Synthesis of High Refractive Index Polyimides Derived from 1,6-Bis(*p*-aminophenylsulfanyl)-3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene and Aromatic Dianhydrides

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ABSTRACT: Highly refractive and transparent polyimides (PIs) containing a 3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene moiety in their main chains have been developed. These PIs were prepared from several dianhydrides such as 4,4′-[*p*-thiobis(phenylsulfanyl)]diphthalic anhydride (3SDEA), 4,4′-[(9*H*-fluorene-9-ylidene)bis(*p*-phenylsulfanyl)]diphthalic anhydride (FPSP), 4,4′-oxidiphthalic anhydride (ODPA), and a new sulfur-containing aromatic diamine, 1,6-bis(*p*-aminophenylsulfanyl)-3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene (BTTA), by a two-step polycondensation procedure. The PIs exhibit good thermal and optical properties such as glass transition temperatures higher than 213 °C, thermal decomposition temperatures ($T_{10\%}$) in the range of 390−443 °C, and optical transparency higher than 80% at 500 nm for a thickness of ca. 10 μm. Because of the very high sulfur content (28.4%) in the polymer main chain, the PI derived from BTTA and 3SDEA exhibits the highest refractive index, i.e., 1.769 at 633 nm.

Introduction

A high refractive index (high-*n*) and low birefringence (Δn) combined with good thermal stability and high optical transparency are the basic concerns in designing optical polymer coatings for advanced display devices, such as organic light-emitting diodes (OLEDs),[1] microlens components for charge coupled devices (CCD), and high-performance CMOS image sensors (CISs), etc.[2−4] Recently, many conventional polymers combined with sulfur atoms have been developed to increase the refractive index of the polymers.[5] In fact, sulfur-containing polymers, including poly(methacrylates),[6] epoxies,[7] polyurethanes,[8] and polyimides, have been used for advanced integrated optical applications.[9−11] Among them, polyimides (PIs) are good candidates for optical application owing to their excellent thermal stability, high chemical resistance, and high mechanical properties.

Quite recently, we developed transparent and sulfur-containing new polyimides derived from various aromatic dianhydrides and aromatic diamines in our laboratory.[12−17] All of them exhibited excellent thermal stability, a high refractive index, good transparency, and low birefringence. In particular, the polyimide derived from 2,7-bis(4-aminophenylsulfanyl)thianthrene (APTT) and 3SDEA exhibited the highest refractive index (up to 1.76) at a wavelength of 633 nm and birefringence lower than 0.01. To obtain further improved refractive indices while maintaining high thermal and optical properties, we designed and synthesized a novel diamine containing tetrathiaanthracene, since the tetrathiaanthracene unit containing four sulfur atoms in its molecular structure increases the sulfur content in the repeating unit. According to the Lorentz−Lorenz equation,[18] two alicyclic units in the tetrathiaanthracene moiety may yield low molar volumes, which are required for high refractive indices. The high polarizability and high percent of the sulfur atoms in the tetrathiaanthracene moiety may increase refractive indices of polymers. Moreover, the bent structures of the alicyclic and thioether units may prevent intermolecular packing between the polymer chains, which is required for high transparency and low birefringence.

In this study, we report the synthesis of 1,6-bis(*p*-aminophenylsulfanyl)-3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene (BTTA) as a novel diamine and PIs derived from BTTA and several dianhydrides (3SDEA), 4,4′-[(9*H*-fluorene-9-ylidene)bis(*p*-phenylsulfanyl)]diphthalic anhydride (FPSP), and 4,4′-oxidiphthalic anhydride (ODPA). In particular, the PI derived from BTTA and 3SDEA exhibited the highest refractive index (1.7692) with a high glass transition temperature (>212 °C), high transparency (>500 nm), and low birefringence (0.0093). The structure−property relationships of the PIs, such as the thermal and optical properties, and the refractive indices of the PIs are investigated in detail.

Experimental Part

Materials. 1,2,4,5-Tetrachlorobenzene, 2-propanethiol, 4,4′-thiobis(benzenethiol), and 1,2-dibromoethane were purchased from Wako, Japan. Pyridine, *N*,*N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone dehydrated (NMP) were used as received. All other chemicals were purchased from TCI Japan. ODPA was dried in vacuum at 120 °C for 4 h prior to use. 3SDEA and FPSP were synthesized in our laboratory according to our previous works.[15,16]

