

Highly Refractive and Organo-Soluble Poly(amide imide)s Based on 5,5'-Thiobis(2-amino-4-methyl-thiazole): Synthesis and Characterization

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ABSTRACT: A new thioether-bridged diimide-diacid (DIDA) monomer was synthesized from the condensation of 5,5'-thiobis(2-amino-4-methyl-thiazole) (DA) and trimellitic anhydride at 1 : 2 molar ratio. A series of novel organic-soluble poly(amide imide)s (PAIs) bearing flexible thioether linkages and heteroaromatic thiazole groups were synthesized from DIDA with various commercially available aromatic diamines (1–5) via a direct polycondensation method with triphenyl phosphite and pyridine. The resulting polymers were obtained in high yields and possessed inherent viscosities in the range of 0.47–0.91 dL g⁻¹. All of the polymers were amorphous in nature, showed good solubility and could be easily dissolved in amide-type polar aprotic solvents (e.g., *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, and *N,N*-dimethylacetamide), and even dissolved in less polar

solvents (e.g., pyridine and tetrahydrofuran). They showed excellent thermal stability with glass transition temperatures between 233–269°C and 10% weight loss temperatures in excess of 480°C in nitrogen and 450°C in air atmosphere. The flexible structure endowed the PAI films with good optical transparency. The optical transmittances of the PAI films at 450 nm were higher than 80% for the thickness of approximately 10 μm. Moreover, the thiazole moieties and flexible thioether linkages in the molecular chains of the PAIs provided them with high refractive indices of 1.7329–1.7509 and low birefringences of 0.0065–0.0098. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1521–1529, 2012

Key words: polyimides; refractive index; high performance polymers; thermal properties; copolymers

INTRODUCTION

The achievement of new functions of advanced optical devices is becoming progressively dependent on the availability of novel functional materials.^{1–3} In recent years, much attention has been paid to high refractive index (high-*n*) polymers with good thermal stability, high optical transparency, and low birefringence (Δn) for their potential applications in advanced optoelectronic fabrications such as optical adhesives or encapsulants for organic light-emitting diode devices (OLED),⁴ antireflective coatings for advanced optical applications,⁵ microlens components for charge-coupled devices (CCD), and high-performance complementary metal oxide semiconductor (CMOS) image sensors (CIS), etc.^{6–8} According to the Lorentz–Lorenz equation, the refractive indices of conventional polymers, which are often in the range of 1.3–1.7, can be improved by the introduction of substituents with high molar refractions (R_M) and low molar volumes (V_M).⁹ Thus, aromatic rings, metallic

elements, sulfur, and halogens except fluorine have been introduced in polymers to enhance their refractive indices.^{10–12} Among the various substituents, sulfur-containing groups, such as linear thioether (–S–), cyclic thioether (thiophene and thianthrene), and sulfone (–SO₂–), seem to be the most optimal candidates because of their combined advantages to develop high-*n* polymers.^{13–17} Consequently, various sulfur-containing polymers, including poly(methacrylates),¹⁸ epoxy resins,¹⁹ polyurethanes,²⁰ poly(arylene sulfide)s,²¹ and polyimides (PIs), have been well investigated as high-*n* optical materials.^{22,23} Among them, PIs are well-known for their excellent thermal stability, high chemical resistance, and good mechanical properties. They also show inherent high refractive indices due to their high polarizable molecular chains and are thus thought to be one of the most promising choices for high-*n* polymers.^{24,25} Recently, Ueda lab developed a series of PIs containing flexible thioether linkages to increase the refractive indices of the conventional PIs.^{10,11,15,16,26–30} These PIs exhibited refractive indices >1.70 at the wavelength of 632.8 nm and birefringences <0.01. Moreover, a facile approach has been recently used by Yen and Liou³¹ to prepare a series of novel optically isotropic, transparent, and thermoplastic polyimidothioethers. These polymers showed good thermal stability and high glass-transition

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temperatures associated with high refractive index and ultra-low birefringence. However, most PIs are generally difficult to process due to their poor solubility and high processing temperature, which limit their widespread applications. Therefore, many attempts have been made to improve their processabilities either by introducing flexible linkages, noncoplanar groups, or heteroaromatic rings into the polymer backbones.^{32–34} Copolymerization is another approach used to obtain soluble and processable PIs. Poly(amide imide) (PAI) is a typical example of copolymerization, which has the property advantages of both polyamides and PIs and thus possesses thermal stability balanced with processability.³⁵ In a previous study,³⁶ we reported a series of PAIs based on a diamine monomer containing flexible thioether linkage. It was found that incorporation of both hydrogen-bonded amide groups and flexible thioether linkages resulted in polymers with enhanced solubility and processability.

Heteroaromatic rings containing $-\text{C}=\text{N}-$ bonding are other candidates as effective substituents to increase the polymers' n values. Indeed, heterocyclic rings such as pyridine, pyrimidine, pyridazine, and triazine units instead of phenyl units could be effective to enhance the refractive indices of polymers while keeping high optical transparency.^{37–39} Thiazole is a rigid heteroaromatic ring containing one $-\text{C}=\text{N}-$ bond. Thiazole-containing polymers have been attracting much attention for their unique properties and have extensive applications in advanced optoelectronic fields, such as organic field-effect transistors⁴⁰ and electroluminescent devices.⁴¹ Also, thiazole-containing PIs have been developed for non-linear optical (NLO) applications.⁴² Although the electrical and optical functions of the thiazole moiety have been widely noticed, to our knowledge, its contribution to the high refractive index of polymers as sulfur-containing substituents has not been addressed until now.

