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ARTICLE

Synthesis and Characterization of Highly Refractive Polyimides Derived from Thiophene-Containing Aromatic Diamines and Aromatic Dianhydrides

Namiko Fukuzaki, Tomoya Higashihara, Shinji Ando, and Mitsuru Ueda*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Aromatic thiophene-containing diamines, 2,5-bis(4-aminophenylsulfanyl)thiophene (APST) and 2,5-bis{2′-[5′-(4″-aminophenyl)sulfanyl]thienyl}thiophene (APSTT), were synthesized and polymerized with a sulfur-containing dianhydride, 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA) and 4,4′-oxydiphthalic anhydride (ODPA), respectively, to afford four poly(amic acid)s (PAAs) with inherent viscosities of 0.41 to 1.68 dL/g. Flexible and tough polyimide (PI) films obtained from the PAA precursors showed good thermal, mechanical, and optical properties. The glass-transition temperatures (T_g) of the PIs were in the range of 157−220 °C, determined by differential scanning calorimetry (DSC), and 160−216 °C by dynamic mechanical analysis (DMA), depending on the dianhydride used. The 10% weight loss temperatures were in the range of 354−456 °C, showing relatively high thermally resistant characteristics of the PI films. The PI films also showed good optical transparency above 500 nm, which agreed well with the calculated absorption spectra using the time-dependent density functional theory. The average refractive indices (n_{av}) measured at 633 nm were 1.7228 to 1.7677, and the in-plane/out-of-plane birefringences (Δn) were 0.0067 to 0.0074. In particular, the n_{av} of PI derived from 3SDEA and APSTT exhibited the highest refractive index, that is, 1.7677 at 633 nm, in the high-refractive-index polyimides. The high refractive indices originate from the high sulfur content, dense molecular packing, and the absence of bulky structures. The relatively small birefringence mainly results from the flexible and bent thioether linkage structures of the diamine.

Introduction

Recently, demand for high-refractive-index (high-*n*) polymers with high transparency and low birefringence has increased for advanced integrated optical applications.[1−3] For instance, polymer microlenses for charge-coupled devices (CCDs) and complementary metal oxide semiconductor (CMOS) image sensors require a higher refractive index exceeding 1.70, even 1.80, where the thermal stability of polymers is also becoming an important consideration in the design of polymer microlens because of the severe heat environment present during fabrication processes.[4] The introduction of substituents with high molar refractions and low molar volumes can efficiently increase the refractive indices of polymers according to the Lorentz−Lorenz equation.[5] Because a sulfur atom has a large atomic refraction, many high-*n* polymers containing sulfur have been reported.[6−13] Aromatic polyimides (PIs) are well-known for their high thermal stability and often show inherent high refractive indices because of their high polarizable molecular chains and high aromatic contents and are thus thought to be one of the best candidates for high-*n* polymers.[14−16]

In our continuous efforts to develop optical polymers exhibiting high refractive indices combined with low birefringence, high thermal stability, and optical transparency, a series of PIs was recently developed on the basis of a diamine containing thioether linkages in the skeletal structure.[17−24] The PIs thus prepared possess good thermal stability, refractive indices >1.70 at the wavelength of 633 nm, and birefringences <0.01.

Thiophene- or dibenzothiophene-containing polymers have been attracting much attention for their unique electronic or photonic properties and have wide applications in advanced optoelectronic fields, such as organic field-effect transistors[25,26] and electroluminescent devices.[27] Thiophene-containing PIs have also been developed for microelectronic or photonic applications.[28,29] Although the electrical and optical functions of the thiophene or dibenzothiophene moiety have been widely noticed, their contribution to the high refractive index of polymers as sulfur-containing substituents has rarely been mentioned.[30]

In a previous paper, we reported highly refractive PIs with high sulfur content (Sc) of 20.5 wt % in the repeating unit derived from 2,8-bis(*p*-aminophenylenesulfanyl)dibenzothiophene and aromatic dianhydrides.[22] These PIs exhibited good transparency in the visible region with a transmittance > 80% at 500 nm, high refractive indices ranging from 1.7353 to 1.7578, and low birefringence between 0.0068 and 0.0106. Furthermore, the highly transparent PI with high Sc of 23.2 wt % obtained from 2,7′-bis(4-aminophenylenesulfanyl)thianthrene (APTT) and 3SDEA was reported to show a refractive index of 1.7600 at 633 nm with low birefringence of 0.0084.[19] A thiophene unit is effective to increase Sc while keeping low molar volumes because the sulfur atom is included in a five-member ring. Therefore, the resulting polymers containing thiophene units are expected to have higher refractive indices than corresponding polymers with thioether linkages.

In this study, we prepared new diamines containing a thiophene unit combining flexible thioether moieties, which provide polymers with high refractive indices, high transparency, and low birefringence. We report the synthesis and properties of optically transparent PIs derived from 2,5-bis(4-aminophenylsulfanyl)thiophene (APST), 2,5-bis{2′-[5′-(4″-aminophenyl)sulfanyl]thienyl}thiophene

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*Corresponding author. E-mail: Ueda.m.ad@m.titech.ac.jp.