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 $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as the reference. The FT-IR spectra were measured by a Horiba FT-120 Fourier transform spectrophotometer. The UV−vis optical transmission spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The transmittance of PI films peeled from substrates was evaluated in the wavelengths range of 250 and 800 nm. Elemental analyses were performed on a Yanaco MT-6 CHN recorder elemental analysis instrument. Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g dL^{-1} NMP solution at 30 °C. The thermal properties were estimated from a Seiko TG/DTA 6300 thermal analysis system (TGA) and a Seiko DSC 6300 differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Melting points of all monomers were measured using DSC analysis unless otherwise indicated. Dynamic mechanical thermal analyses (DMA) were carried out on PI films (30 mm long, 10 mm wide, and 50−80 μm thick) on 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 temperatures values (T_g) were

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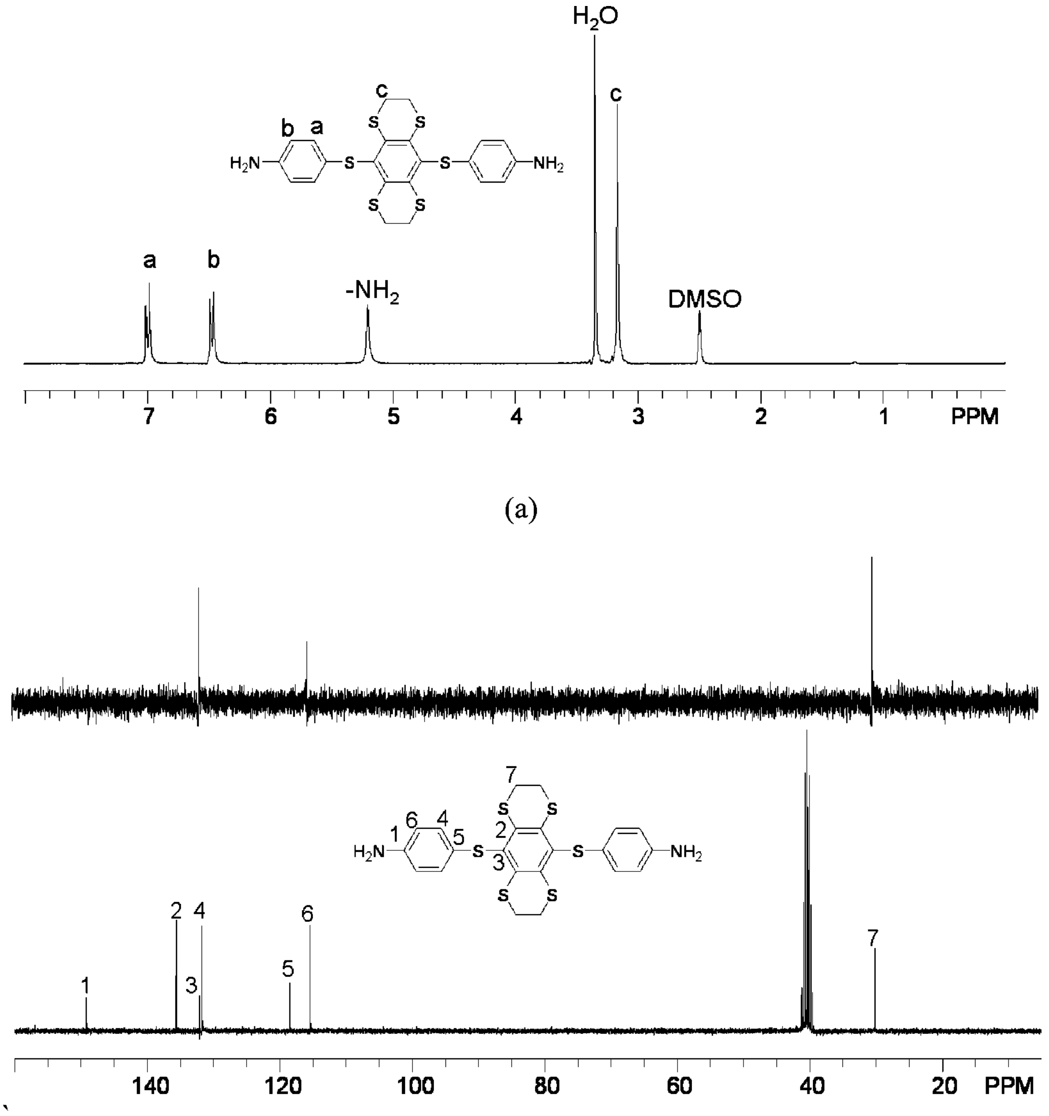
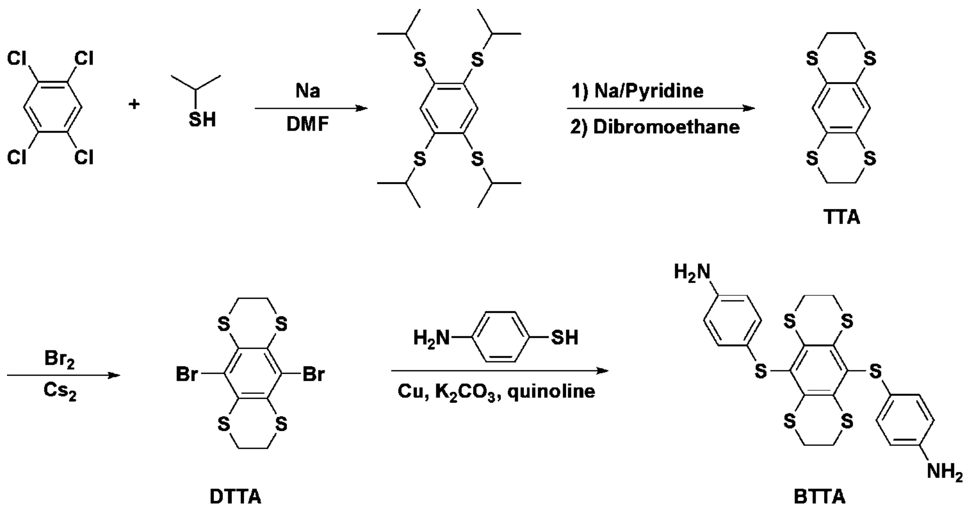


