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Synthesis of Highly Refractive Polyimides Derived from 2,5-Bis(4-aminophenylsulfanyl)-1,4-dithiane and Dianhydrides

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Highly refractive and transparent polyimides (PIs) based on 2,5-bis(4-aminophenylsulfanyl)-1,4-dithiane (BASDT) have been developed. BASDT was polymerized with two dianhhydrides such as 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 4,4'-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA) to afford two PIs. The PI of 3SDEA/BASDT exhibited the glass transition temperature at 156 °C and the 5 % weight loss temperatures ($T_{5\%}$) at 310 ºC. The 1,4-dithiane moiety endowed the PI films with good optical transparency with high refractive indices. The optical transmittance of the PI film from CBDA and BASDT at 400 nm was higher than 90% for the thickness of 1.0 μm. Furthermore, the 1,4-dithiane moiety and flexible thioether linkages in the molecular chains of the PIs provided them with high refractive indices of 1.6929–1.7455 and small birefringence of 0.0056–0.0299.
Keywords: Polyimide; High Refractive Index; 1,4-dithiane; Sulfur-containing Monomers

1. Introduction

High refractive index (high-*n*) polymers have been increasingly desired in many high-tech optical fields as functional components, such as photoresists for 193 nm immersion lithography [1], coatings for long-period-grating refractive index sensors [2], substrates for advanced organic electroluminescent devices [3], and functional coatings for CMOS image sensors (CIS) [4]. Conventional high-*n* optical polymers such as sulfur-containing epoxy [5], poly(methyl methacrylate) (PMMA) [6], and polyurethane [7] can meet most of the requirements. However, the relatively poor thermal stability of the polymers often limits their wide applications. Furthermore, the conventional high-*n* polymers usually exhibit refractive indices of around 1.6, which are not high enough for CIS applications. Polyimide (PI) is one of the most successful candidates used in advanced optical fabrications [8]. As high-*n* polymers, PIs possess many characteristics, including inherent high refractive index, good combination of thermal, mechanical, and dielectric properties [9-12]. However, the large birefringence and deep coloration of the conventional PIs have to be addressed as optical materials. In our previous works, a series of sulfur-containing high-*n* PIs have been developed [13-16]. However, the optical transparency of the sulfur-containing PI films in the visible light region is not sufficiently high and should be improved. The deep colors of PIs are owing to the formation of intra- and intermolecular charge-transfer complexes (CTC) between the electron-donating diamine moiety and the electron-accepting dianhydride moiety. The incorporation of bulky alicyclic unit in a diamine is effective to reduce the CTC formation. Moreover, according to the Lorenz-Lorenz equation, a high molar refraction per unit molecular volume should result in a higher refractive index. Thus, to further improve the refractive indices and the transparency, we focused on the development of a new diamine containing an alicyclic structure with high sulfur content.

In this study, we report optically transparent sulfur-containing PIs with high refractive indices. These PIs were prepared from the dianhydrides, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 4,4'-[*p*-thiobis(phenylenesulfanyl)] diphthalic anhydride (3SDEA), and a new sulfur-containing diamine, 2,5-bis(4-aminophenyl sulfanyl)-1,4-dithiane (BASDT) by a two-step polymerization procedure via the soluble poly(amic acid) (PAA) precursors. The resulting

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PIs exhibited high refractive indices in the range of 1.6929-1.7455 with high transparency (>400 nm) and low birefringence in the range of 0.0056–0.0299.

2. Experimental

2.1. Materials

CBDA kindly supplied by JSR Co. Ltd., was dried in *vacuo* at 120°C for 12 h prior to use. 3SDEA was prepared in-house according to our previous work [15]. All the other reagents and solvents were used without further purification.

2.2. Synthesis of 2,5-diacetoxy-1,4-dithiane (DADT)

To a solution of 2,5-dihydroxy-1,4-dithiane (10.4 g, 68.4 mmol) in dry pyridine (22 mL) cooled at 0°C, acetic anhydride (15.4 g, 149.4 mmol) was added dropwise over 1 h using a dropping funnel under a N_2 atmosphere. During the solution stirred for 1 h, the white solid began to precipitate. The mixture was poured into water. The precipitate was filtered and dried under reduced pressure. Recrystallization from methanol gave a white crystal (9.9 g, yield 61%). M.p.161 °C. IR (KBr, cm^{-1}): ν= 2966, 2935 (alkyl C-H), 1739 (ester C=O), 1431 (alkyl C-H), 1369 (acetyl C-H), 725 (alkyl C-H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 5.58-5.81 (m, 2H), 3.74-3.65 (dd, 2H), 2.86-2.77 (dd, 2H), 2.23-2.16 (s, 6H). E_{LEM}. A_{NAL}. Calcd for $C_8H_{12}O_4S_2$: C, 40.66; H, 5.12. Found: C, 40.75; H 5.04.