In this study, a new thioether-bridged diimide-diacid (DIDA) monomer containing thiazole units was designed and synthesized. A series of sulfur-containing PAIs were prepared by polycondensation of DIDA with various aromatic diamines. The highly polarizable thiazole ring with rigid structure and one $-\text{C}=\text{N}-$ bond is expected to endow the PAIs with high refractive indices and thermal stabilities. Also, the flexible thioether linkage would be beneficial to maintain the high refractive indices and low birefringences of the PAI films. The thermal and solubility properties, as well as refractive index, birefringence, dielectric constant, and optical transparency of the copolyimides are investigated in detail, and the effects of the chemical structures of polymers on the physical properties are also discussed.

EXPERIMENTAL

Materials

5,5'-Thiobis(2-amino-4-methyl-thiazole) (DA) was synthesized in our laboratory according to the reported procedure,⁴³ and recrystallized twice from ethanol. Triphenyl phosphite (TPP, MERCK, Schuchardt, Germany) and trimellitic anhydride (TMA, MERCK, Schuchardt, Germany) were used without further purification. *N*-methyl-2-pyrrolidone (NMP, MERCK, Darmstadt, Germany) and pyridine (Py, Fluka, Buchs, Switzerland) were purified by distillation under reduced pressure over calcium hydride prior to use and stored over 4 Å molecular sieves. LiCl (MERCK, Darmstadt, Germany) was dried for 12 h at 180°C under vacuum before use. 1,4-phenylene diamine (1; MERCK, Darmstadt, Germany), 1,3-phenylene diamine (2; MERCK, Darmstadt, Germany), and 2,6-diaminopyridine (3; MERCK, Darmstadt, Germany) were purified by vacuum sublimation. 4,4'-Oxydianiline (4; MERCK, Darmstadt, Germany) and 4,4'-diaminodiphenyl sulfone (5; MERCK, Darmstadt, Germany) were purified by recrystallization from methanol. The other commercially available reagents were used without further purification.

Measurements

The ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were measured on a Bruker DRX 300 AVANCE apparatus (Bruker BioSpin, Rheinstetten, Germany) at an operating temperature of 25°C. Elemental analysis performed by a Perkin-Elmer 2004 (II) CHN analyzer. The Fourier transform infrared (FTIR) spectra were obtained in potassium bromide (KBr) pellets on a Perkin-Elmer FT spectrum RX1 (Perkin Elmer, Norwalk, CT, USA) over the range 400–4000 cm⁻¹. The ultraviolet-visible (UV-vis) optical absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer (Waltham, MA, USA) at room temperature. PAI films were dried at 100°C for 1 h before testing to remove the absorbed moisture. Inherent viscosities ($\eta_{\text{inh}} = \ln \eta_r / c$ at concentration of 0.5 g dL⁻¹) were measured with an Ubbelohde suspended-level viscometer (Canon Instrument Co., State College, PA, USA) at 30°C using *N,N*-dimethylacetamide (DMAc) as solvent. Melting points (uncorrected) were measured with an Electrothermal engineering LTD 9200 apparatus (Essex, UK). The wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature on a PW 1800 diffractometer (Philips, Eindhoven, Netherlands) with graphite monochromatized Cu K α radiation ($\lambda = 1.5401$ Å). The scanning rate was 0.08°/s over a range of $2\theta = 4$ –80°. Thermogravimetric analyses (TGA) were conducted with a Du Pont 2000 thermal analyzer (Du Pont 2000, Wilmington, DE, USA).

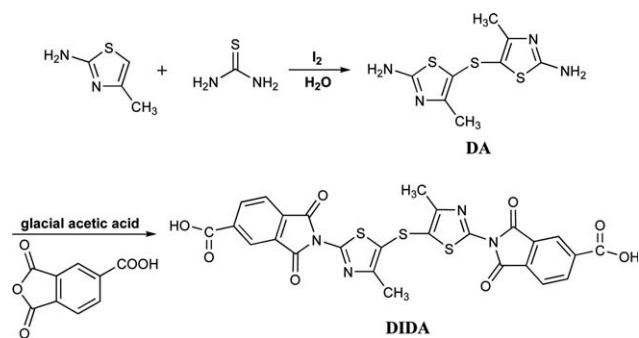
under nitrogen and air atmospheres at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Glass transition temperatures (T_g s), taken as the midpoint of the change in slope of baseline, were measured on a 2010 DSC TA instrument (Brussels, Belgium), with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Refractive indices of the PAI films were measured at room temperature with a prism coupler (Metricron, model PC-2010, Pennington, NJ, USA) equipped with a He-Ne laser light source (wavelength: 632.8 nm). The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were determined using linearly polarized laser light parallel (transverse electric, TE) and perpendicular (transverse magnetic, TM) polarizations to the film plane, respectively. In-plane/out-of-plane birefringence (Δn) was calculated as a difference between n_{TE} and n_{TM} . The average refractive index (n_{AV}) was calculated according to equation: $n_{AV} = [(n_{TE}^2 + n_{TM}^2)/3]^{1/2}$. The dielectric constants (ϵ) were estimated from the measured refractive indices based on the Maxwell equation ($\epsilon = 1.10 n_{AV}^2$).⁴⁴

Synthesis of diimide-diacid monomer (DIDA)

A 100-mL round-bottom flask was charged with a mixture of DA (2.58 g, 10 mmol), TMA (4.23 g, 22 mmol), and glacial acetic acid (40 mL). After this heterogeneous mixture was refluxed for 12 h, it was cooled to the ambient temperature. The mixture was poured into 500 mL of water. The precipitate was collected by filtration, washed with ethanol, and recrystallized from the mixture of *N,N*-dimethylformamide (DMF)/water (v/v = 7 : 1) and dried in vacuum at 100°C for 24 h to afford a light yellow solid. Yield: 92%; m.p. $270\text{--}271^{\circ}\text{C}$; IR (KBr) 3400–2700 (broad), 1791, 1737, 1645, 1572, 1516, 1463, 1327, 1224, 1145, 1110, 1072, 1037, 926, 868, 819, 724, 685, 605 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, DMSO- d_6); δ 2.452 (s, 6H), 8.071–8.097 (d, 2H, $J = 7.8$ Hz), 8.293 (s, 2H), 8.391–8.417 (d, 2H, $J = 7.8$ Hz); $^{13}\text{C-NMR}$ (75 MHz, DMSO- d_6); δ 15.37, 104.97, 124.40, 131.55, 134.30, 150.22, 150.98, 155.31, 163.88, 165.66, 169.59, 173.35 ppm; Analysis calculated for $\text{C}_{26}\text{H}_{14}\text{N}_4\text{O}_8\text{S}_3$: C, 51.48%; H, 2.33%; N, 9.24%. Found: C, 51.39%; H, 2.28%; N, 9.31%.