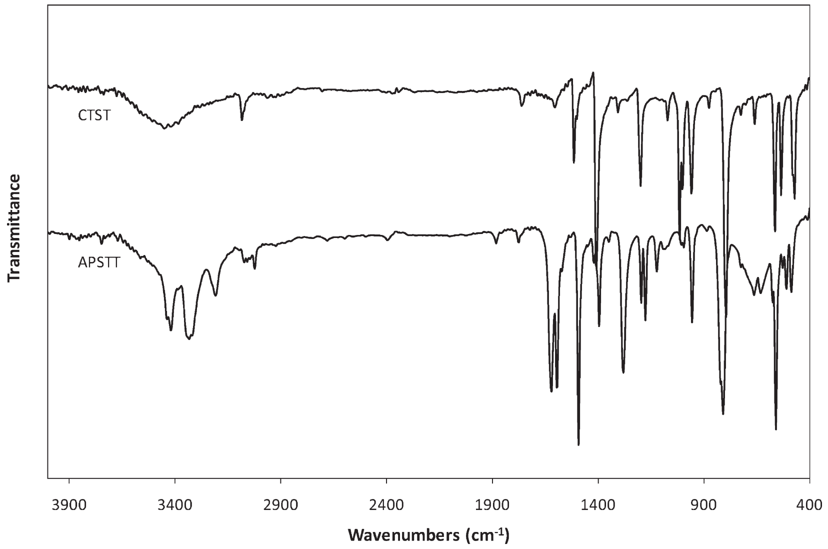
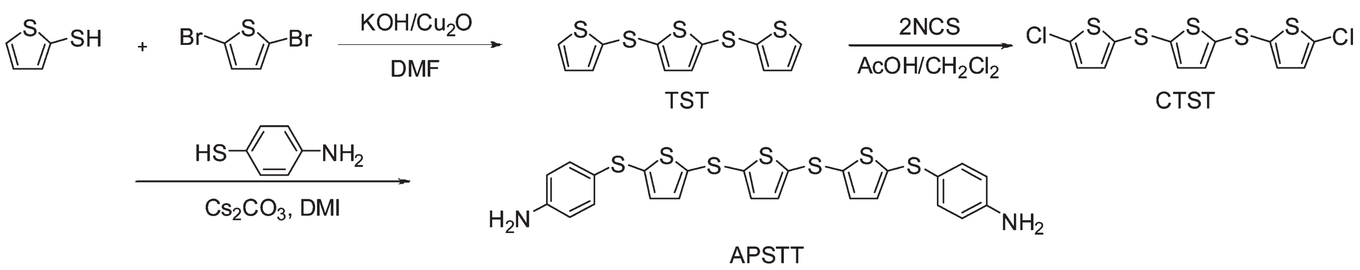


Figure 1. FTIR spectra of CTST and APSTT.

Scheme 1. Synthesis of APSTT



(APSTT), and aromatic dianhydrides such as 4,4′-[*p*-thiobis(phenylsulfanyl)]diphthalic anhydride (3SDEA) and 4,4′-oxydiphthalic anhydride (ODPA). These PIs exhibited high refractive indices in the range of 1.7228 to 1.7677 at 633 nm, high thermal stability (> 350 °C), low birefringence in the range of 0.0067 to 0.0074, and good transmittance > 80% at 500 nm. In particular, the n_{av} of PI derived from 3SDEA and APSTT exhibited the highest refractive index, that is, 1.7677 at 633 nm in the reported highly refractive PIs.[23] The effects of structure on the thermal properties, optical transparency, and refractive indices of the PIs are discussed in detail.

Experimental Section

Materials. All chemicals were purchased from TCI (Tokyo, Japan), if not otherwise specified. 2,5-Dichlorothiophene, 2,5-dibromothiophene, and 4-aminothiophenol were used as received. APST[30] and 3SDEA[18] were prepared according to our previous work. ODPA was dried at 160 °C overnight in vacuo prior to use. *N*-Methyl-2-pyrrolidinone (NMP, Wako, Japan) and *N*,*N*-dimethylformamide (DMF, Wako, Japan) were purified by vacuum distillation from CaH_2 prior to use.

Characterization. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as reference. Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 $g \cdot dL^{-1}$ NMP solution at 30 °C. Fourier transform infrared (FTIR) spectra were obtained with a Horiba FT-120 spectrophotometer. Ultraviolet−visible (UV−vis) optical absorption spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. PI films were dried at 100 °C for 1 h before testing to remove the absorbed moisture. Thermogravimetric analysis (TGA) was recorded on a Seiko TG/DTA 6300 thermal analysis system at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 6300 at a heating rate of 10 °C/min. Dynamic mechanical thermal analysis (DMA) was performed on PI film specimens (30 mm long, 10 mm wide, and 50−60 μm thick) on a Seiko DMS 6300 at a heating rate of 2 °C/min with a load frequency of 1 Hz in air. The glass-transition temperature (T_g) was determined as the peak temperature of the loss modulus (E'') plot.