2.3. Synthesis of 2,5-bis(4-nitrophenylsulfanyl)-1,4-dithiane (BNSDT)

To a solution of DADT (5.29 g, 20.0 mmol) and 4-nitrothiophenol (80% pure, 8.14 g, 42.0 mmol) in dry methylene chloride (50 mL), boron trifluoride ether complex (1 mL) was added dropwise under a N_2 atmosphere. The reaction mixture was stirred for 3 h at room temperature, and the precipitate was collected by filtration. Recrystallization from toluene gave a pale-yellow crystal (9.08 g, yield 94%). IR (KBr, cm^{-1}): ν = 2908 (alkyl C-H), 1573 and 1334 (nitro NO_2). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.21-8.14 (dt, 4H), 7.61-7.54 (m, 4H), 4.61-4.55 (m, 2H), 3.73-3.13 (m, 4H). E_{LEM}. A_{NAL}. Calcd for $C_{16}H_{14}N_2O_4S_4$: C, 45.05; H, 3.31; N 6.57. Found: C, 44.44; H, 3.42; N, 6.52.

2.4. Synthesis of 2,5-bis(4-aminophenylsulfanyl)-1,4-dithiane (BASDT)

The mixture of BNSDT (8.94 g, 21.0 mmol), ethanol (75 mL), and a catalytic amount of 10 w % palladium on activated carbon (1 g) was refluxed and then hydrazine monohydrate (45 mL) diluted with ethanol (15mL) was added dropwise over a period of 1.5 h. After the addition was completed, the reaction mixture was refluxed for 24 h. The hot mixture was filtered to remove the catalyst, and the filtrate was cooled to room temperature to give a crystal BASDT. The product adsorbed in the catalyst was washed with DMF three times, and the DMF was poured into a large amount of water to precipitate the crude BASDT. The total yield was 6.22 g (80.8%). Recrystallization from ethanol gave a white crystal. IR (KBr, cm^{-1}): ν= 3448, 3355 (amine, N-H), 2923, 2854 (alkyl C-H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.38-7.28 (m, 4H), 6.66-6.58 (m, 4H), 4.14 (dd, 1H), 4.05 (dd, 1H), 3.85-3.75 (s, 4H), 3.30-2.97 (m, 4H). E_{LEM}. A_{NAL}. Calcd for $C_{16}H_{18}N_2S_4$: C, 52.42; H, 4.95; N 7.64. Found: C, 52.63; H, 4.75; N 7.74.

2.4. Synthesis of poly(amic acid)s (PAAs) and PIs

A typical polymerization procedure for the synthesis of PAAs is as follows. BASDT (0.552 g, 1.5 mmol), pre-dried at 80ºC for 4 h, and dehydrated NMP (5 mL) were charged into a 30-mL flask equipped with a magnetic stirrer and a nitrogen inlet. Then, the flask was cooled with a water bath under a nitrogen gas flow. When a clear solution was obtained, 3SDEA (0.814 g, 1.5 mmol) was added. The solution was stirred at room temperature for 24 h to afford a viscous PAA solution, which is filtered through a 0.45 μm Teflon syringe filter.

For analysis, the PAA solutions were spin-coated onto a silicon wafer, and the thickness was controlled by spinning rate. For FT-IR and UV-vis measurements, the thicknesses were controlled to be about 2.5 μm. The PI films were prepared by thermal imidization of PAA films at elevated temperatures for 0.5 h each at 80°C and 120°C, and for 2 h at 200°C, respectively, under nitrogen, followed by immersing the silicon wafer into warm water.