Synthesis of poly(amide imide)s

PAIs were prepared by condensation reaction of DIDA monomer with various aromatic diamines (1–5). A typical polycondensation procedure for the PAI-1 is described as follows. A mixture of 0.606 g (1 mmol) of DIDA, 0.108 g (1 mmol) of 1,4-phenylene diamine, 0.3 g of LiCl, 0.5 mL of TPP, 0.5 mL of pyridine, and 3 mL of NMP was heated and stirred at 120°C for 3 h, under nitrogen atmosphere. As the polycondensation proceeded, the reaction mixture became viscous gradually. The viscosity of reaction



Scheme 1 Synthesis of the diimide-diacid monomer (DIDA).

solution increased after 1 h, and additional amount of NMP (1 mL) was added to the reaction mixture. At the end of the reaction, the polymer solution was poured slowly into 250 mL of methanol under rapid stirring. The product was filtered, washed thoroughly with hot water (2×100 mL) and methanol (100 mL), and dried under vacuum at $100\text{ }^{\circ}\text{C}$ overnight. Further purification was carried out by dissolving the polymer in DMAc, filtering the polymer solution, and then precipitating it into methanol. The inherent viscosity of the polymer in DMAc was 0.91 dL g^{-1} , measured at a concentration of 0.5 g dL^{-1} at 30°C . IR (KBr): 3300, 3063, 2920, 1778, 1722, 1671, 1602, 1538, 1500, 1377, 1304, 1237, 1168, 1114, 1092, 1013, 947, 872, 831, 724, 607 cm^{-1} . Analysis calculated for $(\text{C}_{32}\text{H}_{18}\text{N}_6\text{O}_6\text{S}_3)_n$: C, 56.63%; H, 2.67%; N, 12.38%. Found C, 56.50%; H, 2.81%; N, 12.20%. All other PAIs were also prepared using similar procedures.

RESULTS AND DISCUSSION

Monomer synthesis

As shown in Scheme 1, a novel diimide-diacid monomer containing thiazole units (DIDA) was prepared by condensation of DA with two mole equivalents of TMA in refluxed glacial acetic acid. The addition reaction between the amino and anhydride groups, and subsequent cyclodehydration reaction was carried out in heterogeneous solution. After purification by rinsing with ethanol and recrystallization from DMF/water, the structure of the DIDA monomer was confirmed by FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, and elemental analysis. The FTIR spectrum of DIDA revealed distinct peak features of carboxylic acid and cyclic imide groups; absorption bands around $2700\text{--}3400\text{ cm}^{-1}$ (C(O)O–H), 1792 cm^{-1} and 1737 cm^{-1} (asymmetrical and symmetrical stretching vibrations of the C=O of the imide ring). The ^1H - and ^{13}C -NMR spectra of DIDA are presented in Figures 1 and 2, respectively. In the $^1\text{H-NMR}$ spectrum, the resonance signals at downfield regions; 8.071–8.097 (d, $J = 7.8$ Hz), 8.293 (s), and 8.391–8.417 (d, $J = 7.8$ Hz) ppm are ascribed to the protons of

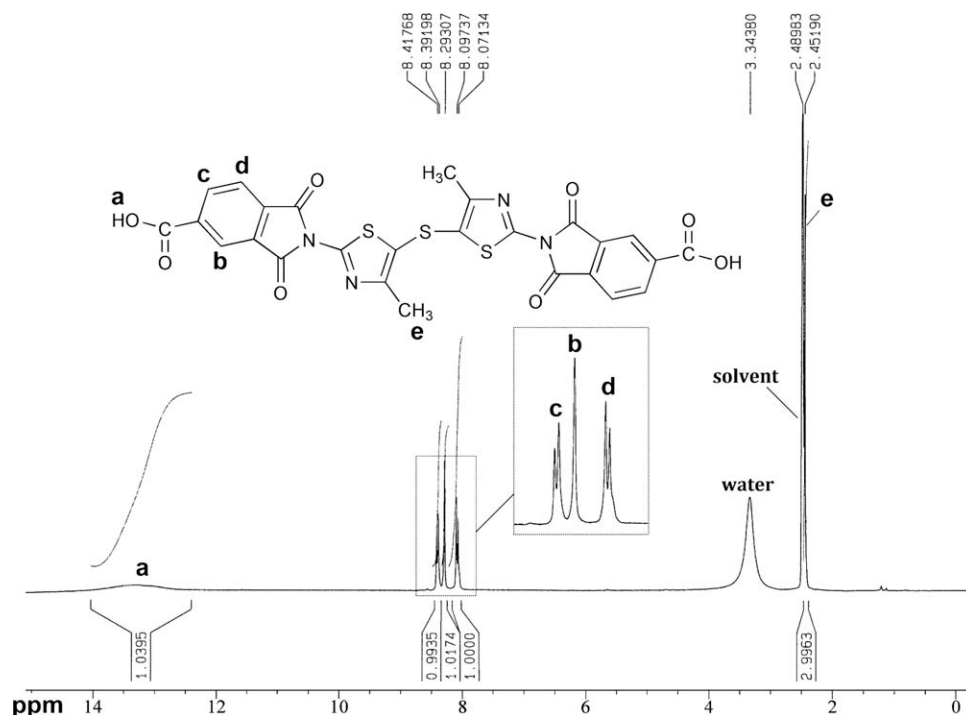


Figure 1 ^1H -NMR spectrum of diimide-diacid monomer (DIDA).

trimellitimido group (H_d , H_b , and H_c). This is because of the conjugation effect by carboxylic acid and imide ring. Also, the area of integration for the protons is in accordance with the assignment. ^{13}C -NMR spectrum of DIDA reveals that carbonyl carbons of carboxylic acid and imide groups resonate in the downfield at 173.35, 165.66, and 163.88 ppm, respectively. The chemical shift in the upfield region (15.38 ppm) is ascribed to the resonance of aliphatic methyl group. In addition to IR and NMR spectra, the elemental analysis results of DIDA also generally

agreed with the calculated values for the proposed structure.