The out-of-plane (n_{TM}) and in-plane (n_{TE}) refractive indices of PI films were measured with a prism coupler (Metricon, model PC-2000) equipped with a He−Ne laser light source (wavelength: 632.8 nm). In plane/out-of-plane birefringence (Δn) was calculated as the difference between n_{TE} and n_{TM}. The average refractive index (n_{av}) was calculated according to eq 1

$$n_{AV} = \sqrt{(2n_{TE}^2 + n_{TM}^2)/3} \qquad (1)$$

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 in the same way as the previous report.[17] One-electron transition energies and the corresponding oscillator strengths of the PI models were also calculated using the time-dependent (TD)-DFT theory to predict the optical absorption in the UV−visible region.[31−33] The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) was used for calculations of 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

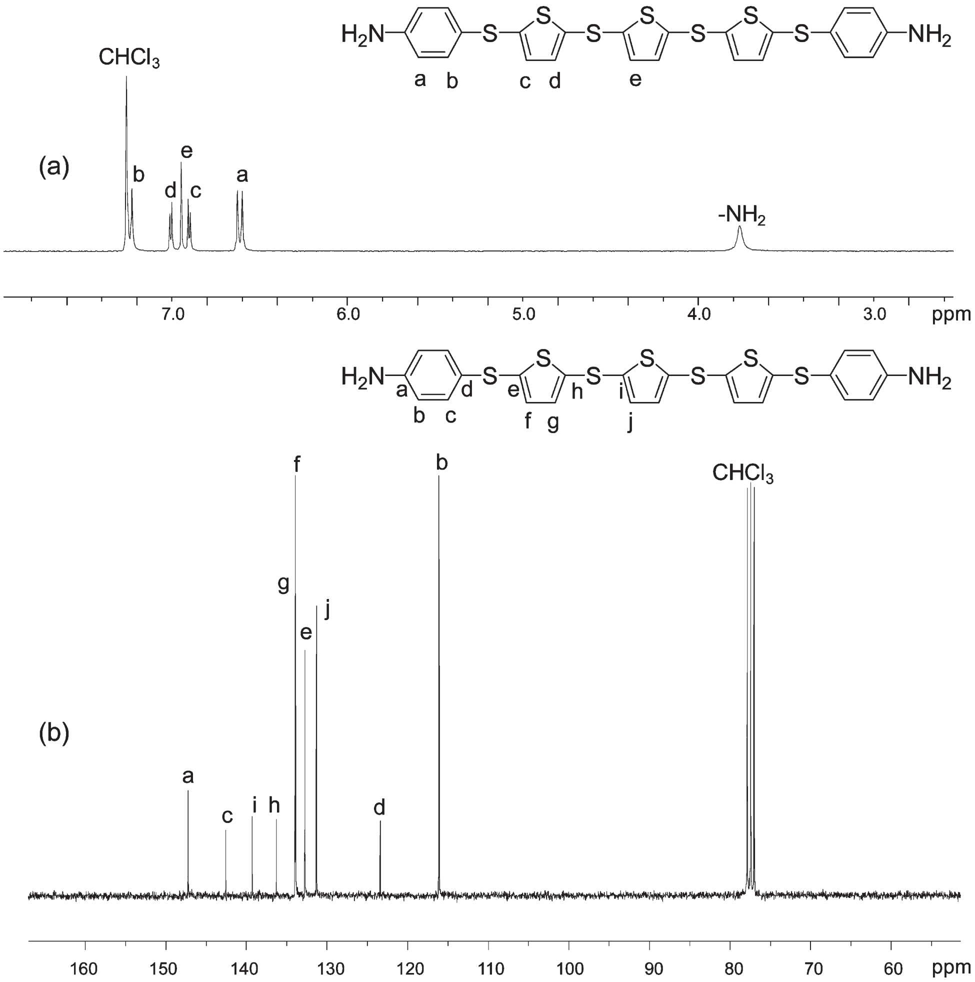


Figure 2. NMR spectra of APSTT (a) ^{1}HNMR and (b) ^{13}CNMR.

(rev. C02 and D01). A typical packing coefficient (K_p) of 0.60 was used for evaluating the intrinsic molecular volumes of models to predict the refractive indices.[14]

Monomer Synthesis. *Synthesis of 2,5-Bis[(2-thienyl)sulfanyl]-thiophene (TST).* A solution of 2-thiophenethiol (4.81 g, 44.1 mmol) in DMF (15 mL) was added to a stirred mixture of 2,5-dibromothiophene (2.75 g, 18 mmol), KOH (2.32 g, 41.4 mmol), and copper oxide (5.67 g, 39.6 mmol) in DMF (30 mL). The mixture was heated at 135 °C for 24 h, cooled to room temperature, and poured in 6 M HCl (80 mL), and toluene (300 mL) was added. The resulting two-phase mixture was stirred for a while and filtered through a pad of Celite. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (hexane) to give TST. Yield: 2.51 g (45%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.10−7.12 (d, 4H), 6.91 (s, 2H), 6.54−6.56 (d, 4H), 5.36 (s, 4H).

Synthesis of 2,5-Bis[2′-(5′-chlorothienyl)sulfanyl]thiophene (CTST). NCS (2.14 g, 16 mmol) was added in small portions to a stirred solution of 2.50 g (8.00 mmol) of TST in acetic acid (12 mL) and dichloromethane (16 mL) over a period of 1.5 h at room temperature. The mixture was poured into water (200 mL), and the organic layer was separated, washed with saturated aqueous $NaHCO_3$ solution and water, dried over $MgSO_4$, and evaporated. The obtained solid was recrystallized from hexane to afford white crystals. Yield: 2.60 g (80%). mp: 58−59 °C. FT-IR (KBr, cm^{-1}): 1515, 1408, 1200, 1014, 1003, 960, 795, 563,536. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.02 (d, 2H), 6.99 (s, 2H), 6.79 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$/TMS, δ): 139.2, 133.9, 133.7, 132.5, 127.0. Anal. Calcd for $C_{12}H_6Cl_2S_5$: C, 37.79; H, 1.59. Found: C, 37.66; H, 1.78.

