High Refractive Index Polyimides Derived from 2,7-Bis(4-aminophenylenesulfanyl)thianthrene and Aromatic Dianhydrides

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ABSTRACT: High refractive aromatic polyimides (PIs) containing a thianthrene-2,7-disulfanyl moiety in their main chain have been developed. The PIs were prepared from a newly developed aromatic diamine 2,7-bis(4-aminophenylenesulfanyl)thianthrene (APTT) and several aromatic dianhydrides by a two-step polycondensation procedure. The relationships between the structures and the thermal, mechanical, and optical properties of the flexible, tough, transparent, and amorphous PI films were established. Introduction of the thianthrene-2,7-disulfanyl group endowed the PIs with good combined properties, including high thermal stability with 10% weight loss temperatures ($T_{10\%}$) higher than 500 °C in nitrogen and the glass transition temperatures (T_gs) higher than 200 °C, good transparency with transmittances higher than 80% at 500 nm, and refractive indices higher than 1.73 at 632.8 nm. Because of higher sulfur content, the refractive indices of the PIs we synthesized are higher than those of PIs derived from the other sulfur-containing diamines such as 4,4′-(*p*-phenylenedisulfanyl)dianiline (2SPDA) and 4,4′-thiobis[(*p*-phenylenesulfanyl)aniline] (3SDA). The PI derived from APTT and 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA) has the highest sulfur content (23.2%) in its repeating units, and hence, it exhibits the highest refractive index, i.e., 1.7600.

Introduction

In recent years, there is an increasing demand for high refractive index polymers with high transparency and low birefringence for advanced integrated optical applications.[1−3] Many conventional sulfur-containing polymers characterized by high optical transparency,[4] a high dielectric constant,[5] good adhesion to the substrates,[6] and a high refractive index[7] have been reported. On the other hand, the thermal stability of polymers is becoming an important consideration in the design of advanced optical devices due to the severe heat environment present during fabrication processes.[8] Therefore, the applications of conventional sulfur-containing polymers are greatly limited owing to their poor combined properties at elevated temperatures. Aromatic polyimides (PIs), known for their excellent physical and chemical properties, have been studied and developed for many years from the point of view of both academic and technical interests.[9−12]

Recently, high refractive index PIs with high thermal stability have been proposed for optoelectronic applications such as charge-coupled device (CCD) image sensors, complementary metal oxide semiconductor (CMOS) image sensors, etc.[13−15] However, thus far, the high refractive index values reported in the literature have mainly been achieved by the incorporation of metal oxide compounds such as titanium dioxide or zirconium oxide.[13]

Recently, we have synthesized a series of sulfur-containing PIs in our laboratory from various aromatic dianhydrides and two aromatic diamines 4,4′-(*p*-phenylenedisulfanyl)dianiline (2SPDA) and 4,4′-thiobis[(*p*-phenylenesulfanyl)aniline] (3SDA) that contain linear thioether moieties.[16,17] The resulting PIs possessed good thermal stability, high refractive index, good transparency, and low birefringence. To further improve the refractive indices without forfeiting other optical and thermal properties, we focused on the thianthrene-2,7-disulfanyl moiety because the inclusion of a thianthrene with two sulfur atoms in its molecular structure increases the sulfur content of the repeating units. Furthermore, the bent structures of the thianthrene ring and thioether unit may suppress packing between the polymer chains, which is required for high transparency and low birefringence. Polymers containing thianthrene rings have been studied for many years either for developing functional polymers such as polyamides,[18] PIs,[19,20] and poly(aryl ethers)[21] or for developing functional agents such as i-line-sensitive photoacid generators.[22] However, there have been limited experimentations with high refractive index polymers containing thianthrene groups.[23]

This paper presents the synthesis of 2,7-bis(4-aminophenylenesulfanyl)thianthrene (APTT), a novel diamine, and PIs from APTT and various aromatic dianhydrides. The PI derived from APTT and a sulfur-containing dianhydride 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA) exhibited the highest refractive index of 1.7600 with high thermal stability (>500 °C), high transparency (>450 nm), and low birefringence (0.0084). The structure−property relationships of the PIs are reported.

Experimental Part

Materials. *p*-Fluorothiophenol and *p*-aminothiophenol were purchased from Aldrich and used as received. Fuming sulfuric acid (60% oleum) was purchased from Wako, Japan, and used as received. *N*-Methyl-2-pyrrolidinone (NMP, Wako, Japan) and *N,N*-dimethylformamide (DMF, Wako, Japan) were purified by vacuum distillation over CaH_2 prior to use. All the other chemicals were purchased from TCI, Japan, and used directly. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (sBPDA) and 4,4′-oxydiphthalic anhydride (ODPA) were dried at 160 °C overnight in vacuo prior to use. 2,3,3′,4′-Biphenyltetracarboxylic dianhydride (aBPDA) was synthesized according to a modified reported procedure.[24] 4,4′-[*p*-

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Thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA) was synthesized in-house according to our previous work.[17]

Monomer Synthesis. 2,7-Difluorothianthrene. The compound was prepared according to a reported procedure;[21,25] mp 156 °C [differential scanning calorimetry (DSC) peak temperature] (lit. 156 °C). IR (KBr, cm^{-1}): 1592.9, 1454.1, 1253.5, 1207.2, 894.8, 856.2, and 802.2. ^1H NMR (300 MHz, DMSO-d_6, ppm): 6.96−7.03 (m, 2H), 7.22−7.25 (m, 2H), and 7.41−7.45 (m, 2H).

