (s, C=O), and 1365 cm^{-1} (C—N), are observed, as shown in Figure 4. In addition, an absorption peak of aromatic thioether groups (Ar—S—Ar) is observed at 1099 cm^{-1}. Furthermore, the elemental analysis also supported the formation of the expected PIs.

Thermal Properties of PIs

The thermal properties of the PIs, such as 10% weight loss temperatures (T_d^{10}) and glass transition temperatures (T_g), were evaluated by TGA, DSC, and DMA measurements. The results are summarized in Table 1. All PIs exhibit good thermal stability, such as the T_d^{10} values at 460–505 °C (Fig. 5). The T_gs of the PIs estimated by DSC (see Supporting Information) and DMA (Fig. 6) show similar values. All PIs show high T_gs in the range of 179–218 in the order of PI-2 > PI-1 > PI-3. This trend is related to the structural effects of the diamines. The results indicate that the introduction of methyl groups at the *ortho* position of amino groups is effective to increase the T_gs due to the increase in the chain rigidity of PI-1 and PI-2, that is, the methyl groups significantly restrict the bond rotation at the C—N imide bond. Figure 6 illustrates the variations in the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) measured by DMA at a heating rate of 2 °C min^{-1} under air. The modulus remains constant or slightly decreased on heating over a wide temperature range below the T_gs. Above the T_g, the modulus dramatically decreases, as shown in Figure 6(a). The T_gs determined from the peak temperatures of E'' were close to the T_gs estimated from DSC.

Optical Properties

Figure 7 shows the optical transmission spectra of PI films with PMDA-ODA as the reference PI (~10 μm thick). All PIs show much better transparency with the cutoff wavelengths (λ_{cutoff}) at 402–375 nm compared with PMDA-ODA. The transmittances of PI-1 and PI-2 measured at 425 nm are significantly higher than that of PI-3 derived from **6** and 4,4′-thiobis[(*p*-phenylenesulfanyl)aniline].[28] This is attributable to the *ortho* methyl groups in the aromatic diamines, which induce significant steric hindrance around the C—N imide bond. This is supported by the fact that the dihedral angles at the C—N bonds in the optimized geometry of the models are 66°, 73°, and 42° for PI-1, PI-2, and PI-3, respectively, as

TABLE 1 Thermal Properties of the Polyimides

PI	$[\eta]_{inh}$[a] of PAA (g dL^{-1})	Film[b]	T_g (°C)[c]		$T_{10\%}$[d] (°C)
			DSC	DMA	
PI-1	0.68	Pale yellow	197	194.3	474
PI-2	0.32	Pale yellow	218	216.7	475
PI-3[e]		Pale yellow	179	173.8	500

[a] Measured at a concentration of 0.5 g dL^{-1} of NMP solution at 30 °C.
[b] Color at the thickness of ~10 μm.
[c] T_g, glass transition temperature.
[d] $T_{10\%}$, temperatures at 10% weight loss.
[e] **6**-3SDA (ref. 29).

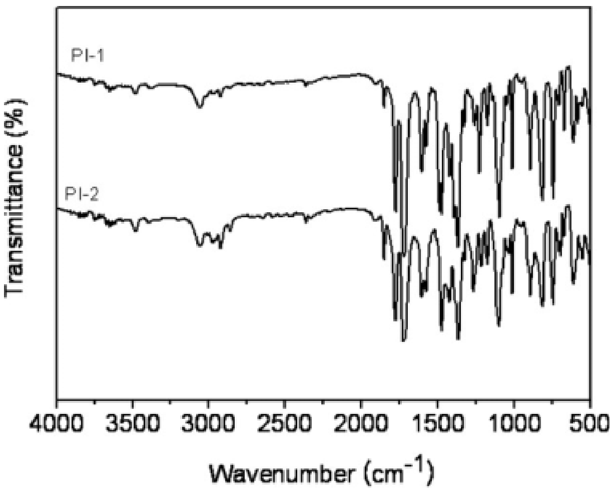


FIGURE 4 FTIR spectra of PI films.

shown in Figure 1. The significantly distorted conformations in PI-1 and PI-2 effectively reduce the formation of intramolecular and intermolecular CTCs in the main chains.

The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the PI films were measured at 633 nm in the range of 1.7160–1.7505 and 1.7084–1.7437, as listed in Table 2. The n_{TE} values are slightly higher than those of n_{TM}, which indicates that the PI chains are preferentially oriented in the film plane.[29] The n_{av} of PI films is in the range of 1.7135–1.7482 in the order of PI-3 > PI-1 > PI-2. The highest n_{av} observed for PI-3 could have originated from two factors. First, the introduction of methyl groups into the diamines reduces the sulfur content, which is the primary factor of the high refractive indices of sulfur-containing PIs. Second, the distorted conformation around the C—N imide bond lowers the intermolecular packing of PIs, which increases the molar volumes of PIs.

All of the PIs show low birefringence (Δn) in the range of 0.0066–0.0076 compared with PMDA-ODA as reference PI. The relatively low Δn value is related to the highly flexible and phenyl-sulfanyl-phenyl linkages in the main chains. The results indicate that aromatic diamines with *ortho* methyl groups are effective to improve the optical transparency of the resulting PIs while maintaining high refractive indices and low birefringences of the PIs.