Synthesis of 2,5-Bis{2′-[5′-(4″-aminophenyl)sulfanyl]thienyl}-thiophene. In a 200 mL round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, a Dean−Stark trap, and a condenser was placed *p*-aminothiophenol (1.38 g, 11.0 mmol), cesium carbonate (2.12 g, 6.50 mmol), DMI (5 mL), and toluene (5 mL). The mixture was heated with stirring at 140 °C for 4 h under a nitrogen atmosphere. After complete removal of water, residual toluene was distilled off. Then, the mixture was cooled to room temperature, and CTST (1.90 g, 5.00 mmol) dissolved in DMI (2.0 mL) was added dropwise to the mixture. After addition, the reaction mixture was heated to 140 °C and maintained at this temperature for 24 h. The mixture was poured in water and extracted with acetic acid. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The crystalline residue was passed through a silica gel column chromatography (elution with a 1:1 mixture of acetic acid and hexane). Evaporation of the solvent gave a solid substance, which was further purified by HPLC (chloroform) to give APSTT. Yield: 0.714 g (25%). mp: 95−98 °C. FTIR (KBr, cm^{-1}): 3421, 3209, 1620, 1597, 1493, 1396, 1281, 1176, 957, 810. ^{1}H NMR (300 MHz, $CDCl_3$/TMS, δ): 7.23−7.26 (d, 4H), 7.00−7.01 (d, 4H), 6.95(s, 2H), 6.90−6.91 (d, 4H), 6.60−6.63 (d, 4H), 3.76 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$/TMS, δ): 147.0, 142.4, 139.0, 136.0, 133.7, 133.6, 132.5, 131.1, 123.2, 115.8. Anal. Calcd for $C_{24}H_{18}N_2S_7$: C, 51.58; H, 3.25; N, 5.01. Found: C, 51.41; H, 3.33; N, 4.93.

Polyimide Synthesis. A typical polymerization procedure for the synthesis of poly(amic acid) (PAA) was as follows. APSTT (0.2794 g, 0.5 mmol) and newly distilled NMP (1.0 mL) were charged in a 20 mL flask equipped with a magnetic stirrer, a

Scheme 2. Synthesis of Polyimides

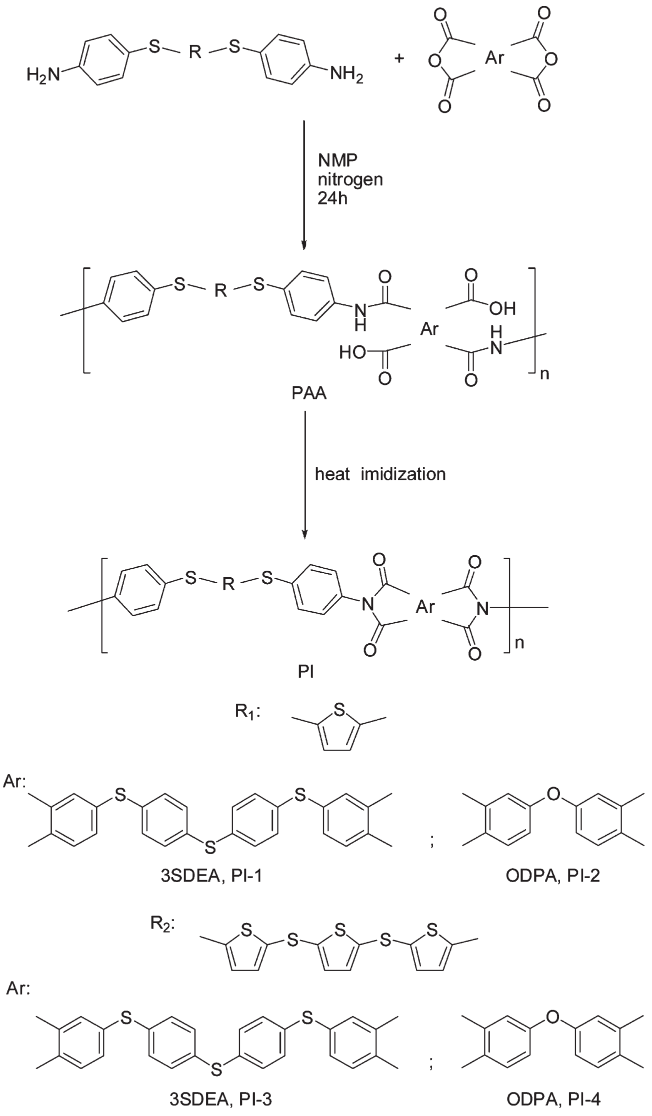


Table 1. Synthesis and Characterization of Polyimides

PI	$[\eta]_{\text{inh}}$ of PAA[a] [dL/g]	elemental analysis	C (%)	H (%)	N (%)
PI-1	1.68	calcd	63.13	2.89	3.35
		found	63.26	3.08	3.26
PI-2	0.48	calcd	63.56	2.67	4.63
		found	63.19	2.99	4.50
PI-3	0.61	calcd	58.62	2.65	2.63
		found	58.61	2.76	2.65
PI-4	0.41	calcd	58.67	2.42	2.63
		found	57.49	2.64	3.41