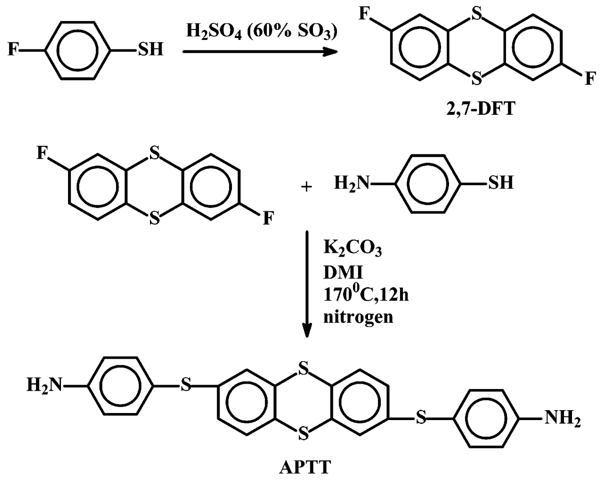
2,7-Bis(4-aminophenylenesulfanyl)thianthrene (APTT). *p*-Aminothiophenol (9.39 g, 75 mmol), anhydrous potassium carbonate (5.39 g, 39 mmol), NMP (30 mL), and toluene (50 mL) were placed in a 200 mL three-necked flask equipped with a magnetic stirrer, a Dean−Stark trap, a nitrogen inlet, and a reflux condenser. The mixture was heated to reflux (140−145 °C) in an oil bath for 4 h until the theoretical amount of water was collected in the trap. Residual toluene was removed by distillation. The reaction mixture was cooled to 120 °C, and a slurry of 2,7-difluorothianthrene (7.57 g, 30 mmol) and 15 mL of NMP was added. The reaction mixture was then heated to 170 °C and stirred for 12 h. Next, the mixture was cooled to room temperature and poured into water (500 mL) with stirring. The precipitated yellow solids were collected by filtration and washed thoroughly with water. The solids were heated with ethanol (250 mL) for 1 h. Then, the mixture was filtered hot. The pale yellow solids obtained in the filter were washed twice with cold ethanol and dried in vacuo at 80 °C overnight. The solids (10.34 g, yield: 74.5%) were analyzed to check whether they were target compound; mp 185.2 °C (DSC peak temperature). IR (KBr, cm^{-1}): 3428.8, 3332.4, 2360.4, 1619.9, 1592.9, 1565.9, 1492.6, 1442.5, 1361.5, 1292.1, 1176.4, 1103.1, and 817.7. ^1H NMR (300 MHz, DMSO-d_6, ppm): 5.49 (s, 4H), 6.61−6.64 (d,4H), 6.94−6.98 (d, 4H), 7.06 (s, 2H), 7.14−7.17 (d, 4H), and 7.36−7.38 (d, 2H). ^{13}C NMR (300 MHz, DMSO-d_6, ppm): 151.2, 142.2, 137.5, 136.7, 131.0, 129.9, 126.2, 125.9, 115.8, and 114.3. Anal. Calcd for $C_{24}H_{18}N_2S_4$: C, 62.31; H, 3.92; N, 6.05. Found: C, 62.22; H, 3.96; N, 6.01.

Polyimide Synthesis. The polymers were synthesized from APTT and four dianhydrides via a two-step procedure. For example, PI-1 was prepared as follows. sBPDA (1.4711 g, 5.0 mmol) was added to a stirred solution of APTT (2.3133 g, 5.0 mmol) in NMP (21.4 g) with a solid content of 15 wt %. The reaction mixture was stirred in nitrogen at room temperature for 24 h to afford a viscous brown solution. The obtained poly(amic acid) (PAA) solution was filtered through a 0.45 μm Teflon syringe filter to eliminate any particulates that might affect the quality of the cured film. The purified PAA solution was spin-coated on a silicon (Si) wafer or quartz substrate, and the thickness was controlled by regulating the spinning rate. The thickness of the specimen for Fourier transform infrared (FT-IR) and ultraviolet−visible (UV−vis) measurements was controlled to be ∼10 μm, and the thickness of the specimen to be used for measuring thermal properties was adjusted to be 30−50 μm. The PI-1 film was obtained by thermally curing the PAA solution in an oven at 80, 150, 250, and 300 °C for 1 h each. The PI-1 film, which was brown in color, was obtained by immersing the Si wafer in warm water.