(a)

(b)

Figure 1. NMR spectra of BTTA (a) ^{1}H NMR and (b) ^{13}C NMR and DEPT-135.

Scheme 1. Synthesis of BTTA



determined 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 measured with a prism coupler (Metricon, model PC-2000) equipped with a half-wave plate in the light path and a He−Ne laser light source (wavelength: 633 mm). The in-plane (n_{TE})/out-of-plane (n_{TM}) and birefringence (Δn) were calculated as a difference between n_{TE} and n_{TM}. The average refractive index was calculated according to the equation $n_{AV} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$. All films were dried at 100 °C for 30 min under vacuum before testing to remove the absorbed moisture.

Monomer Synthesis. 1,2,4,5-Tetrakis(2-propylthio)benzene. A solution of 2-propanethiol (44.1 g, 0.57 mol) in DMF (250 mL) was added dropwise to sodium (13.2 g, 0.57 mol). The reaction mixture was stirred for 24 h at room temperature. After all the sodium dissolved, 1,2,4,5-tetrachlorobenzene (24.6 g, 0.11 mol) was added. The mixture was heated with stirring at 150 °C for 5 h, and then the reaction mixture was poured on ice. The white precipitate was filtered and washed with water. The white solid was purified by recrystallization from methanol to give white crystals (82.4% yield); mp 81.5 °C (DSC peak temperature) (lit.[19] 80−81.5 °C). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 7.29$ (s, 2H), 3.56−3.38 (m, 4H), 1.34−1.31 (d, 16H).

2,3,7,8-Tetrahydro-1,4,6,9-tetrathiaanthracene (TTA). A mixture of 1,2,4,5-tetrakis(2-propylthio)benzene (15.0 g, 40.0 mmol) and sodium (5.00 g, 200 mmol) was added into pyridine (150 mL). The mixture was heated with stirring at 110 °C for 5 h and cooled to −10 °C. To this mixture was added a slight excess of 1,2-dibromoethane (30.1 g, 160 mmol). The mixture was stirred at room temperature for 12 h and then poured into water. The precipitate was washed with water and methanol. The crude product was purified by column chromatography using dichloromethane. The product was recrystallized from dichloromethane and hexane (vol %: 5:1) to give white crystals (30.9% yield); mp 224.5 °C (DSC peak temperature) (lit.[20] 224−224.5 °C). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): $\delta = 7.00$ (s, 2H), 3.21 (s, 4H).

1,4-Dibromo-3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene (DTTA). To a solution of TTA (2.00 g, 7.73 mmol) in carbon disulfide (20 mL) was added bromine (1.59 mL, 30.9 mmol) at room temperature for 30 min. The reaction mixture was stirred at room temperature for 24 h under nitrogen. After the reaction, the obtained solid was filtered and washed with ethanol. The crude solid was purified by recrystallization from toluene to give green crystals (71.4% yield); mp 306 °C (DSC peak temperature). FT-IR (KBr, cm^{-1}): $\nu = 1415.4$, 1319, 1280.5, 1234.2, 1068.3, 871.6. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 3.36$ (s, 8H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 130.6$, 30.6. Anal. Calcd for $C_{10}H_8Br_2S_4$; (416.24): C, 28.86; H, 1.94. Found: C, 28.86; H, 1.94.