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

nitrogen inlet, and a cold water bath. 3SDEA (0.2713 g, 0.5 mmol) was added, and dehydrated NMP (1.2 mL) was used to adjust the solid content of the reaction systems to 20 wt %. The pale-yellow solution was stirred at room temperature for 24 h to yield a viscous PAA solution. The PAA solution was spin-coated on a silicon wafer, and the thickness was controlled by spinning rate. For example, the thickness of a specimen for FT-IR and UV−vis measurements was controlled to be ~10 μm, and the specimen for thermal properties measurement was adjusted to be 30−50 μm. PI-1 film was obtained by thermally curing the PAA solution in an oven for 1 h each at 80, 150, 250, and 280 °C, respectively, under a nitrogen atmosphere. The PI-1 film was obtained by immersing the silicone wafer in warm water. The films of PIs 2−4 were prepared by a similar method from PAA solutions.

Results and Discussion

Monomer Synthesis. A new thiophene-containing aromatic diamine APSTT was prepared in three steps, as shown in Scheme 1. The reaction of thiophene-2-thiol with 2,5-dibromothiophene in DMF under the Ullman reaction condition yielded TST, which was treated with *N*-chlorosuccinimide to yield CTST. CTST was directly reacted with 4-aminothiophenol to give the diamine APSTT, which was purified by HPLC to remove a small amount of impurity. Figure 1 compares the FTIR spectra of CTST and APSTT. The absorption band at 1072 cm^{-1}, assignable to the C−Cl stretching in CTST, disappears in the spectrum of APSTT. Alternatively, the characteristic absorptions of the amino groups at 3436 and 3421 (N−H stretching) and 1597 cm^{-1} (N−H deformation) are obviously observed. All peaks detected in the ^{1}H and ^{13}C NMR spectra of APSTT were consistently assigned (Figure 2). The signal at 3.76 ppm in Figure 2a was assigned to the amino groups, and the aromatic proton (H$_a$) ortho to the amino groups was observed at 6.61 ppm. In the ^{13}C NMR spectrum (Figure 2b), 10 signals were observed, which are consistent with the expected structure. The structure of the diamine was also confirmed by elemental analysis.

Polyimide Synthesis. The PIs were prepared by the polycondensation of diamines APST and APSTT with aromatic tetracarboxylic dianhydrides 3SDEA and ODPA via soluble PAA precursors, followed by thermal imidization at elevated temperatures (Scheme 2). The PAA solutions have inherent viscosities of 0.41 to 1.68 dL/g, indicating moderate to high molecular weights of the polymers (Table 1). Flexible and tough PI films were cast from the PAA solutions. The FTIR spectra of the PIs (Figure 3) show the characteristic absorptions of the imide ring at 1774 (asymmetrical stretching of carbonyl) and 1724 cm^{-1} (symmetrical stretching of carbonyl) and the C−N bond at 1373 cm^{-1}. In addition, absorption peaks at ~1222 cm^{-1} attributed to aromatic thioether (Ar−S−Ar) are observed. The elemental compositions of the PIs were checked by elemental analysis. These results clearly indicate the formation of the expected PIs.

Thermal Properties. The thermal decomposition and deformation behavior of the PIs was investigated by TGA, DSC, and DMA measurements. The results are presented in Table 2. The PIs derived from APST exhibit good thermal stability up to 350 °C under nitrogen (Figure 4), whereas it is inferior to that of the PIs from the phenylene analogue, 3SDEA. The PIs derived from APSTT exhibit somewhat lower thermal stability with a 10% weight-loss temperature of 354 °C.

The T_g values of the PIs were determined by DSC (Figure 5) and DMA (Figure 6) analyses, respectively. T_g is one of the key parameters of high-*n* optical polymers when considering the high-temperature circumstance during fabrication and the long-term heat-releasing environment resulting from the miniaturization of optoelectronic devices.[34] In the DMA analysis, the T_g is determined to be the peak temperature of loss modulus (E'') curves. The T_g values obtained from these two methods are nearly the same. The small differences are mainly attributed to the different frequency responses of the PIs, that is, $f = 0$ Hz for DSC and 1 Hz for DMA. The crucial factor that contributed to the lower T_g of PI-3 is the flexible molecular chains. PI-3