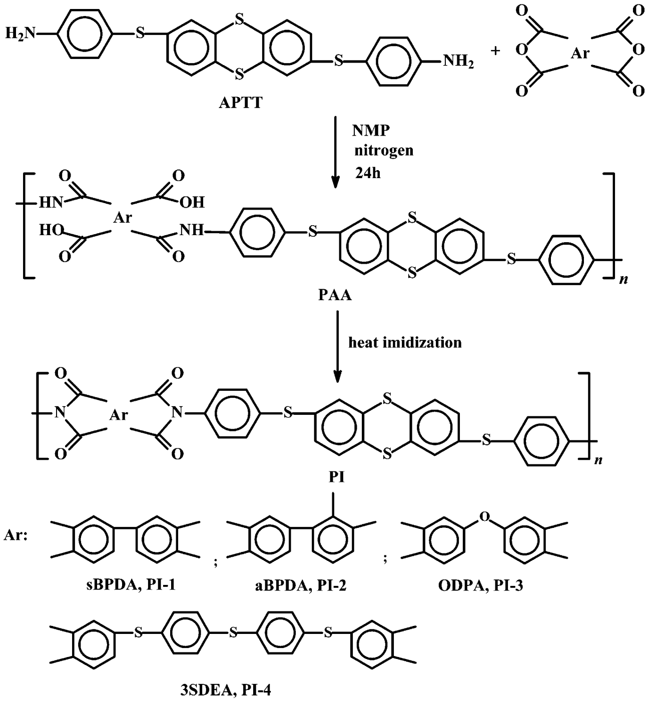
Other PI films were prepared by a procedure similar to that mentioned above, except that sBPDA was substituted with aBPDA (PI-2), ODPA (PI-3), or 3SDEA (PI-4).

Measurements. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the reference. Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g/dL solution in NMP at 30 °C. The FT IR spectra were obtained with a Horiba FT-120 Fourier transform spectrophotometer. The UV vis spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The PI films were dried at 100 °C for 1 h prior to testing to remove any absorbed moisture. Wide-angle X-ray diffraction was conducted on a Rigaku D/max-2500 X-ray diffractometer using Cu Kα_1 radiation; the instrument was operated at 40 kV and 200 mA. Thermogravimetric analysis (TGA) was performed using the Seiko TG/DTA 6300 thermal analysis system at a heating rate of 10 °C/min in nitrogen. DSC was performed using the Seiko 6300 at a heating rate of 10 °C/min. Dynamic mechanical thermal analysis (DMA) was performed on the PI film specimens (length, 30 mm; width, 10 mm; thickness, 50−60 μm) by using the Seiko DMS 6300 at a heating rate of 2 °C/min with a load frequency of 1 Hz in air. The peak temperature of the loss modulus (E'') plot was determined to be the glass transition temperature (T_g).

Scheme 1. Synthesis of APTT



Scheme 2. Synthesis of PIs

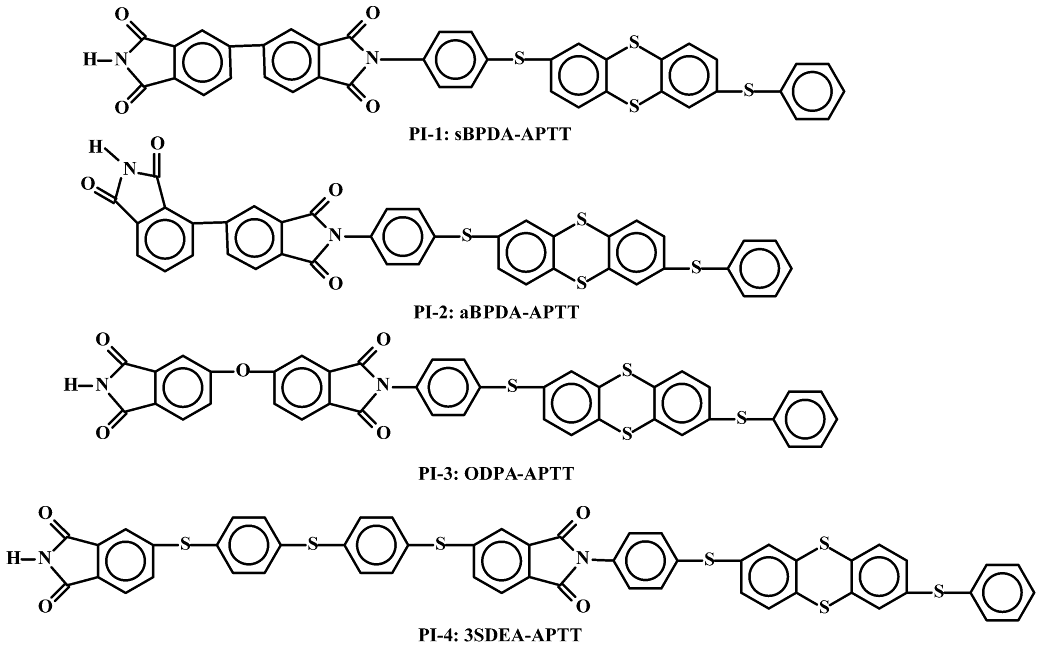


The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the PI films were measured using a prism coupler (Metricon, model PC-2000) equipped with a He−Ne laser light source (wavelength: 632.8 nm). The in-plane (n_{TE})/out-of-plane (n_{TM}) birefringence (Δn) was calculated as the difference between the n_{TE} and n_{TM}. The average refractive index (n_{av}) was calculated by