2.5. Measurements.

The FT-IR spectra were obtained on a Horiba FT-720 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX300S spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent and trimethylsilane as the reference. The UV-vis transmittance spectra were recorded on a JASCO V-560 UV/Vis spectrometer in the range 250–800 nm. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. 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-2010) equipped with a He-Ne laser light source (wavelength: 632.8 nm). The polarization of the incident light guided from a linearly polarized laser was controlled by inserting a half-waveplate in the light path. The prism attachable to the surface of PI films was made of a single crystal of gallium-gadolinium-garnet (GGG).

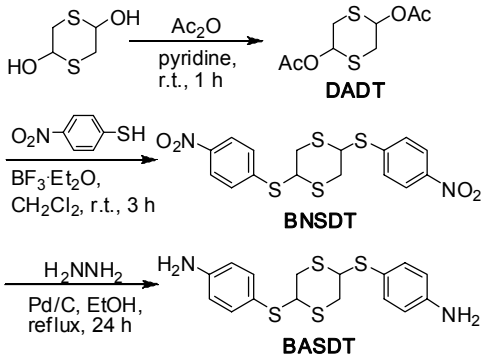
In plane (n_{TE})/out-of-plane (n_{TM}) birefringence (Δn) was calculated as a difference between n_{TE} and n_{TM}. The average refractive index (n_{av}) was calculated according to equation (1):

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

3. Results and Discussion

3.1. Monomer Synthesis

As a monomer having a high sulfur content (35.0 wt %) with an alicyclic ring structure, BASDT was selected, and it was prepared via three steps from 2,5-dihydroxy-1,4-dithiane as shown in Scheme 1. 2,5-Dihydroxy-1,4-dithiane was converted to DADT by treatment with acetic anhydride, which was reacted with 4-nitrothiophenol in the presence of boron trifluoride ether complex to produce BNSDT. Finally, the BNSDT was hydrogenated to BASDT with hydrazine in the presence of Pd catalyst. BASDT was obtained as the mixture of *trans* and *cis* stereo-isomers. The structure of BASDT was characterized on the basis of elemental analysis as well as FT-IR and ^{1}H NMR spectroscopies. The IR spectrum of BASDT showed characteristic absorptions at 3448 and 3355 cm^{-1} which are assignable to the amino group. Figure 1 shows the ^{1}H NMR spectrum of BASDT, and the inset indicates the assignment of each resonance. All peaks agreed with the assignment to the expected structure of BASDT. The characteristic singlet signal due to the amino group resonated at 3.80 ppm and doublet-doublet signals at 4.14 and 4.05 ppm assignable to the methine protons next to the thioether group of the *trans* and *cis* stereoisomers, respectively, are clearly observed. Using these signals, the ratio of trans and *cis* isomers in the mixture was estimated to be 1.8 : 1. The structure of BASDT was also confirmed by the elemental analysis.



Scheme 1. Synthesis of diamine (BASDT).

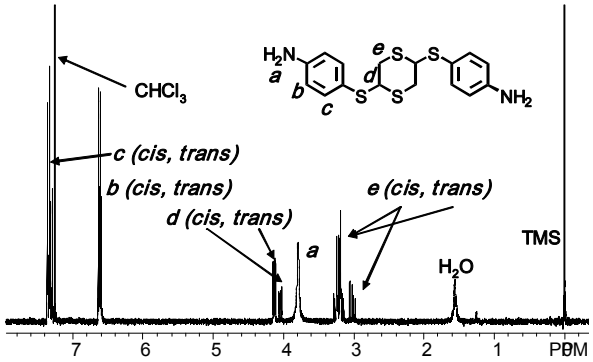
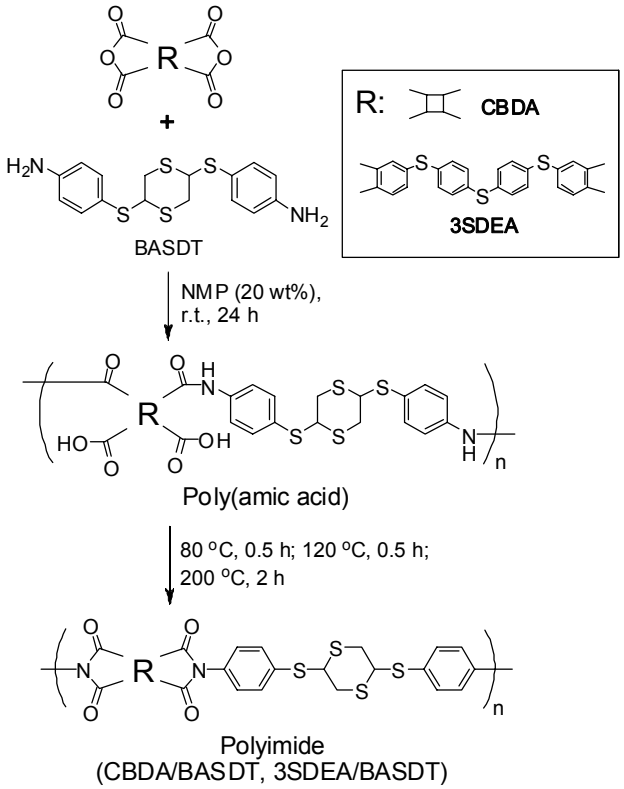