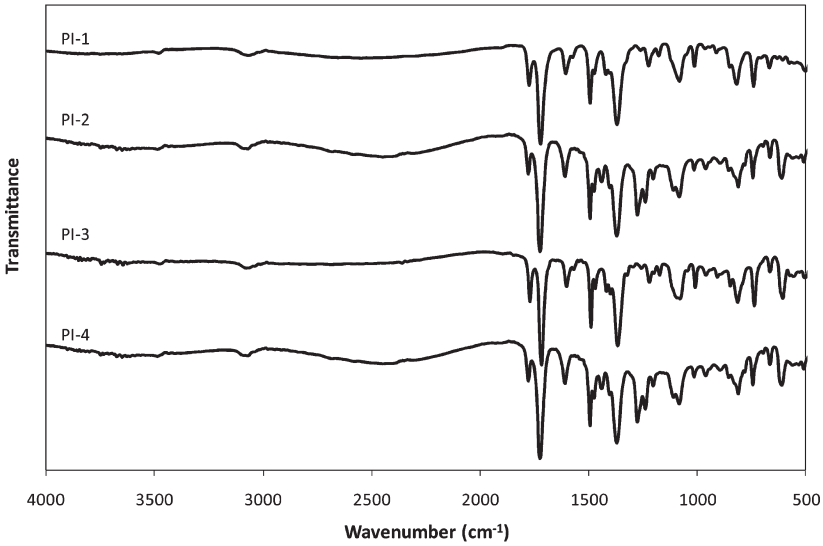


Figure 3. FTIR spectra of PI films.

Table 2. Thermal Properties of Polyimides

	T_g (°C)[a]		$T_{5\%}$[b]	$T_{10\%}$[b]
PI	DSC	DMA	(°C)	(°C)
PI-1	185	186	428	456
PI-2	220	216	396	443
PI-3	177	177	338	374
PI-4	157	160	331	354

[a] T_g: glass-transition temperature. [b] $T_{5\%}$, $T_{10\%}$: temperatures at 5 and 10% weight loss, respectively.

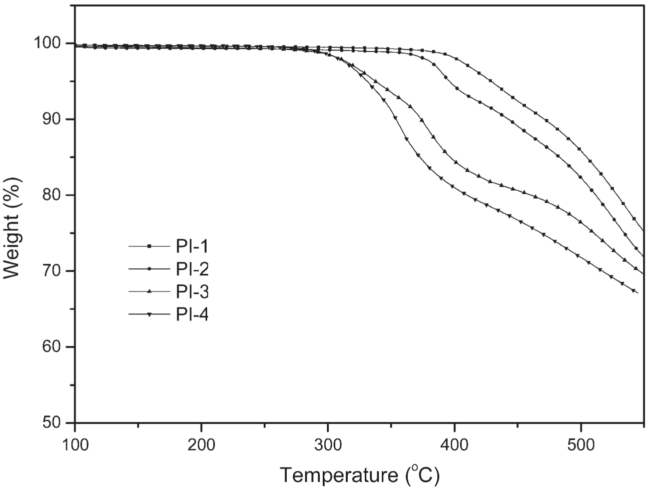


Figure 4. TGA curves of PI films (under a nitrogen atmosphere, 10 °C/min).

possesses flexible thioether linkages in both the dianhydride and diamine moieties, which should undergo reorientation at elevated temperatures. According to the thermal decomposition temperatures and T_g, it can be concluded that the PIs derived from APST exhibit better thermal stability than those of APSTT, which can be mainly attributed to the lower thioether contents.

Optical Properties. Table 3 summarizes the sulfur content and optical properties of the PI films, including transmittances at 450 nm (T_{450}), film thicknesses, in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, average refractive indices (n_{av}), birefringences (Δn), and calculated refractive indices (n_{calcd}). Figure 7 shows the experimental UV/vis transmission spectra of the PI films and the calculated absorption spectra of the PIs. The absorptions of the experimental spectra were normalized at a thickness of 10 μm. The PI films show pale-yellow to yellow colors with T_{450} values of 62−86%. The PI-2 obtained from ODPA and APST exhibited the highest optical transparency with the smallest value of λ_{cutoff}, where the PI-3 from 3SDEA and APSTT showed the lowest. The introduction of plural thiophene rings in the main chain slightly deteriorates the optical transparency of the films. This could be due to the enhanced delocalization of lone-pair electrons of sulfur atoms and π-electrons of the thiophene rings in APSTT. The calculated ionization potential (Ip) of APSTT diamine (6.85 eV) is smaller than that of APST (6.92 eV), which indicates that the former possesses a higher electron-donating property than the latter. In addition, APSTT has a smaller band gap (4.28 eV) than APST (4.52 eV), which should be due to the electron delocalization around the thiophene−*S*−thiophene moieties. The calculated absorption spectra agree with the experimental features of the transmission spectra. The PIs derived from 3SDEA dianhydride displayed longer cutoff wavelengths with higher absorption at 400 nm than those of the PIs from ODPA.

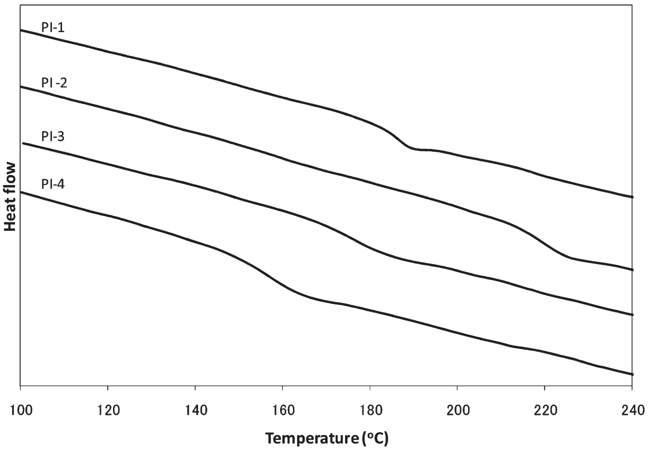


Figure 5. DSC curves of PI films (under a nitrogen atmosphere, 20 °C/min).