1,6-Bis(*p*-aminophenylsulfanyl)-3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene (BTTA). To a solution of *p*-aminothiophenol (1.32 g, 10.5 mmol) in quinoline (10 mL) and toluene (10 mL) was added potassium carbonate (1.74 g, 12.6 mmol). The mixture was heated with stirring at 140 °C for 4 h in a nitrogen atmosphere to remove water with a Dean−Stark apparatus. After complete removal of the water, the residual toluene was distilled off. To this suspension were added copper powder (0.033 g, 0.520 mmol) and DTTA (2.00 g, 4.80 mmol), followed by heating the mixture at 200 °C for 24 h under a nitrogen atmosphere. Then, the reaction mixture was extracted with dichloromethane and washed with ethanol. The solvent was evaporated, and the residual solids were crystallized from pyridine to give brown crystals (49.5% yield); mp 301 °C (DSC peak temperature). FT-IR (KBr, cm^{-1}): $\nu = 3440$, 3355, 3023, 2908, 1616, 1492, 1280, 817. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 6.90{-}6.88$ (d, 4H), 6.38−6.35 (d, 4H), 5.09 (s, 4H), 3.06 (s, 8H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 149.1$, 135.6, 132.1, 131.7, 118.5, 115.4, 30.1. Anal. Calcd for $C_{22}H_{20}N_2S_6$; (504.80): C, 52.34; H, 3.99; N, 5.55. Found: C, 52.83; H, 4.04; N, 5.49.

Polyimide Synthesis. A typical polymerization procedure for the synthesis of poly(amic acid) was as follows. BTTA (0.650 g, 1.28 mmol) previously dried at 100 °C for 4 h and dehydrated NMP (3.0 mL) were charged into a 20 mL flask equipped with a magnetic stirrer in a nitrogen atmosphere (Scheme 2). 3SDEA (0.698 g, 1.28 mmol) was added, and dehydrated NMP (2.4 mL) was used to adjust the solid content of the reaction systems to 20 wt %. The solution was stirred to room temperature for 24 h to afford a viscous poly(amic acid) (PAA) solution, which was filtered through a 0.45 μm Teflon syringe filter.

Table 1. Synthesis and Characterization of Polyimides

PI	$[\eta]_{inh}$[a] of PAA [dL/g]	film quality[b]		elemental analysis C (%)	H (%)	N (%)
PI-1	0.64	F, T	calcd	59.32	3.09	2.77
			found	58.65	3.09	2.64
PI-2	0.60	F, T	calcd	58.51	2.97	3.59
			found	58.31	3.02	3.75
PI-3	0.58	F, T	calcd	66.11	3.43	2.45
			found	66.23	3.62	2.50

[a] Measured with PAA at a concentration of 0.5 g/dL of NMP solution at 30 °C. [b] F: flexible; T: tough.

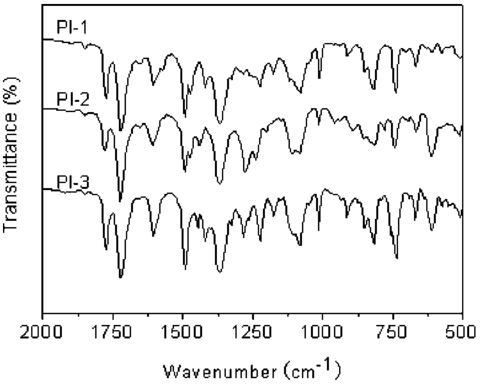


Figure 2. FT-IR spectra of PI films.

To control the film thickness, the PAAs solutions were spin-coated on silicon wafers at different spinning rates. The thickness of PIs films was controlled to be ∼10 μm for UV and FT-IR measurements. To measure thermal properties, the thickness of PI films was adjusted to 50−100 μm. The PI films were prepared by thermal imidization of PAAs solutions (Scheme 2). PI-1 film was obtained by thermal curing of the PAA-1 solution in an oven for 1−2 h each step at 80, 120, 150, 200, 250, and 15 min at 300 °C, followed by immersing the silicon wafers in warm water. The films of PIs 2 and 3 were prepared by a similar process from PAA solutions.