Polymer synthesis

The direct polycondensation of aromatic dicarboxylic acids with aromatic diamines using TPP and pyridine as condensing agents has been known to be an efficient method for the preparation of aromatic polyamides on laboratory scale.⁴⁵ This method was successfully adopted here to prepare aromatic PAIs,

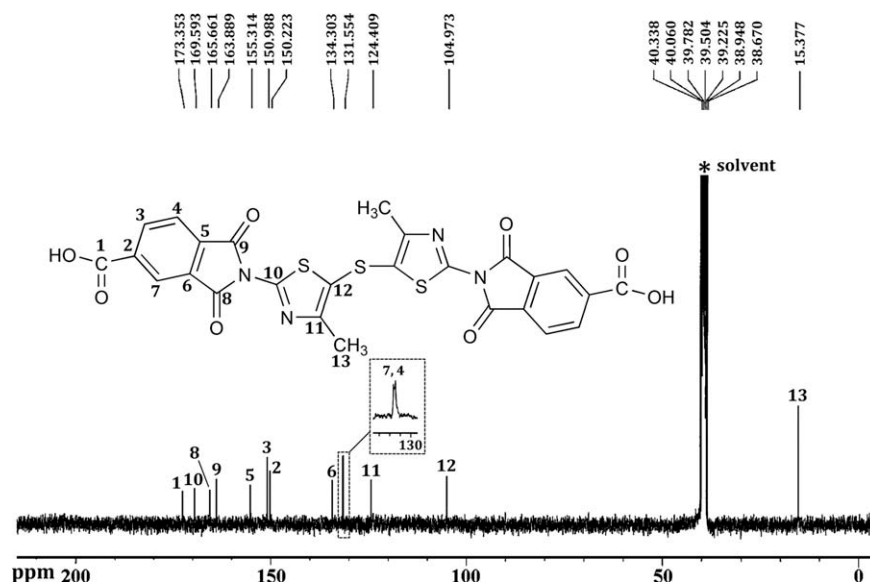
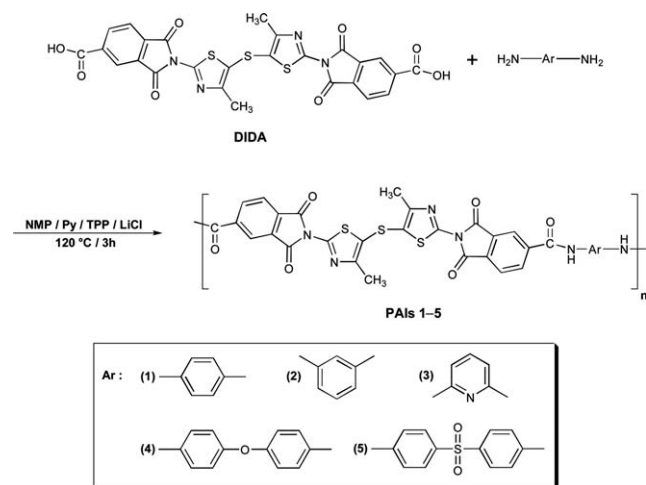


Figure 2 ^{13}C -NMR spectrum of diimide-diacid monomer (DIDA).



Scheme 2 Synthesis of the PAIs.

PAI-1–PAI-5, from DIDA with various aromatic diamines 1–5, as shown in Scheme 2. Synthesis conditions and inherent viscosities of the polymers are summarized in Table I. All the polycondensations in NMP proceeded readily in a homogeneous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol. These PAIs were obtained in high yields (91–95%), and the inherent viscosities were in the range of 0.47–0.91 dL g⁻¹ which were measured in DMAc solutions. The PAIs films were prepared by spin-coating the PAIs–DMAc solutions on silicon (Si) wafer, and the thickness was controlled by regulating the spinning rate. The thickness of PAIs films for UV measurements was controlled to be ~ 10 μm. The structural features of these PAIs were verified by elemental analysis and FTIR spectroscopy. The elemental analysis values generally agreed with the calculated values for the proposed structures of polymers (Table II). However, because of the hygroscopic nature of the amide groups, the values of carbon were lower than the calculated values for the

TABLE I
Synthesis Conditions and Inherent Viscosities of Poly(amide imide)s

Polymer code	Amount of reagent used ^a			η_{inh}^c (dL/g)
	NMP (mL)	Pyridine (mL)	LiCl (g)	
PAI-1	3 + 1 ^b	0.5	0.30	0.91
PAI-2	3	0.5	0.25	0.79
PAI-3	2.5	0.6	0.25	0.47
PAI-4	2.5	0.5	0.25	0.85
PAI-5	3 + 1	0.6	0.30	0.69

^a Amount of each DIDA and diamine monomer = 1.0 mmol; TPP = 0.5 mL; reaction temperature = 120°C; reaction time = 3 h.

^b “3 + 1” means that an initial amount of 3 mL NMP was used and an additional 1 mL of NMP was added when the reaction solution became too viscous.