$$n_{av} = \sqrt{(2n_{TE}{}^2 + n_{TM}{}^2)/3}$$

Calculations. The refractive indices of the models for the aromatic PIs synthesized in this study were calculated on the basis of the Lorentz−Lorenz theory as reported previously.[16] The model structures used for the density functional theory (DFT) calculations are shown in Scheme 3. One-electron transition energies and the

Scheme 3. Model Compounds for the Calculation of the Refractive Index



PI-1: sBPDA-APTT

PI-2: aBPDA-APTT

PI-3: ODPA-APTT

PI-4: 3SDEA-APTT

corresponding oscillator strengths of the PI models were also calculated using time-dependent DFT (TD-DFT) to predict optical absorptions in the UV−vis region.[26−28] The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) was used for calculating linear polarizabilities, transition energies, and oscillator strengths. The three-parameter Becke-style hybrid functional (B3LYP) was adopted as a function, and all calculations were performed using the software package of Gaussian-03 (Rev. C02 and D01). A typical packing coefficient (K_p) of 0.60 was used to evaluate the intrinsic molecular volumes of the models and predict the refractive indices.[29]

Results and Discussion

Monomer Synthesis. As shown in Scheme 1, APTT was synthesized by a two-step procedure with *p*-fluorothiophenol as the starting material. First, the intermediate 2,7-DFT was prepared according to a reported procedure and purified by sublimation under a reduced pressure.[21] Second, 2,7-DFT was reacted with *p*-aminothiophenol to afford APTT with a yield of 74.5%. The attempt to prepare APTT from 2,7-dichlorothianthrene (2,7-DCT) had limited success. The yield was lower (less than 25%), and much more solvent (NMP) had to be used due to the low solubility of 2,7-DCT. In contrast to the aromatic diamines with linear thioether moieties, such as 2SPDA and 3SDA, APTT has lower solubility in absolute ethanol. Thus, it is difficult to recrystallize APTT with ethanol. However, we observed that after APTT was boiled with ethanol at a solid content of 25 wt % it was obtained as a white solid with high purity. The structure of the diamine was confirmed by FT IR, ^{1}H NMR, and ^{13}C NMR spectroscopies and elemental analysis. The IR spectrum of APTT shows characteristic absorptions at 3428 and 3332 cm^{-1} due to the N−H stretching of a primary amino group (Figure 1). In addition, the absorptions of the thioether (C−S−C) and 1,3,4-substituted benzene rings are observed at 1103 and 817 cm^{-1}, respectively. The ^{1}H NMR and ^{13}C NMR spectra of APTT are presented in Figure 2. The characteristic amino protons and the protons ortho to the thianthrene ring (H_e) are observed at 5.49 and 7.37 ppm, respectively (Figure 2a). In Figure 2b, 10 carbon signals in the range of 114−151 ppm appear in the spectrum; this is consistent with the expected structure of the diamine. In addition, the measured elemental compositions of C, H, and N elements agree well with the calculated values. From the above data, it is obvious that the new diamine APTT is obtained with high purity for the polymerization.

Polyimide Synthesis. The syntheses of the PIs are depicted in Scheme 2. High molecular weight poly(amic acid)s (PAAs) with inherent viscosities in the range 0.92−1.24 dL/g are prepared easily (Table 1). Flexible and tough PI films were obtained by heating the corresponding PAAs cast onto a quartz substrate (diameter, 10 cm) in nitrogen, followed by immersion in warm water. The resulting PI films were dried in vacuo at 100 °C for 10 h prior to performing measurements. The FTIR spectra of the PIs show characteristic absorptions due to the imide ring at 1780 ($\upsilon_{as,C=O}$), 1720 ($\upsilon_{s,C=O}$), and 1387 cm^{-1} ($\upsilon_{as,C-N}$) (Figure 3). The absorption due to C−S stretching of an Ar−S−Ar unit is also observed at 1083 cm^{-1} (indicated by asterisks in the spectra). Furthermore, the structures of the PIs were confirmed by elemental analysis. X-ray diffractions performed on thin films indicated that the obtained PIs are amorphous polymers in the solid state; this can be further confirmed by the DSC measurements, in which no melting peaks were observed.