In addition, the longest cutoff wavelength of PI-3 and the lowest absorption (i.e., highest transmittance) of PI-2 at 340−380 nm are also reproduced in the calculations. These results indicate that the optical transparency of the PI films prepared in this study is essentially determined by the inherent electronic structure of PI chains, whereas

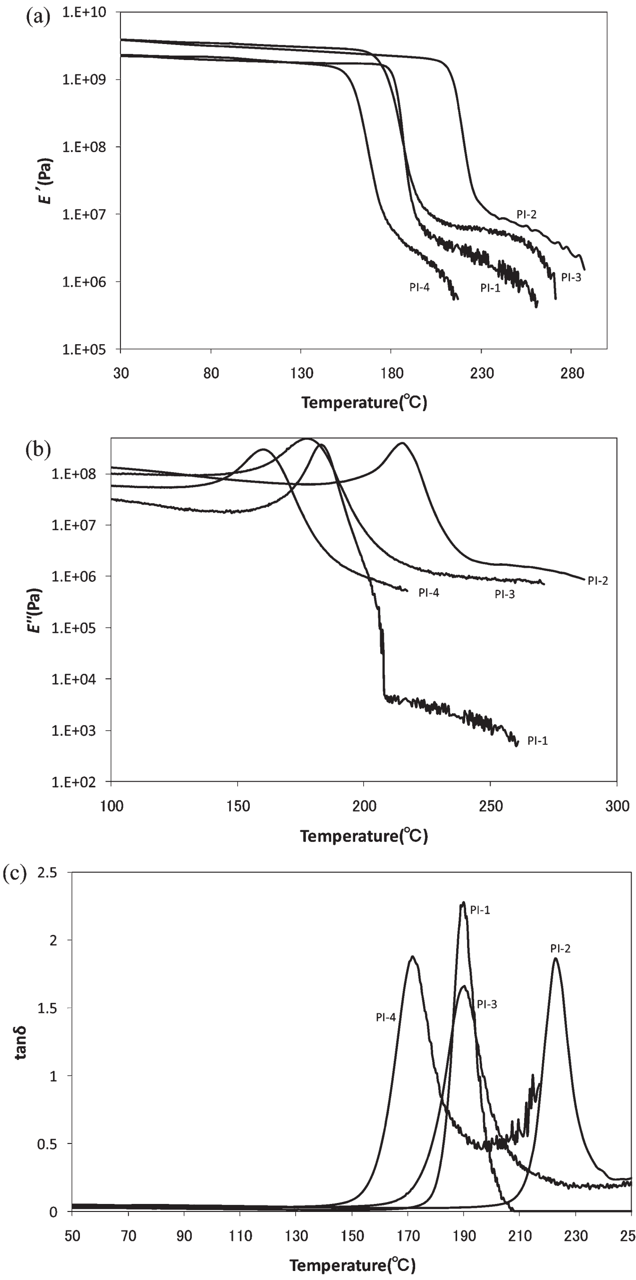


Figure 6. DMA curves of PIs (1 Hz, 2 °C/min): (a) Storage modulus E', (b) loss modulus E'', and (c) tan δ.

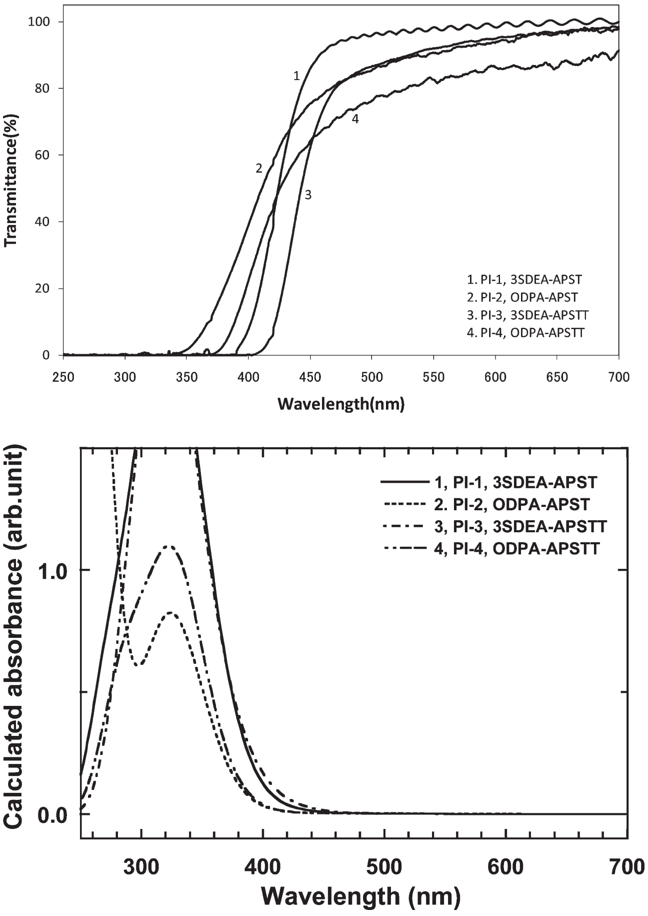


Figure 7. Experimental UV/vis transmission spectra of the PI films (top) and the calculated absorption spectra of the PIs (bottom).