^c Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

proposed structures.⁴⁶ IR spectrum of a representative PAI, PAI-1, is shown in Figure 3. The FTIR spectra of these PAIs exhibited the characteristic absorption bands for the imide ring at ~ 1780 cm⁻¹ and ~ 1720 cm⁻¹ (asymmetrical and symmetrical C=O stretching), ~ 1380 cm⁻¹ (C–N stretching), ~ 1092 cm⁻¹ and 725 cm⁻¹ (imide ring deformation). The absorption of amide group appears at ~ 3300 cm⁻¹ (N–H stretching) and ~ 1670 cm⁻¹ (C=O stretching).

Polymer solubility

Solubility of the polymer is a major factor that shows its processability for different applications. The solubility behavior of these sulfur-containing PAIs was determined by dissolving 0.05 g of polymers in 1 mL of solvent, including NMP, DMSO, DMAc, DMF, THF, pyridine, acetone, and chloroform for 24 h at room temperature (25°C) or upon

TABLE II
Elemental Analysis and Moisture Uptake of PAIs

Polymer code	Formula (Formula weight)		Elemental analysis (%)			Moisture uptake ^a (%)
			C	H	N	
PAI-1	(C ₃₂ H ₁₈ N ₆ O ₆ S ₃) _n (678.72) _n	Calcd.	56.63	2.67	12.38	2.03
		Found	56.50	2.81	12.20	
PAI-2	(C ₃₂ H ₁₈ N ₆ O ₆ S ₃) _n (678.72) _n	Calcd.	56.63	2.67	12.38	2.07
		Found	56.48	2.88	12.17	
PAI-3	(C ₃₁ H ₁₇ N ₇ O ₆ S ₃) _n (679.70) _n	Calcd.	54.78	2.52	14.42	2.23
		Found	54.59	2.75	14.33	
PAI-4	(C ₃₈ H ₂₂ N ₆ O ₇ S ₃) _n (770.81) _n	Calcd.	59.21	2.88	10.90	2.19
		Found	59.03	3.03	10.77	
PAI-5	(C ₃₈ H ₂₂ N ₆ O ₈ S ₄) _n (818.88) _n	Calcd.	55.74	2.71	10.26	2.35
		Found	55.58	2.94	10.09	

^a Moisture uptake (%) = $(W - W_0/W_0) \times 100\%$; W: weight of polymer sample after standing at room temperature, W₀: weight of polymer sample after being dried in vacuum at 100°C for 12 h.

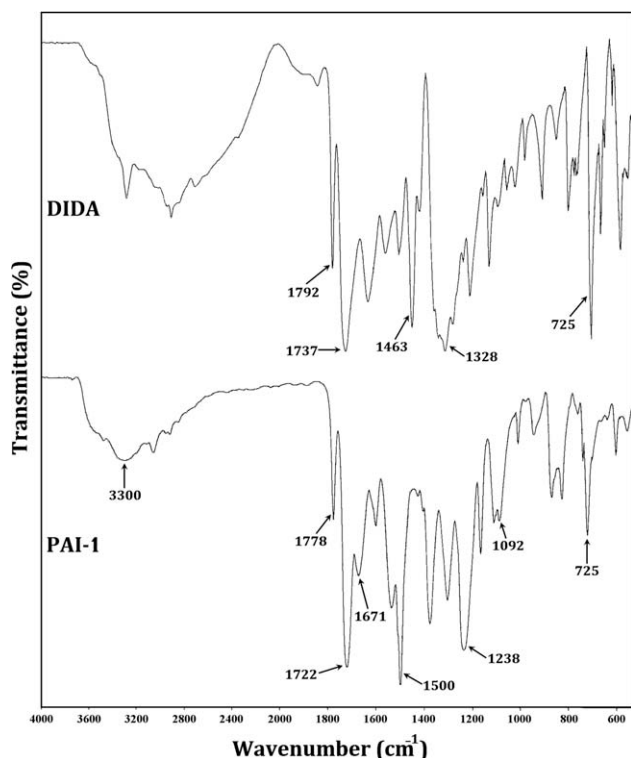


Figure 3 IR spectra of diimide-diacid monomer (DIDA) and PAI-1.

heating in tightly closed vials. Enhancement of solubility of PIs in common low-toxic solvents has been successfully achieved by introduction of flexible thioether linkages and hydrogen-bonded amide groups in our previous works.^{36,47} Similarly, in the present study, almost all the polymers were dissolved not only in highly polar solvents such as NMP, DMSO, DMAc, and DMF, but also in moderate polar solvents such as pyridine and THF. As indicated in Table III, PAI-4 derived from 4,4'-oxydianiline showed an improved solubility compared with other polymers, especially in some low boiling point solvents. Also the unique enhanced solubility of the *meta*-related polymers (PAI-2 and PAI-3) might be attributed to the higher entropy state of the polymer

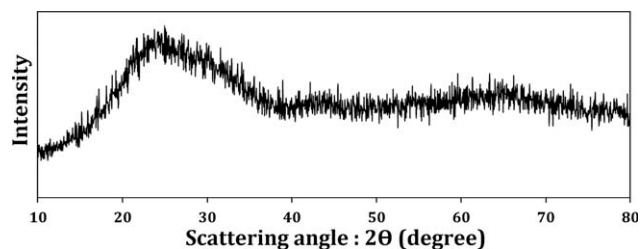


Figure 4 WAXD pattern of PAI-1.

chains resulting from the *meta* linkages. In general, the good solubility of these PAIs is mainly attributed to the synergic effects of flexible thioether linkages and also hydrogen-bonded amide groups which could inhibit close packing and reduce the interchain interactions to enhance solubility. The good solubility of the present PAIs in low-toxic solvents facilitates their applications in high-tech fields.