Thermal Properties. The thermal properties of the PIs were evaluated by TGA, DSC, and DMA measurements. The results are summarized in Table 2. As shown in Figure 4 (TGA), the PIs exhibit good thermal stability up to 450 °C. Residual weights ranging from 64% to 71% are observed at 750 °C in nitrogen.

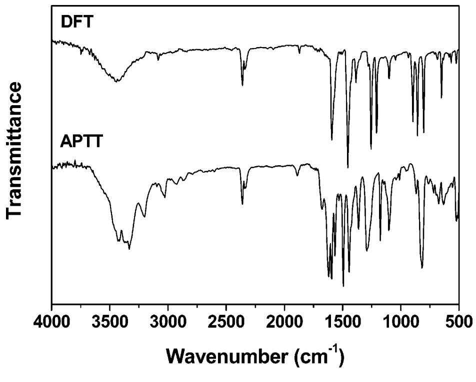


Figure 1. FTIR spectra of APTT.

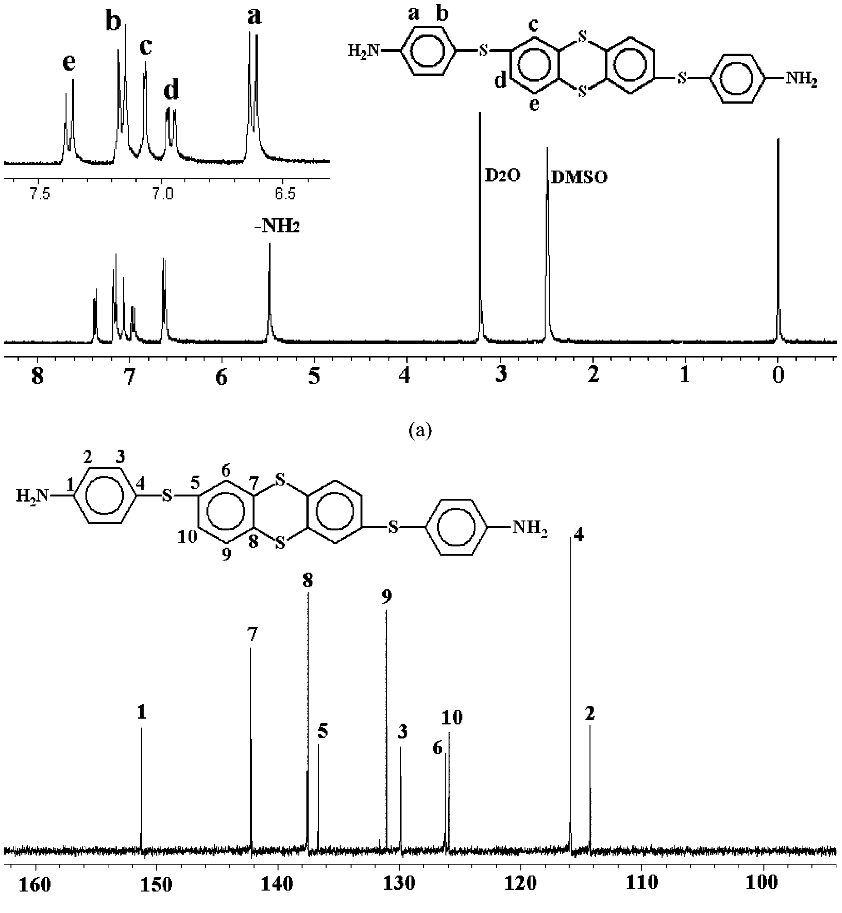


Figure 2. NMR spectra of APTT (a) ^{1}H NMR and (b) ^{13}C NMR.

Table 1. Synthesis and Characterization of PIs

PI	dianhydride	yield (%)	$[\eta]_{inh}$[a] (dL/g)	elemental analysis	C	H	N
PI-1	sBPDA	98	1.24	calcd	66.65	2.80	3.89
				found	66.21	3.02	3.66
PI-2	aBPDA	98	0.92	calcd	66.65	2.80	3.89
				found	66.37	3.03	3.47
PI-3	ODPA	98	1.16	calcd	65.20	2.74	3.80
				found	64.79	2.92	3.64
PI-4	3SDEA	99	1.03	calcd	64.44	2.91	2.89
				found	63.89	3.11	2.62

[a] Measured with PAA at a concentration of 0.5 g/dL in NMP solution at 30 °C.

Table 2. Thermal and Mechanical Properties of the PI Films

	T_g (°C)[a]						
PI	DSC	DMA	$T_{5\%}$[a] (°C)	$T_{10\%}$[a] (°C)	R_{w750}[a] (%)	E'[b] (GPa)	E''[b] (MPa)
PI-1	252	226	519	563	71	2.89	89.1
PI-2	229	217	506	546	70	2.73	88.4
PI-3	240	221	513	527	66	2.45	66.1
PI-4	201	202	494	508	64	1.74	55.0

[a] T_g = glass transition temperatures; $T_{5\%}$ and $T_{10\%}$ = temperatures at 5% and 10% weight loss, respectively; R_{w750} = residual weight ratio at 750 °C in nitrogen. [b] E' = storage modulus at 30 °C; E'' = loss modulus at 30 °C, 1 Hz.