Results and Discussion

Synthesis of Monomers. A new aromatic diamine containing sulfur atoms, BTTA, was synthesized by a four-step procedure, as shown in Scheme 1. First, TTA was prepared from 1,2,4,5-tetrakis(2-propylthio)benzene and 1,2-dibromoethane in the presence of sodium in pyridine.[19,20] Second, bromination of TTA yielded DTTA. Finally, DTTA was converted to BTTA by the Ullman reaction with aminothiophenol. The structure of BTTA was confirmed by IR and NMR spectroscopies. The IR spectrum of BTTA shows characteristic absorptions of amino and thioether groups at 3355 and 1280 cm^{-1}, respectively. The ^{1}H NMR and ^{13}C NMR spectra of BTTA are presented in Figure 1 with assignments of all peaks. The signal at 5.09 ppm in Figure 1a is assigned to the amino groups. The protons of an aromatic ring containing an amine moiety (Ha, Hb) are observed at 6.89 and 6.37 ppm in the spectrum. The symmetric methylene protons are observed at 3.06 ppm. In the ^{13}C NMR spectrum (Figure 1b), seven signals are observed, which are consistent with the expected structure. Among these peaks, three quaternary carbon peaks are assigned by DEPT-135 measurement. In addition, the measured elemental compositions of the C, H, and N elements agree well with the

Scheme 2. Synthesis of Polyimides

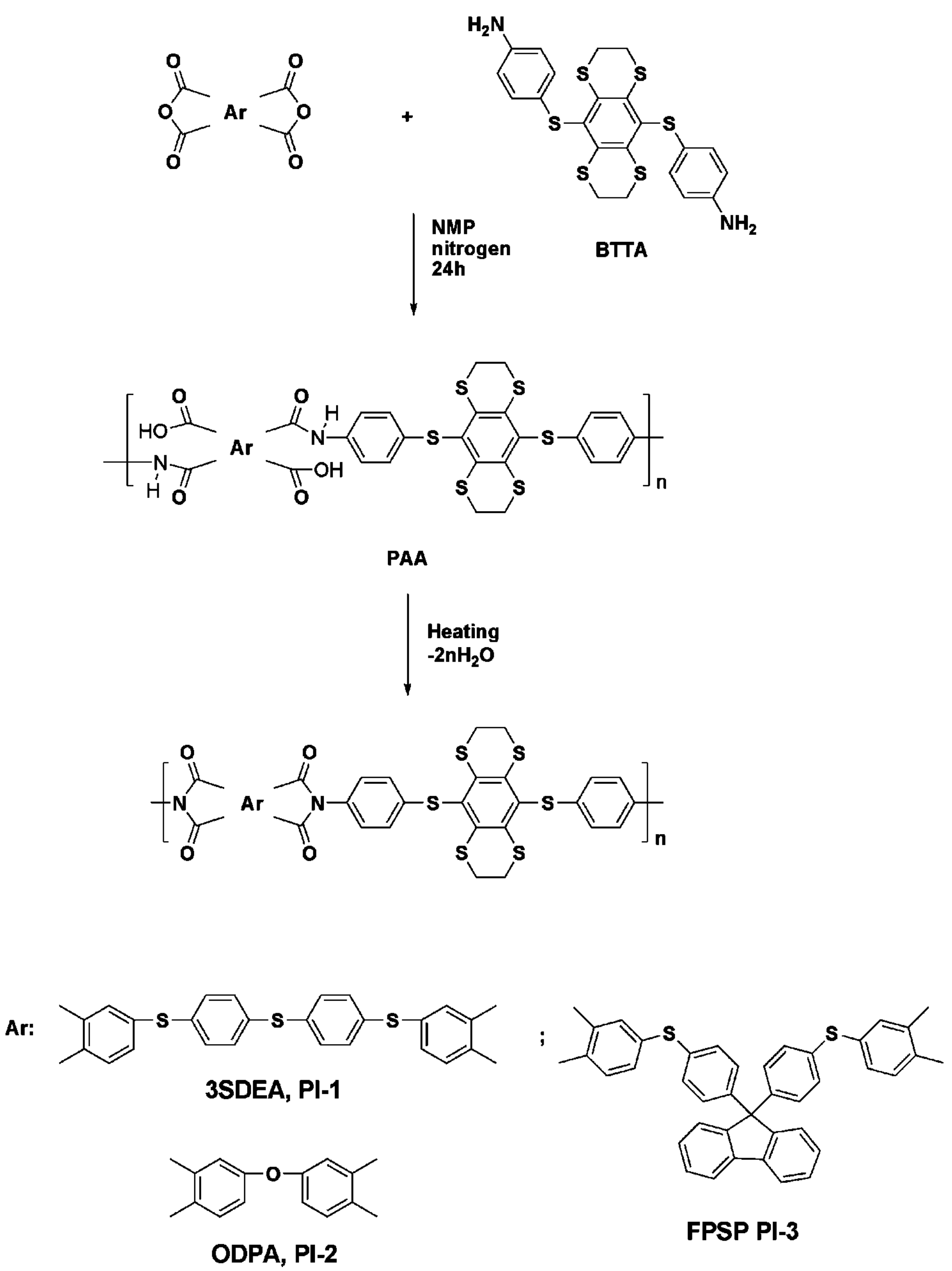


Table 2. Thermal Properties of the Polyimides

			T_g (°C)				
PI	S[a] (wt %)	film[b]	DSC	DMA	$T_{5\%}$[c] (°C)	$T_{10\%}$[c] (°C)	R_{w750}[c] (%)
PI-1	28.48	pale yellow	212	229	380	443	64
PI-2	24.63	pale yellow	247		365	391	59
PI-3	22.39	pale yellow	266	267	386	424	66