Figure 1. ^{1}H NMR spectrum of BASDT (*cis* and *trans* mixture).

3.2. Polyimide Synthesis

Two PIs were prepared from two dianhydrides of CBDA and 3SDEA, and BASDT via the PAA precursors, followed by thermal imidization at 200 °C for 2 h (Scheme 2). Table 1 summarizes the results of polymerization. Relatively high molecular weight PAAs with inherent viscosities in the range of 0.62–0.63 dL/g were prepared easily. Flexible PI films were obtained by heating the

corresponding PAAs cast on a fused silica substrate in nitrogen, followed by immersion in warm water. The resulting PI films were dried in *vacuo* at 100°C for 10 h prior to measurements.



Scheme 2. Synthesis of polyimides.

Table 1. Polymerization and thermal properties of polyimides.

	$[\eta]_{inh}$[a] (dL/g)	Film color	$T_{5\%}$ (°C)	T_g (°C)[a]
CBDA/BASDT	0.61	almost colorless	303	-
3SDEA/BASDT	0.63	pale-yellow	311	151
ref-CBDA/3SDA	-	-	440	262
ref-3SDEA/3SDA	-	-	488	174

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

The successful thermal conversion from PAAs to PIs can be confirmed by the FT-IR spectra (Figure 2), in which the characteristic absorptions due to the imide moiety at 1774 cm^{-1} ($\upsilon_{as,C=O}$), 1720 cm^{-1} ($\upsilon_{s,C=O}$), and 1365 cm^{-1} (υ_{C-N}) are clearly identified. No peaks due to the N–H stretching at 3260 cm^{-1} and C=O stretching of the amide groups at 1560 cm^{-1} are observed. Furthermore, elemental analysis also supported the formation of PIs.

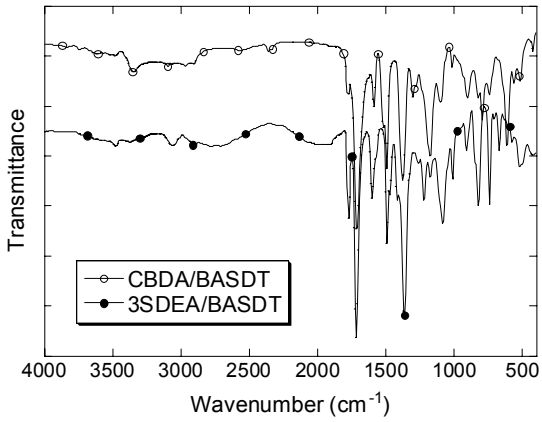


Figure 2. IR spectra of CBDA/BASDT and 3SDEA/BASDT.

3.3. Thermal Properties

The thermal stability of PIs was evaluated by TG and DSC under a nitrogen atmosphere. The results are summarized in Table 1, in which the thermal properties of the reference PIs from 4,4'-thiobis[(*p*-phenylenesulfanyl)aniline] (3SDA) that is a representative sulfur-containing diamine giving a highly refractive PI [13-16] are presented. Figure 3 shows the traces of TG for PIs. All the PIs show thermal stability with the 5% weight loss temperatures ($T_{5\%}$) in the range of 300–310 ºC.