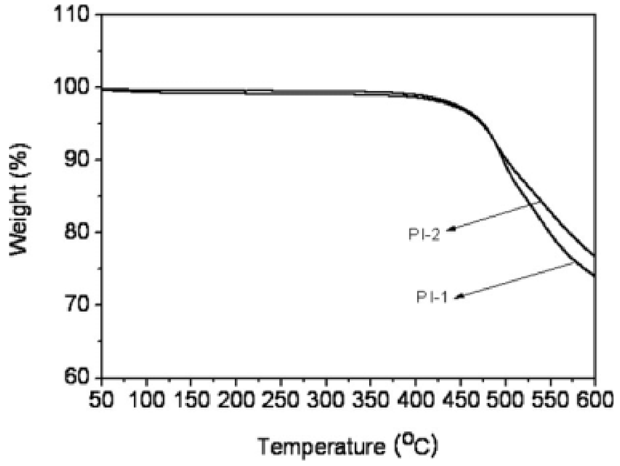


FIGURE 5 TGA curves of PI films (in nitrogen atmosphere, 10 °C min^{-1}).

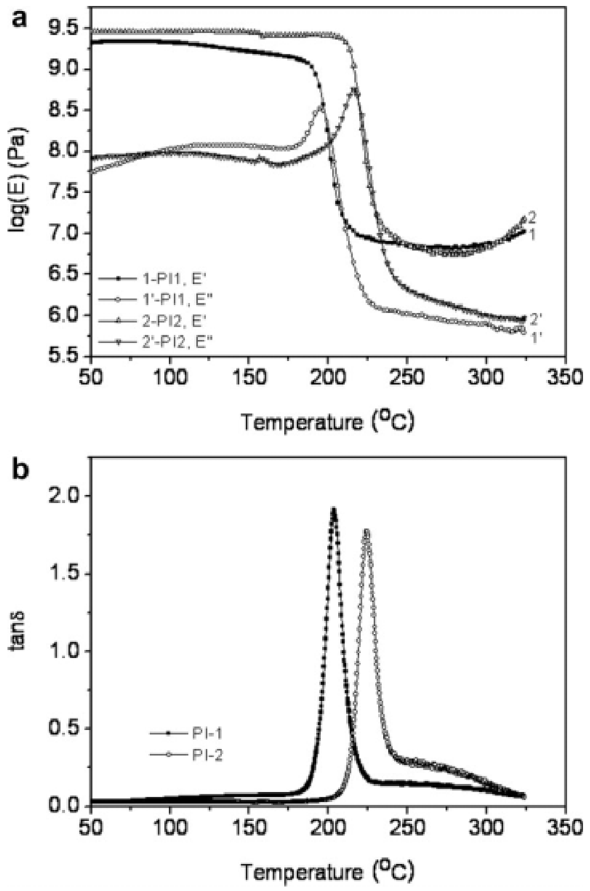


FIGURE 6 DMA curves of PI-1 and PI-2 (1 Hz, 2 °C min^{-1}): (a) modulus and (b) tan δ.

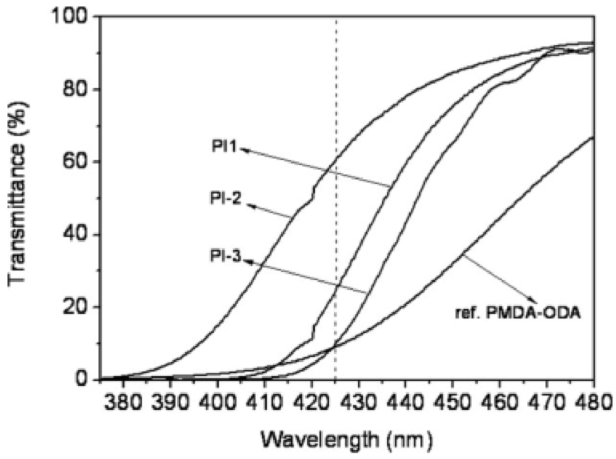


FIGURE 7 UV–vis spectra of PI films (film thickness: ~10 μm).

TABLE 2 Optical Properties of the PI Films

				Refractive Indices and Birefringence at 633 nm[d]			
PI	S_c[a] (%)	λ_{cutoff}[b] (nm)	d[c] (μm)	n_{TE}	n_{TM}	n_{av}	Δn
PI-1	19.9	400	12.9	1.7323	1.7256	1.7301	0.0066
PI-2	19.3	375	14.2	1.7160	1.7084	1.7135	0.0076
PI-3[e]	20.4	402	9.3	1.7505	1.7437	1.7482	0.0068
Ref-PI[f]	0	415	9.2	1.7207	1.6427	1.6950	0.0780

[a] Sulfur content.

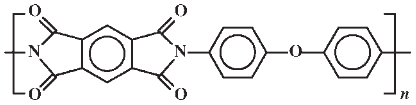
[b] Cutoff wavelength.

[c] Film thickness for refractive index measurement.

[d] Measured at 632.8 nm, see Measurements section.

[e] **6**-3SDA (ref. 29).

[f] PMDA-ODA with the chemical structure as follows.



CONCLUSIONS

Aromatic diamines containing methyl groups at the *ortho* positions of amino groups were newly synthesized to enhance the optical transparency of the resulting PIs. The PIs derived from **2** and **5** showed higher transparency compared with **6**-3SDA, while maintaining relatively high refractive indices. At the same time, the glass transition temperatures of the PI films were increased and exhibited low birefringences. The experimental results indicate that the introduction of methyl groups at the *ortho* position of aromatic diamines is an effective way to improve the optical transparency of PIs. These high optical transparency, high refractive index, and high thermal stability factors make the resulting PIs promising candidates for advanced optical device applications.

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