X-ray diffraction of the polymers

The morphological structure of the PAIs was estimated by WAXD in a spectral window ranging from $2\theta = 4^\circ$ to 80° . The curves of all the polymers were broad and without obvious peak features, which indicate that they are all amorphous. The highly amorphous nature of these PAIs is mainly attributed to the presence of the pendent methyl groups in the polymer backbone. The incorporation of pendant groups decreases the backbone symmetry and regularity, through weakening intermolecular forces such as hydrogen bonding between the polymer chains, and a lowering chain packing efficiency which results in decreased crystallinity. Thus, the amorphous structure of these PAIs also reflected in their good solubility in common organic solvents and good film forming ability. A representative diffractogram of the polymers (PAI-1) is shown in Figure 4.

Thermal properties

The thermal properties of the polymers, which were evaluated by DSC and TGA methods, are listed in

TABLE III
Solubility^a of Poly(amide imide)s

Polymer code	Solvent ^b							
	NMP	DMSO	DMAc	DMF	THF	Pyridine	Acetone	Chloroform
PAI-1	+	+	+	+	±	-	-	-
PAI-2	++	+	+	+	S	±	-	-
PAI-3	++	++	+	+	±	S	-	-
PAI-4	++	++	++	++	+	+	+	±
PAI-5	++	+	+	+	±	±	-	-

(++) Soluble at room temperature, (+) soluble after heating, (±) partially soluble, (S) swelling, (-) insoluble.

^a Solubility: measured at a polymer concentration of 0.05 g/mL.

^b NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; THF: tetrahydrofuran.

TABLE IV
Thermal Characterizations of PAIs

Polymer code	TGA			Char yield ^b (%)
	DSC	Decomposition temperature ^a (°C)		
		In air	In nitrogen	
PAI-1	T_g^c (°C)			
PAI-1	269	466	510	66
PAI-2	250	457	496	59
PAI-3	255	461	503	61
PAI-4	233	453	482	53
PAI-5	261	466	507	64

^a Temperature of 10% weight loss determined in nitrogen and air atmospheres.

^b Residual weight (%) at 700°C in nitrogen.

^c T_g measured by DSC at scanning rate of 10 °C/min in flowing nitrogen.

Table IV. The DSC analysis shows that in each sample there is no evidence of crystallization and melting processes. Therefore, the polymers are in a full amorphous state and do not show any tendency to crystallize, even during the cooling step. T_g is one of the important parameters of high- n optical polymers when considering the high-temperature circumstance during fabrication and the long-term heat-releasing environment due to the miniaturization of optoelectronic devices.⁴⁸ The T_g values of aromatic PAIs were in the range of 233–269°C, which follows the decreasing order of the chain flexibility and steric hindrance of the polymers backbones. For example, PAI-2 with *meta*-substituted phenylene rings had a T_g of 250°C, whereas a higher value of 269°C was observed for PAI-1, which had *para*-substituted phenylene rings. PAI-1 showed the highest T_g value of all the PAIs, which could be attributed to its rigid *para*-phenylene segments in the polymer backbone. Also, PAI-5 having the rigid sulfone groups in polymer backbones showed higher T_g value than corresponding PAI-4.

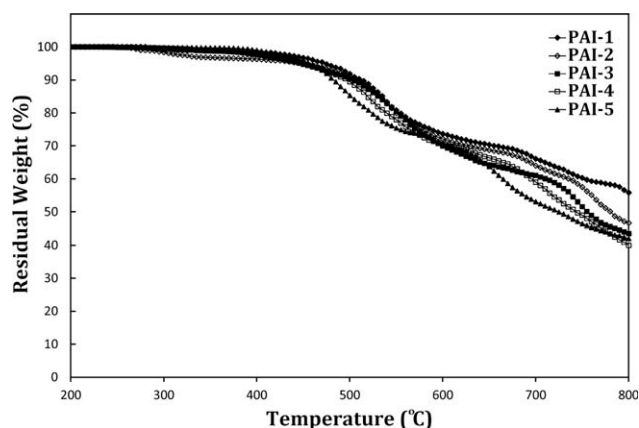


Figure 5 TGA curves of PAIs with a heating rate of 10 °C/min in nitrogen atmosphere.

The thermal and thermo-oxidative stabilities of the polymers were characterized by TGA measurements in both nitrogen and air atmospheres. The temperatures at 10% weight loss (T_{10}) were determined from the original thermograms and are tabulated in Table IV. These PAIs showed good thermal stability and had no notable weight loss below 480°C in nitrogen atmosphere. T_{10} values of the PAIs were in the range of 482–510°C in nitrogen and in the range of 453–466°C in air, respectively. The amount of residue of all PAIs at 700°C in nitrogen atmosphere was higher than 50%, especially, PAI-1 had highest yield up to 66%. The thermogravimetric curves of the PAIs in nitrogen atmosphere are shown in Figure 5. As expected, these polymers possessed excellent thermal stability which could withstand the elevated processing. Thus, the introduction of flexible thio-ether linkages and pendant methyl groups did not deteriorate their thermal stability significantly.

Optical properties

Table V summarizes the sulfur content and optical properties of the PAI films, including transmittances

TABLE V
Optical Properties of PAIs Films

Polymer code	S_c (wt %) ^a	Refractive indices and birefringence					Dielectric constants ^g
		T_{450} (%) ^b	n_{TE} ^c	n_{TM} ^d	n_{AV} ^e	Δn ^f	
PAI-1	14.17	81	1.7410	1.7312	1.7377	0.0098	3.32
PAI-2	14.17	83	1.7388	1.7305	1.7360	0.0083	3.31
PAI-3	14.15	83	1.7447	1.7368	1.7421	0.0079	3.34
PAI-4	12.48	85	1.7351	1.7286	1.7329	0.0065	3.30
PAI-5	15.66	88	1.7533	1.7462	1.7509	0.0071	3.37

^a Sulfur content.

^b Transmittance at 450 nm (10 μm thick).

^c n_{TE} : the in-plan refractive index at 632.8 nm at ambient temperatures.