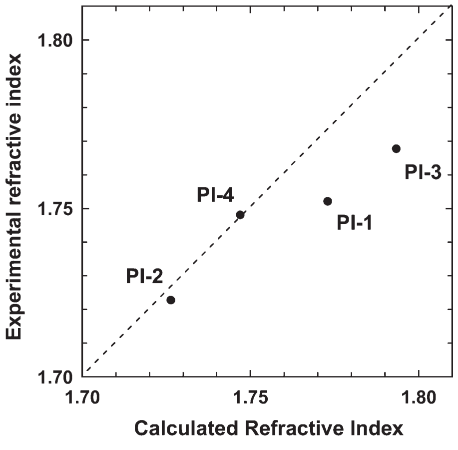


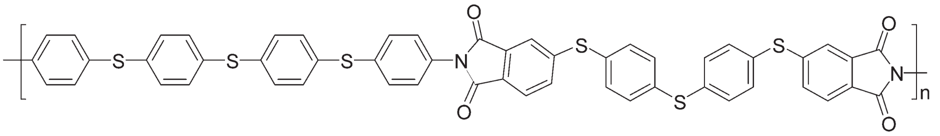
Figure 8. Relationship between the experimental and calculated refractive indices of the PIs.

Table 3. Optical Properties of PIs Films

			refractive indices and birefringence at 633 nm[c]				
PI	S_c (wt %)[a]	T_{450} (%)[b]	n_{TE}	n_{TM}	n_{av}	Δn	n_{calcd}
PI-1	23.0	86	1.7546	1.7472	1.7521	0.0074	1.7730
PI-2	15.9	75	1.7251	1.7183	1.7228	0.0068	1.7264
PI-3	30.1	62	1.7700	1.7629	1.7677	0.0072	1.7934
PI-4	26.0	64	1.7503	1.7436	1.7481	0.0067	1.7470
ref-PI	20.5	64	1.7505	1.7437	1.7482	0.0068	1.7708

[a] Sulfur content. [b] Transmittance at 450 nm (10 μm thick). [c] See measurements.

Scheme 3. Structure of 3SDEA-3SDA (ref-PI)



the intermolecular interactions do not exert a significant influence.

The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the PI films measured at 633 nm, respectively, ranged from 1.7251 to 1.7700 and 1.7183 to 1.7629, as listed in Table 3. The n_{TE} values are slightly higher than those of n_{TM}, which indicates that the PI chains are preferentially oriented parallel to the film plane.[35] All PI films exhibited high n_{av} values in the range of 1.7228 to 1.7677, and the n_{av} observed for PI-3 (1.7677) is the highest of any high refractive PI ever reported.[23] Such a high refractive index is primarily due to the very high sulfur content (30.1 wt %) and the relatively dense molecular packing originating from the thiophene−*S*−thiophene structures. The Abbe number (ν_D) of PI-3 was 21.6, which is a typical ν_D for sulfur-containing aromatic PIs.[36] Figure 8 shows the relationship between the experimental (n_{av}) and calculated refractive indices (n_{calcd}) of the PIs. The n_{calcd} values show an approximately linear relationship with the n_{av} values, though the n_{calcd} of the PIs synthesized from 3SDEA (PI-1 and PI-3) was slightly overestimated ($n_{av} < n_{calcd}$). This indicates that the 3SDEA dianhydride having two diphenylthioether linkages in its skeletal structure reduces the molecular packing density of PI chains, which is supported by the fact the data points of PI-1 and PI-3 equally deviate from the reference line of $n_{av} = n_{calcd}$. In contrast, the calculations successfully reproduce the n_{av} values of the PIs from ODPA dianhydride. Furthermore, all PIs show very small birefringence values (Δn) in the range of 0.0067 to 0.0074. Such low birefringences should be related to the highly flexible phenyl−*S*−thiophene and thiophene−*S*−thiophene linkages in the main chain. These results indicate that aromatic diamines having highly polarizable aromatic−*S*−aromatic linkages are effective in increasing the refractive indices of PIs. In particular, the plural thiophene and flexible thioether linkages in the APSTT diamine endow the PIs with high refractive indices, low birefringence, and relatively good optical transparency. The transparency was comparable to that of our previous high-*n* PI sample, such as ref-PI (Scheme 3), indicating 64% transmittance at 450 nm.[18]

Conclusions

Thiophene-containing diamines were synthesized and polymerized with aromatic tetracarboxylic dianhydrides to afford high-*n* PIs. The n_{av} values measured at 633 nm range from 1.7228 to 1.7677, depending on the sulfur content of the PIs. In particular, the n_{av} of the PIs derived from 3SDEA and APSTT exhibited the highest refractive index, that is 1.7677 at 633 nm, among all high refractive PIs ever reported. As expected, the thiophene and flexible thioether linkages in the APSTT diamine endow the PIs with high refractive indices, low birefringences, and relatively good optical transparency. Although the T_g values are slightly decreased compared with the previously reported high-*n* PIs, they can fulfill the thermal stability requirements as optical polymers. All of their properties are desired for advanced optical applications, such as the components for advanced optical device fabrications.

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