The PI films had $T_{10\%}$ values of 508−563 °C in the following decreasing order: PI-1 > PI-2 > PI-3 > PI-4. This trend is consistent with the structural characteristics of the PIs. For example, in contrast to the rigid molecular structures of PI-1 and PI-2, that of PI-4 is more flexible due to the flexible thioether linkages present in its molecular chains; therefore, the $T_{10\%}$ value of PI-4 is much lower. A similar trend is also observed with regard to the DSC measurements (Figure 5). PI-1 has the highest T_g, which is ~51 °C higher than that of PI-4 (201 °C). It should be also noted that PI-4, which is derived from 3SDEA and APTT, has a higher T_g than its analogous PIs (179 °C for 3SDEA−3SDA and 191 °C for 3SDEA−2SPDA), indicating that the introduction of a cyclic thianthrene group prohibits with the free motions of the molecular chains at elevated temperatures.

The temperature dependence of the dynamic storage modulus (E'), loss modulus (E''), and tan δ of the representative PIs (PI-1 and PI-4) are shown in Figure 6 and Table 2. The initial values of E' (30 °C) are in the range 1.74−2.89 GPa, which remains constant or decreases slightly on heating over a wide temperature range up to ~200 °C. The corresponding E'' curves show a

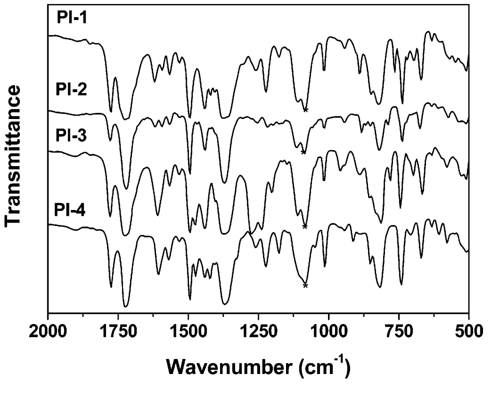


Figure 3. FTIR spectra of PI films.

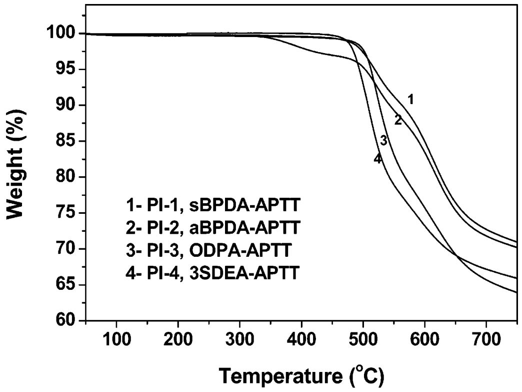


Figure 4. TGA curves of PI films (in nitrogen, 10 °C/min).

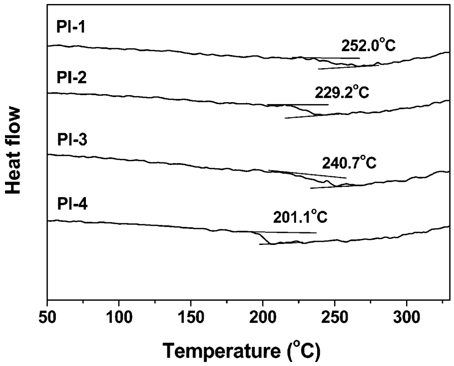
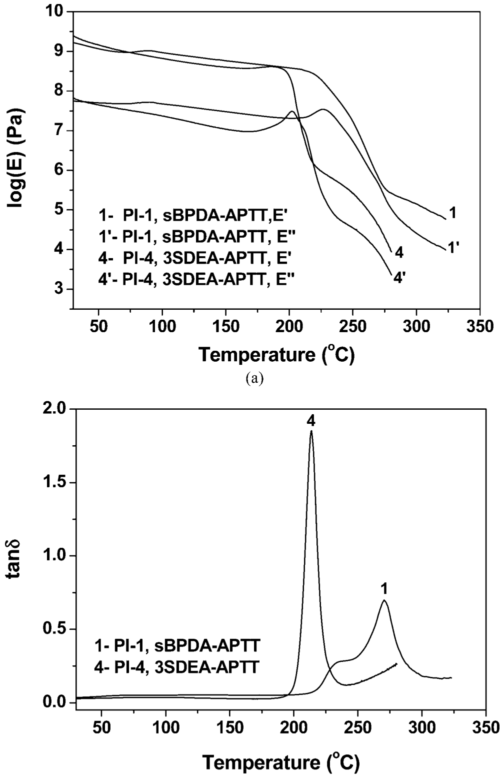


Figure 5. DSC curves of PI films (in nitrogen, 10 °C/min).