[a] Sulfur content. [b] Color at the thickness of ~10 μm. [c] T_g: glass transition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively; R_{w750}: residual weight ratio at 750 °C in nitrogen.

calculated values. These results clearly support the formation of BTTA.

Synthesis and Characterization of Polyimides (PIs). Scheme 2 shows the synthetic route of aromatic PIs. A series of PIs were prepared by the polycondensation of aromatic dianhydrides, such as 3SDEA, FPSP, and ODPA, with BTTA via soluble poly(amic acid) (PAA) precursors, followed by thermal imidization at elevated temperatures (Scheme 2). PAAs with inherent viscosities in the range of 0.58−0.64 dL/g were produced (Table 1). Flexible and tough PI films were obtained by heating the PAAs cast onto silicone wafers in nitrogen, followed by immersion in warm water. The successful thermal conversion from PAAs to PIs was characterized by the FT-IR spectra shown in Figure 2. The characteristic absorptions due to the imide moiety are observed at 1770 cm^{-1} ($\nu_{\mathrm{as,C=O}}$), 1720 cm^{-1} ($\nu_{\mathrm{s,C=O}}$), and 1370 cm^{-1} ($\nu_{\mathrm{C-N}}$). The absorption due to the thioether groups at 1083 cm^{-1} also appeared. Furthermore, the structures of the PIs were confirmed by elemental analysis (Table 1).

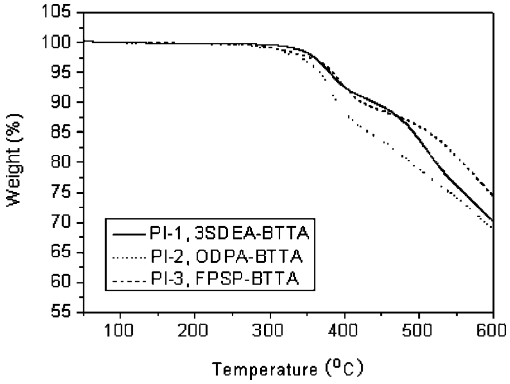


Figure 3. TGA curves of PI films (in nitrogen atmosphere, 10 °C/min).

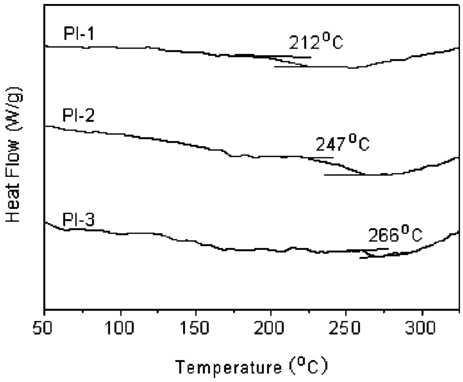


Figure 4. DSC curves of PI films (in nitrogen atmosphere, 10 °C/min).

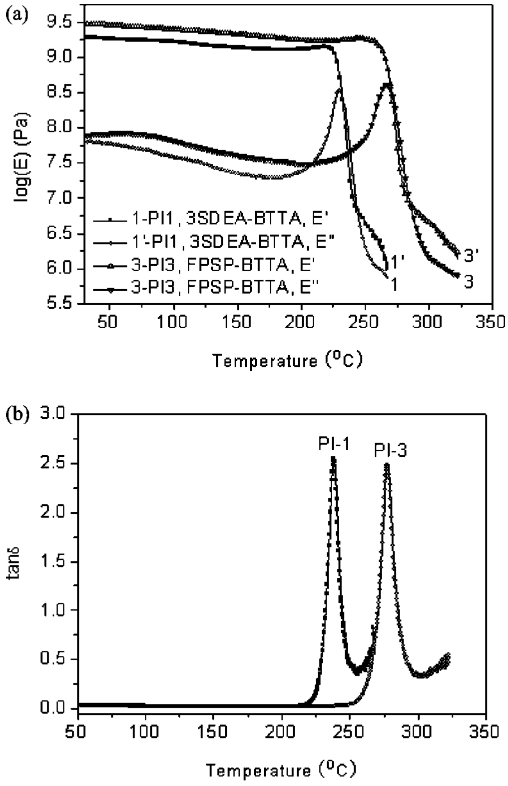


Figure 5. DMA curves of PI-1 and PI-3 (1 Hz, 2 °C/min): (a) modulus; (b) tan δ.