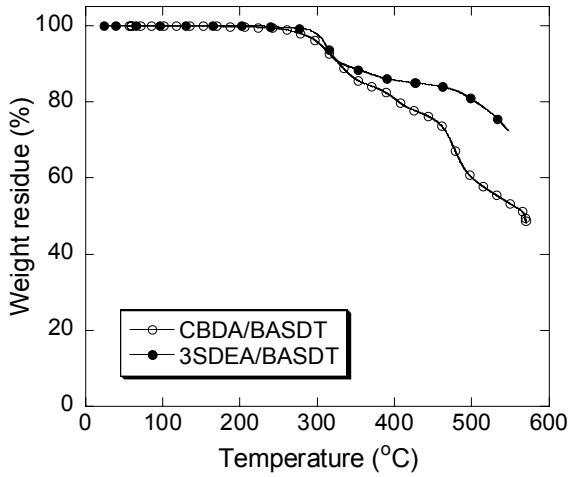


Figure 3. TG curves of polyimides (CBDA/BASDT, 3SDEA/BASDT).

The glass transition temperatures (T_gs) were evaluated by DSC measurements (Figure 4). The PI from 3SDEA and BASDT shows T_g at 151 ºC. On the other hand, no T_g was observed for CBDA/BASDT below 200 °C.

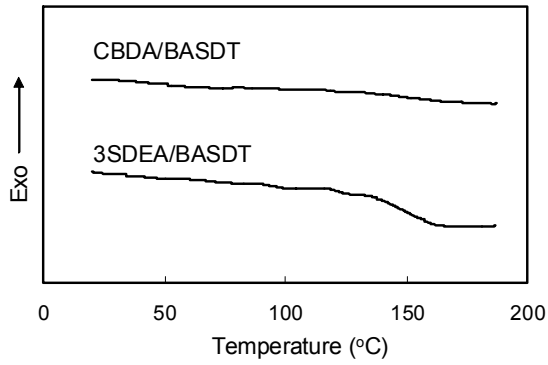


Figure 4. DSC curves of Polyimides.

The temperature dependences of the dynamic storage modulus (*E'*), loss modulus (*E"*), and tan δ of 3SDEA/BASDT are shown in Figure 5, which indicates that the modulus remains constant below the T_g. Whereas, the modulus drops dramatically above the T_g,. The *E"* curve exhibits T_g at 156 ºC. These results reveal that the heat deformation temperatures of the PIs were decreased by the incorporation of the alicyclic structure.

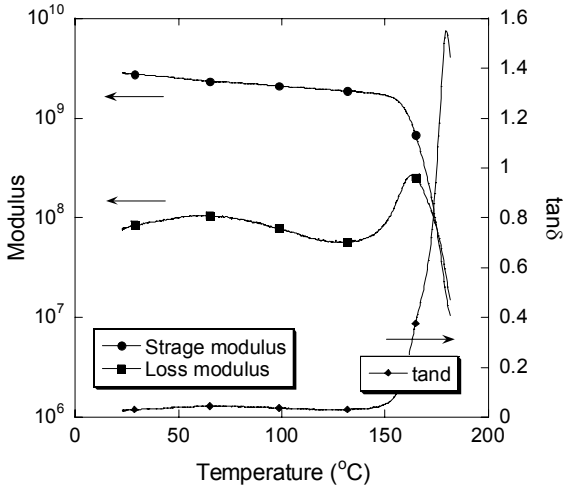


Figure 5. DMA curves of polyimide films (3SDEA/BASDT).

3.4. Optical Properties

Figure 6 shows the UV/vis optical transmission spectra of CBDA/BASDT and 3SDEA/BASDT (pale-yellow, 2–3 μm–thick) with those of the reference PIs (CBDA/3SDA and 3SDEA/3SDA). The absorbance of the films was normalized to a 2.4 μm-thick. The CBDA/BASDT exhibits higher transparency in the UV region than that of the reference CBDA/3SDA, and the transmittances in the visible region are higher than 90% even at 400 nm. Note that the experimental transmission spectra of the PIs agree well with the calculated spectra (Figure 7) based on the TD-DFT [17], in which the higher transparency of CBDA/BASDT at the shorter wavelengths is well reproduced, which is presumably due to the sulfur-containing alicyclic structure. On the other hand, 3SDEA/BASDT shows a similar spectrum to 3SDEA/3SDA, in which the alicyclic structure does not improve the transparency of the resulting PIs because the absorbance of the aromatic PIs mainly depends on the dianhydrides structure [18].