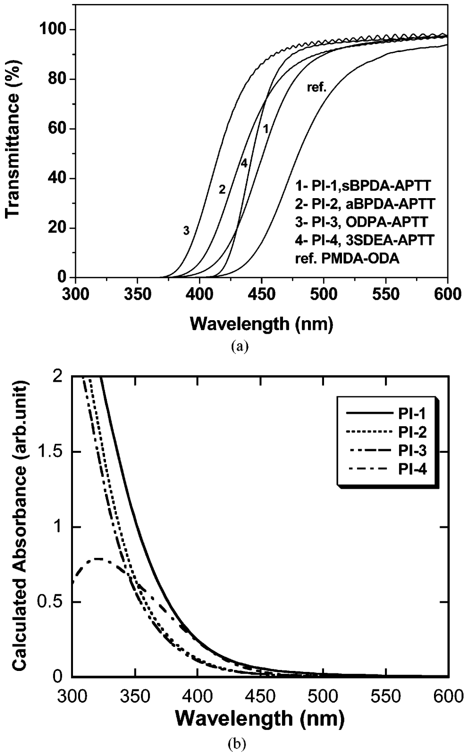


(a)

(b)

Figure 6. DMA curves of PI-1 and PI-4 (1 Hz, 2 °C/min): (a) modulus and (b) tan δ.

similar trend. The difference is that the E'' curve has a maximum peak, indicating the glass transition of the PI. The T_g values range from 202 to 226 °C, which are lower than those measured by DSC, except for PI-4.



(a)

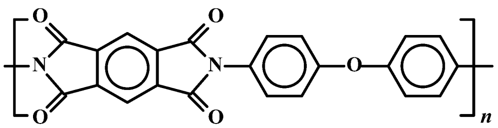
(b)

Figure 7. UV vis spectra of PI films: (a) experimental and (b) calculated results.

Table 3. Optical Properties of the PI Films

				refractive indices and birefringence					
PI	S_C[a] (%)	λ_{cutoff}[b] (nm)	d[c] (μm)	n_{TE}[d]	n_{TM}[d]	n_{av}[d]	Δn[d]	n_{cal}[e]	ϵ[f]
PI-1	17.8	376	9.0	1.7595	1.7452	1.7547	0.0143	1.7703	3.39
PI-2	17.8	374	11.9	1.7429	1.7358	1.7405	0.0070	1.7487	3.33
PI-3	17.4	367	8.5	1.7403	1.7302	1.7370	0.0101	1.7623	3.32
PI-4	23.2	400	11.8	1.7628	1.7545	1.7600	0.0084	1.7886	3.41
ref[g]	0	415	9.2			1.6950	0.0780		

[a] Sulfur content. [b] Cutoff wavelength. [c] Film thickness. [d] See Measurements section. [e] Calculated refractive index; see Calculations section. [f] Dielectric constant estimated from modified Maxwell's equation as $\epsilon = 1.10n_{av}^2$. [g] Reference 31. PMDA-ODA with the following chemical structure:



Optical Properties. Optical transparency of the PI films is a crucial factor for their use in optical applications. Generally, wholly aromatic PI films exhibit colors ranging from pale-yellow to deep brown, depending on their structures, due to the formation of intra- or intermolecular charge-transfer complexes (CTC).[30] External factors that affect the colors of the PI films include purity of the polymers, residual solvent, film-forming conditions, etc. Thus, in the current study, the PI specimens used for optical properties evaluations were prepared from highly purified monomers in a nitrogen atmosphere to eliminate other effects. By these procedures, the PI films with colors ranging from brown-yellow (40 ± 1 μm, for thermal properties evaluation) to pale-yellow (10 ± 0.5 μm, for optical properties evaluation) were obtained. Parts a and b of Figure 7 depict the experimental UV−vis spectra of PI films that were ~10 μm thick and the calculated absorption spectra, respectively. The data are summarized in Table 3. The films have cutoff wavelengths (λ_{cutoff}) of 367−400 nm, which decrease approximately to the same extent as the decrease in the sulfur

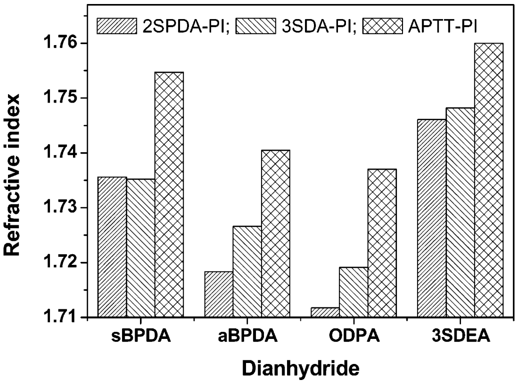


Figure 8. Comparison of the refractive indices of PIs (632.8 nm).