Thermal Properties. The thermal properties of all PIs were evaluated by TGA, DSC, and DMA measurements under a nitrogen atmosphere. The results are summarized in Table 2. As shown in Figure 3, the PIs exhibit good thermal stability with 5% weight loss temperatures ($T_{5\%}$) up to 350 °C and $T_{10\%}$ in the range of 391−443 °C. Weight residues at 750 °C ranging from 59% to 66% are observed in nitrogen. The glass transition temperatures (T_gs) were determined by DSC (Figure 4) and DMA (Figure 5). The T_g values estimated from these two methods are nearly the same. The difference is mainly attributable to the different responses of the polymers to the evolution systems. One of the most important key parameters is the T_g of the optical device fabrication. All of the PIs show high T_gs exceeding 200 °C measured by DSC. PI-3 has the highest T_g, which is ~54 °C higher than those of PI-1 and PI-2. The significantly high T_gs of PI-3 could mainly be attributed to the rigid and steric hindrance of the bulky fluorenyl unit. Additionally, DMA analyses were carried out for PIs 1−3 in air condition at a heating rate of 2 °C min^{-1}. Figure 5 illustrates the variations in the storage modulus (E'), loss modulus (E'), and loss factor (tan δ) at various temperatures. It can be seen from Figure 5 that the modulus remains constant or decreased slightly before their corresponding T_gs. After their T_gs, which are determined as the peak temperatures of E', the modulus drops dramatically. PI-3 exhibits the highest T_g (267 °C) owing to the rigid and bulky fluorenyl unit. These results reveal that the heat deflection temperatures of the PIs can be improved by the incorporation of rigid or cyclic substituents.

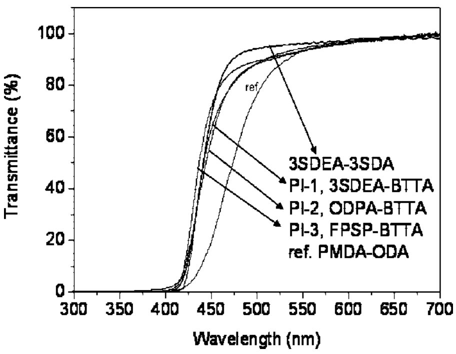


Figure 6. UV−vis spectra of PI films (film thickness: ~10 μm).

Optical Properties. Figure 6 exhibits the UV−vis absorption spectra of PI films (pale yellow, ~10 m thick). The data are summarized in Table 3. The cutoff wavelengths (λ_{cutoff}) of the films are in the range of 418−421 nm. The spectral shapes of the five PIs are similar to each other, and the transmittances of the film measured at 500 nm are higher than 80% in the visible region, which is much higher than that of the PI derived from pyromellitic dianhydride (PMDA) and 4,4′-oxidianiline (ODA).[17] The transmittance of PI-3 measured at 450 nm is 73%, while that of PI-1 and PI-2 is 65% and 63%, respectively. The highest transparency of PI-3 is attributable to the bulky and twisted fluorene structures in the main chains which effectively weaken the intermolecular packing by increasing the free volumes among the PI chains. All the PI films show higher optical transparency than conventional aromatic PI (PMDA/ODA). The in-plane (n_{TE}), out-of-plane (n_{TM}), average refractive indices (n_{av}), and in-plane/out-of-plane birefringences (Δn) for the PIs are summarized in Table 3. The n_{av} of 1.7692 observed for PI-1 (3SDEA-BTTA) at 633 nm is the highest value for sulfur-containing PIs ever synthesized by the authors, while the n_{av} of 1.7600 observed for 3SDEA-APTT PI is the highest so far reported in previous studies.[12−17] The notable difference between the molecular structures of APTT and BTTA is the two 1,4-dithiane structures which project normal to the main chains of BTTA. The central component of BTTA is a 3,4,8,9-tetrahydro-2,5,7,10-tetrathiaanthracene structure attached to two

Table 3. Optical Properties of the PIs Films

			refractive indices and birefringence at 633 nm					
PI	$\lambda_{\mathrm{cutoff}}$[a] (nm)	d[b] (μm)	n_{TE}[c]	n_{TM}[d]	n_{av}[e]	Δn[f]	n_∞[g]	D ($\times 10^2$)[h]
PI-1	418	19.0	1.7723	1.7630	1.7692	0.0093	1.7120	2.286
PI-2	419	13.9	1.7444	1.7336	1.7408	0.0108	1.6976	1.745
PI-3	421	30.3	1.7445	1.7375	1.7422	0.0070	1.6908	2.069
ref[i]	415		1.7163	1.6322	1.6883	0.0841	1.6412	1.887