^d n_{TM} : the out-of-plan refractive index at 632.8 nm at ambient temperatures.

^e Average refractive index; $n_{AV} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$.

^f Birefringence; $\Delta n = n_{TE} - n_{TM}$.

^g Optically estimated dielectric constant; $\epsilon = 1.10 n_{AV}^2$.

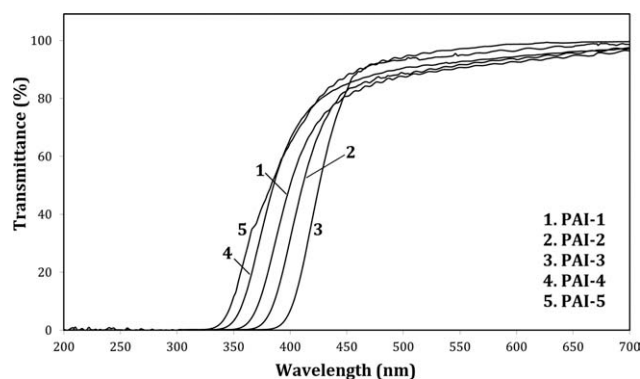


Figure 6 UV-vis spectra of PAI films (film thickness: $\sim 10 \mu\text{m}$).

at 450 nm (T_{450}), in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, average refractive indices (n_{av}), birefringences (Δn), and optical dielectric constants (ϵ). The UV-vis transmission spectra of the PAI films with thicknesses of approximately $10 \mu\text{m}$ are shown in Figure 6. The spectral shapes of the five PAIs were similar to each other and the cutoff wavelengths of the films were in the range of 332–386 nm. The optical transmittances of the films measured at 450 nm were entirely higher than 80% because the flexible thioether ($-\text{S}-$) linkages would effectively prevent interchain molecular packing. In particular, PAI-5 obtained from DIDA and 4,4'-diaminodiphenyl sulfone exhibited the highest optical transparency with the smallest value of λ_{cutoff} , which is attributable to the reduction of the intermolecular interactions by the bulky sulfonyl substituents. These results indicate that the optical transparency is not deteriorated by the introduction of thiazole units into the PAIs.

It has been established that the refractive indices of PIs are affected by several factors including sulfur content, molecular geometry, molecular polarizability, flexibility of polymer backbone, and degree of molecular packing.⁴⁹ As listed in Table V, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the PAI films measured at 632.8 nm ranged from 1.7351 to 1.7533 and 1.7286 to 1.7462, respectively. All the PAI films exhibited higher n_{TE} values than n_{TM} , indicating that the molecular chains were preferentially aligned in the film plane. The average refractive indices (n_{av}) estimated from the n_{TE} and n_{TM} values ranged between 1.7329 and 1.7509 in the order of PAI-5 (1.7509) > PAI-3 (1.7421) > PAI-1 (1.7377) > PAI-2 (1.7360) > PAI-4 (1.7329). The fact that the n_{av} value for PAI-2 is lower than that for the isomeric PAI-1 clearly indicates the *meta*-catenated diamine moiety in PAI-2 causes a lowering of molecular packing, leading to the reduction of n_{av} . Furthermore, the highest n_{av} observed for PAI-5 (1.7509) could mainly attribute to its highest sulfur content among the PAIs. In general, the high refractive index of the PAIs is obviously attributed to the

introduction of highly polarizable thiazole units and thioether linkages into the polymers.

Birefringence expresses the level of optical anisotropy in the film, and it is defined as the difference in refractive index between two orthogonal planes of polarization.⁵⁰ Moreover, the birefringence of polymer materials comes mainly from the preferred orientation of rigid groups and polymer chains.⁵¹ In this work, all the PAI films exhibited very small birefringence values (Δn) in the range of 0.0065–0.0098. Highly flexible thiazole–S–thiazole linkages in the main chain contributed to lowering the film birefringence by increasing the chain mobility and decreasing the chain packing.

The dielectric constants (ϵ) of the PI films can be roughly estimated from the refractive indices using the modified Maxwell equation ($\epsilon = 1.10n_{\text{AV}}^2$), where ϵ is the dielectric constant at around 1 MHz. Thus, the estimated ϵ values of the PAIs were in the range of 3.30–3.37 which were slightly lower than those of the wholly aromatic PIs ($\epsilon = 3.50$ –3.60).¹⁴

CONCLUSIONS

A new thioether-bridged diimide-diacid monomer containing thiazole rings (DIDA), was synthesized and polymerized with various aromatic diamines to afford a series of sulfur-containing PAIs. The n_{av} values measured at 632.8 nm range from 1.7329 to 1.7509 depending on the different sulfur contents of the PAIs. As expected, the thiazole groups and flexible thioether linkages in the DIDA monomer endow the PAIs with high refractive indices, low birefringences (0.0065–0.0098), and relatively good optical transparency. Moreover, these PAIs exhibited good solubility in various organic solvents and excellent thermal and thermo-oxidative stability. According to the X-ray diffractograms and solubility data, the flexible thioether linkages which prevent polymer chains from packing well, are responsible for the amorphous and good solubility characteristics of all polymers. Thus, the good combined properties make the present PAIs good candidates for advanced optical device fabrications.

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References

1. Ma, H.; Jen, A. K. Y.; Dalton, L. R. *Adv Mater* 2002, 14, 1339.
2. Pagliaro, M.; Ciriminna, R. *J Mater Chem* 2005, 15, 4981.
3. Shacklette, L. W. *Opt Photon News* 2004, 15, 22.
4. Ju, Y. G.; Almuneau, G.; Kim, T. H.; Lee, B. W. *Jpn J Appl Phys* 2006, 45, 2546.
5. Krogman, K. C.; Druffel, T.; Sunkara, M. K. *Nanotechnology* 2005, 16, S338.