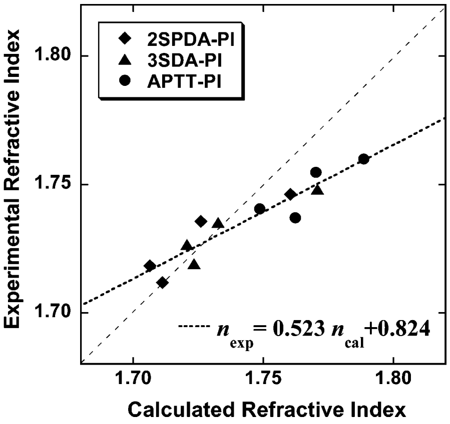


Figure 9. Experimental and calculated refractive indices of PIs (632.8 nm).

contents in the order of PI-4 > PI-1 ≈ PI-2 > PI-3. The PI films exhibit good transparency over 500 nm with the transmittance higher than 80%. The transmittance of PI-3 at 450 nm is 86.2%, while that of PI-1, PI-2, and PI-4 is 48.1%, 68.5%, and 65.7%, respectively. Thus, PI-3 shows the best optical transparency, which is consistent with the calculated results (Figure 7b). All the films exhibit much better optical transparency than the standard aromatic PI derived from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) at a similar thickness (Figure 7a).

As shown in Table 3, the refractive index (n_{av}) increases from a minimum of 1.7370 (PI-3) to a maximum of 1.7600 (PI-4) with increasing sulfur content. These values are all higher than the n_{av} value of PMDA-ODA (1.6950).[31] The calculated n_{av} values show similar trends. Despite identical sulfur contents, the n_{av} value of PI-1(1.7547) is higher than that of PI-2 (1.7405), since PI-2 has a larger molecular free volume due to asymmetric bulky molecular packing. The values of in-plane/out-of-plane birefringence (Δn) of the PI films range from 0.0084 to 0.0143, which are much lower than that of the typical aromatic PI PMDA-ODA (0.0780).[31] The low birefringence values of the PIs we synthesized are due to the flexible thioether linkages in their molecular chains, which increase chain mobility and decrease chain packing.[32]

Figure 8 compares the n_{av} values (measured at 632.8 nm) of the PIs derived from 2SPDA, 3SDA, and APTT. Within a given dianhydride family, the n_{av} values increase with increasing of sulfur content of the diamine in the order of 2SPDA < 3SDA < APTT. Initially, the incorporation of nonplanar thianthrene moieties was expected to increase the molecular free volume of the obtained PIs[18] and thus cause a possible decrease in the n_{av} values according to the Lorentz−Lorenz equation.[16] However, the n_{av} values continued to increase. For example, PI-4 has a n_{av} value of 1.7600, which is higher than that of 3SDEA−3SDA and 3SDEA−2SPDA by 0.0118 and 0.0139, respectively. This might be a result of the competition between the increasing sulfur contents and molecular free volumes. Figure 9 shows the relationships between the experimental n_{av} (measured at 632.8 nm) and calculated n_{cal} for the PIs shown in Figure 8. The experimental n_{av} values show a linear relationship with the calculated n_{cal}, indicating that DFT calculation is a very useful tool for predicting the refractive indices of polymers. Further, it should be noted that the relationship expressed as $n_{av} = 0.523n_{cal} + 0.824$ is apparently a deviation from the quantitative prediction of n_{exp} (i.e., $n_{av} = n_{cal}$ as indicated by a dotted line). The cause of the deviation is directly attributed to the use of a constant packing coefficient (K_p) of 0.60 for evaluating molecular volumes. The significantly smaller values of n_{av} compared with the corresponding n_{cal} values are observed for the PIs exhibiting n_{av} higher than 1.74. This fact indicates that the degree of molecular packing decreases (i.e., larger molecular free volumes with smaller K_p) with increasing thioether linkages. If similar degrees of molecular packing (K_p) are attained for all the PIs, refractive indices higher than 1.785 can be expected.

The dielectric constants of the PI films estimated by using the average refractive indices in the modified Maxwell equation: $\epsilon = 1.10n_{av}^2$ are shown in Table 3.[33] The PI films are expected to demonstrate the ϵ values ranging from 3.32 to 3.41.

Conclusion

To increase the refractive indices of sulfur-containing PIs without forfeiting their other optical and thermal properties, APTT, which is a thianthrene-2,7-disulfanyl moiety-containing diamine, was synthesized. The PIs derived from APTT showed refractive indices higher than 1.73 because of the high sulfur content of their repeating units. The bent structure of the thianthrene ring and the flexible thioether linkages afforded the PIs with high transparency and low birefringences. In particular, PI-4 demonstrated good combined characteristics, including a $T_{5\%}$ of 494 °C, T_g of 201 °C, n_{av} of 1.7600, and Δn of 0.0084; hence, it is a good candidate for advanced optical applications.

References and Notes

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