[a] $\lambda_{\mathrm{cutoff}}$: cutoff wavelength. [b] d: film thickness. [c] n_{TE}: the in-plane refractive index. [d] n_{TM}: the out-of-plane refractive index. [e] n_{av}: average refractive index $[(2n_{\mathrm{TE}}^2 + n_{\mathrm{TM}}^2)/3]^{1/2}$. [f] See Measurements section. [g] n_∞: refractive index at the infinite wavelength. [h] D: coefficient of wavelength dispersion determined by fitting with the simplified Cauchy's formula (see text). [i] PMDA−ODA employed as reference.[21]

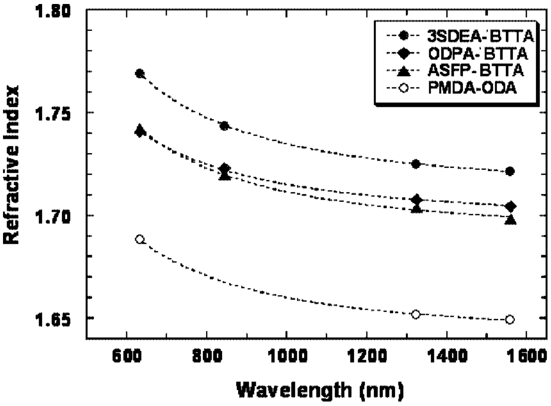


Figure 7. Wavelength dispersion of the refractive indices of PIs.

thiophenyl groups. It is noteworthy that this spatially spreading component possesses a disklike planar structure containing six sulfur atoms located at similar distances from the center. This unique structure makes possible a dense assembly of sulfur atoms, which leads to the high refractive indices. In addition, the molecular packing coefficient (K_{p}) estimated from the calculated van der Waals volumes (V_{vdw}), molecular polarizabilities (α), and the observed refractive indices at 1558 nm for PI-1 (0.5816) is significantly higher than that of 3SDEA-3SDA (0.5596). The relatively dense molecular packing in PI-1 could be an essential reason for the highest value of n_{av}.

The average refractive indices of PIs (n_{av}), measured at $\lambda =$ 633, 845, 1324, and 1558 nm, are plotted in Figure 7. As indicated by the dotted lines, the wavelength-dependent refractive indices (n_λ) are fitted by a simplified form of Cauchy's formula, $n_\lambda = n_\infty + D/\lambda^2$, where n_∞ is the refractive index at an infinite wavelength and D is the coefficient of dispersion. The values of n_∞ and D thus obtained are listed in Table 3. PI-1 with the highest n_{av} at 633 nm exhibits the largest values of n_∞ and D of the four, which agree with the linear relationship between n_∞ and D obtained from a series of aromatic PIs.[21] In contrast, PI-2 shows the second-highest n_∞ despite an n_{av} value lower than that of PI-3, which is caused by the smallest D value of PI-2. We previouly reported that another PI derived from ODPA dianhydride yields a small D in aromatic PIs.[21]

As seen in Table 3, all PI films exhibit higher n_{TE} values than n_{TM}, indicating that they have positive birefringence and that the molecular chains are preferentially aligned in the film plane. The Δn values of the PI films range from 0.0070 to 0.0108. The low birefringence of the PIs may arise from the flexible diphenyl sulfide linkages, which effectively reduces the in-plane orientation of the PI main chains. The relatively small birefringence of PI-3 implies that the PI chain is randomly oriented in the film due to the bulky and twisted structure of FPSP in contrast to the rigid and highly birefringent PI of PMDA/ODA. The significant decrease in Δn by the use of FPSP dianhydride has been reported elsewhere.[15]

Conclusions

The new diamine BTTA containing a tetrathiaantracene-1,4-disulfanyl moiety was designed and synthesized. A series of PIs were prepared by the polycondensation of BTTA with sulfur-containing aromatic dianhydrides including 3SDEA, ODPA, and FPSP, followed by thermal imidization. The PIs based on BTTA show a refractive index higher than those of common sulfur-containing PIs owing to the high sulfur content in the polymer main chain. The series of PIs shows good optical transparency and relatively high glass transition temperatures. In particular, PI-1 containing the highest sulfur content of the molecular chains (28.4%) showed the highest refractive index (1.7692), with a low birefringence of 0.0093.

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