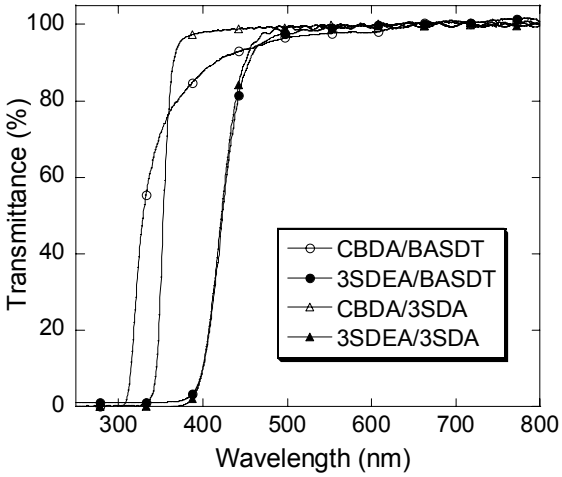


Figure 6. UV-vis spectra of polyimides. CBDA/BASDT, 3SDEA/BASDT, CBDA/3SDA, 3SDEA/3SDA (normalizing to 2.4 μm thickness).

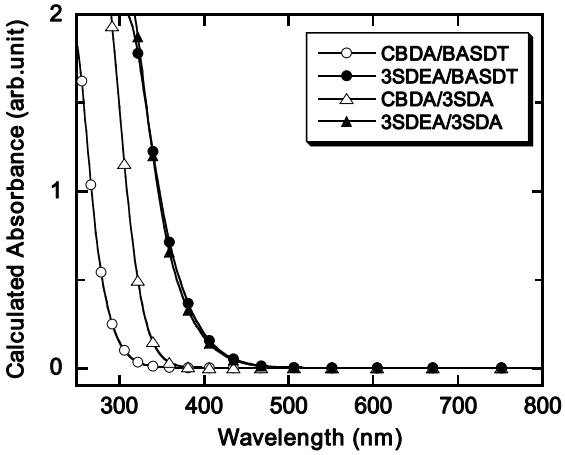


Figure 7. Calculated optical absorption spectra of polyimides using the TD-DFT method.

Table 2 summarizes the in-plane (n_{TE}), out-plane (n_{TM}), average refractive indices (n_{av}), and the birefringences (Δn) for the two PIs with the reference PIs exhibiting high n_{av}s. The CBDA/BASDT and 3SDEA/BASDT show the significantly high n_{av} values of 1.6929 and 1.7455,

Table 2. Optical properties of polyimides

	thickness	λ_{cutoff}[a] (nm)	n_{TE}[b]	n_{TM}[b]	n_{av}[b]	Δn[c]
CBDA/BASDT	1.0	290	1.7028	1.6729	1.6929	0.0299
3SDEA/BASDT	2.4	375	1.7474	1.7418	1.7455	0.0056
ref-CBDA/3SDA	4.9	344	-	-	1.6951	0.0203
ref-3SDEA/3SDA	4.0	402	-	-	1.7485	0.0068

[a] Cutoff wavelength. [b] Refractive indices at 632.8nm. [c] Birefringence.

respectively. Each value is comparable to that of the each reference PI. These results clearly indicate that the effect of the high sulfur content in BASDT is comparable to the phenyl rings having high molar refraction. The reduction of the number of phenyl rings in the repeating unit of BASDT-derived PIs is advantageous to improve the optical transmission at the shorter wavelengths in the UV region. The introduction of 1,4-dithiane moiety in the PI main chains will lead us to a new series of highly refractive semi-aromatic PIs.

4. Conclusions

A diamine of BASDT with a high sulfur-content and an alicyclic structure was newly designed and prepared to develop highly refractive transparent polyimides (PIs). The experimental results demonstrated that the synergic effects of sulfur and acyclic structure is effective to develop PIs with high refractive indices, low birefringence, and good optical transparency. The CBDA/BASDT and 3SDEA/BASDT PIs show the high values of n_{av} of 1.6929 and 1.7455, respectively, and excellent transparency higher than 90% even at 400 nm. The high-sulfur content in BASDT increases the refractive indices of the resulting PIs. On the other hand, a reduction of a number of aromatic units in BASDT does not increase the refractive index. However, in all cases, the increasing of sulfur contents in the repeating units is positive in improving the refractive indices of the PIs without deteriorating the other properties.

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