6. Suwa, M.; Niwa, H.; Tomikawa, M. *J Photopolym Sci Technol* 2006, 19, 275.
7. Nakai, J.; Aoki, T. U.S. Pat.7,087,945 (2006).
8. Regolini, J. L.; Benoit, D.; Morin, P. *Microelectron Reliab* 2007, 47, 739.
9. Ando, S.; Fujigaya, T.; Ueda, M. *Jpn J Appl Phys* 2002, 41, L105.
10. Liu, J. G.; Nakamura, Y.; Terraza, C. A.; Suzuki, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromol Chem Phys* 2008, 209, 195.
11. Liu, J. G.; Nakamura, Y.; Ogura, T.; Shibasaki, Y.; Ando, S.; Ueda, M. *Chem Mater* 2008, 20, 273.
12. Choi, M. C.; Wakita, J.; Ha, C. S.; Ando, S. *Macromolecules* 2009, 42, 5112.
13. Gao, C. Y.; Yang, B.; Shen, J. C. *J Appl Polym Sci* 2000, 75, 1474.
14. Li, C.; Li, Z.; Liu, J. G.; Zhao, X. J.; Yang, H. X.; Yang, S. Y. *Polymer* 2010, 51, 3851.
15. Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromolecules* 2007, 40, 4614.
16. Fukuzaki, N.; Higashihara, T.; Ando, S.; Ueda, M. *Macromolecules* 2010, 43, 1836.
17. Suzuki, Y.; Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym J* 2008, 40, 414.
18. Liu, J. G.; Ueda, M. *J Mater Chem* 2009, 19, 8907.
19. Lu, C. L.; Cui, Z. C.; Wang, Y. X.; Yang, B.; Shen, J. C. *J Appl Polym Sci* 2003, 89, 2426.
20. Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. *J Appl Polym Sci* 2000, 76, 45.
21. Robb, M. J.; Knauss, D. M. *J Polym Sci Part A: Polym Chem* 2009, 47, 2453.
22. Nakamura, A.; Fujii, H.; Juni, N.; Tsutsumi, N. *Opt Rev* 2006, 13, 104.
23. Li, S.; Kang, H.; Wu, W.; Ye, C. *J Appl Polym Sci* 2008, 110, 3758.
24. Terui, Y.; Ando, S. *J Photopolym Sci Technol* 2005, 18, 337.
25. Chang, C. M.; Chang, C. L.; Chang, C. C. *Macromol Mater Eng* 2006, 291, 1521.
26. Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym J* 2007, 39, 543.
27. Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *J Polym Sci Part A: Polym Chem* 2007, 45, 5606.
28. Terraza, C. A.; Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *J Polym Sci Part A: Polym Chem* 2008, 46, 1510.
29. You, N. H.; Suzuki, Y.; Yorifuji, D.; Ando, S.; Ueda, M. *Macromolecules* 2008, 41, 6361.
30. You, N. H.; Suzuki, Y.; Higashihara, T.; Ando, S.; Ueda, M. *Polymer* 2008, 50, 789.
31. Yen, H. J.; Liou, G. S. *J Mater Chem* 2010, 20, 4080.
32. Wang, X. L.; Li, Y. F.; Zhang, S. J.; Ma, T.; Shao, Y.; Zhao, X. *Eur Polym J* 2006, 42, 1229.
33. Abouzari-Lotf, E.; Shockravi, A.; Javadi, A. *Polym Degrad Stab* 2011, 96, 1022.
34. Zhao, X.; Li, Y. F.; Zhang, S. J.; Shao, Y.; Wang, X. L. *Polymer* 2007, 48, 5241.
35. Behniafar, H.; Jafari, A. *J Appl Polym Sci* 2006, 100, 3203.
36. Shockravi, A.; Abouzari-Lotf, E.; Javadi, A.; Atabaki, F. *Eur Polym J* 2009, 45, 1599.
37. You, N. H.; Nakamura, Y.; Suzuki, Y.; Higashihara, T.; Ando, S.; Ueda, M. *J Polym Sci Part A: Polym Chem* 2009, 47, 4886.
38. You, N. H.; Higashihara, T.; Oishi, Y.; Ando, S.; Ueda, M. *Macromolecules* 2010, 43, 4613.
39. Li, Z.; Liu, J. G.; Yang, S. Y. *High Perform Polym* 2010, 22, 468.
40. Osaka, I.; Sauvé, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Adv Mater* 2007, 19, 4160.
41. Jung, I. H.; Jung, Y. K.; Lee, J.; Park, J. H.; Woo, H. Y.; Lee, J. I.; Chu, H. Y.; Shim, H. K. *J Polym Sci Part A: Polym Chem* 2008, 46, 7148.
42. He, M.; Zhou, Y.; Miao, J.; Liu, C.; Cui, Y.; Zhang, T. *Dyes Pigm* 2010, 86, 107.
43. Woodbridge, R. G.; Dougherty, G. *J Am Chem Soc* 1949, 71, 1744.
44. Bose, D.; Lee, H.; Yoon, D. Y.; Swalen, J. D.; Rabolt, J. F. *J Polym Sci Part B: Polym Phys* 1992, 30, 1321.
45. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Part A: Polym Chem* 1975, 13, 1373.
46. Liaw, D. J.; Liaw, B. Y. *J Polym Sci Part B: Polym Chem* 1998, 36, 2301.
47. Shockravi, A.; Abouzari-Lotf, E.; Javadi, A. *Des Monomers Polym* 2009, 12, 119.
48. Maier, G. *Prog Polym Sci* 2001, 26, 3.
49. Ando, S.; Matsuura, T.; Sasaki, S. *Polym J* 1997, 29, 69.
50. Liaw, D. J.; Huang, C. C.; Chen, W. H. *Polymer* 2006, 47, 2337.
51. Lee, K. S.; Kim, J. P.; Lee, J. S. *Polymer* 2010, 51, 632.