

Optically Transparent Sulfur-containing Semi-alicyclic Polyimide with High Refractive Index

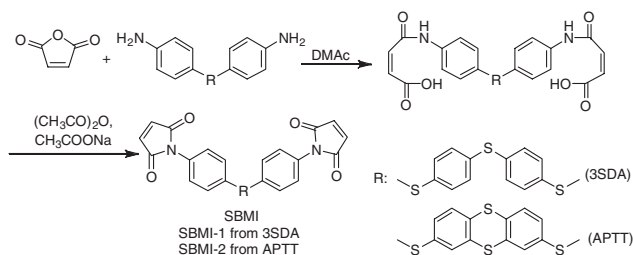
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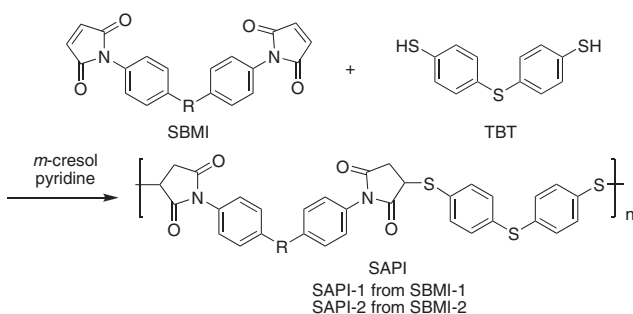
Sulfur-containing semi-alicyclic polyimides (PIs) with high refractive indices up to 1.7272 at 632.8 nm have been prepared by the Michael polyaddition of sulfur-containing bismaleimides (SBMIs) with 4,4'-thiobis(benzenethiol) (TBT). These PIs also showed high transparency in the visible region, low birefringence (Δn), and a high glass transition temperature.

High refractive index polymers have been developed in recent years for optoelectronic applications,^{1–3} such as encapsulants for organic light-emitting diode devices (OLED),⁴ charge-coupled devices (CCDs), and complementary metal oxide semiconductor (CMOS) image sensors (CISs).⁵ The general approach to enhance the refractive index in polymers is the introduction of substituents with high molar refraction, low molar volume, or high density, according to the Lorentz–Lorenz equation.⁶ Thus, the introduction of heavy halogen atoms,⁷ sulfur atoms,^{8–12} and metal atoms¹³ with high molar refractions is effective to increase the refractive indices of polymers.

Our previous work on high- n PIs revealed that the incorporation of sulfide-containing moieties could effectively increase the refractive indices and decrease the Δn values of the PIs.^{11,14,15} However, the optical transparency of sulfur-containing PI films in the visible light region is not sufficiently high and should be improved. To remedy this problem, we recently reported optically transparent sulfur-containing PI–TiO₂ nanocomposite film with a high refractive index and negative pattern formation from poly(amic acid) (PAA)–TiO₂ nanocomposite film,¹⁶ where semi-alicyclic PIs were prepared from alicyclic dianhydrides, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 1,2,4,5-cyclohexanetetracarboxylic dianhydride (CHDA), and the sulfide-linked aromatic diamines, 4,4'-thiobis(*p*-phenylenesulfanyl)aniline] (3SDA) and 2,7-bis(4-aminophenylenesulfanyl)thianthrene (APTT), by a two-step polymerization procedure via soluble PAA precursors. Although the PI derived from CBDA and APTT showed a high refractive index of 1.7203 at 632.8 nm, it exhibited significantly large Δn (0.0220) due to the planar structure of the CBDA moiety. Thus, it was not adopted to be combined with TiO₂ nanoparticles. The refractive indices of nanocomposites can be approximately estimated by the equation of $n_{\text{comp}} = \phi_p n_p + \phi_{\text{org}} n_{\text{org}}$,^{17,18} where n_{comp} , n_p , and n_{org} are the refractive indices of the nanocomposite, nanoparticle, and organic matrix, respectively. ϕ_p and ϕ_{org} are the volume fractions of the nanoparticles and organic matrix, respectively. Thus, it can be concluded from the equation that, in order to achieve a definite n_{comp} value with a definite type of nanoparticle, the higher the value of n_{org} is, the lower the value of ϕ_p . This is important for the design of high- n nanocomposites for optical applications because an overload of the nanoparticles often increases the optical loss and decreases the processability of the organic matrix.¹⁹



Scheme 1. Synthesis of SBMIs.



Scheme 2. Synthesis of SAPIs.

In this study, we report an optically transparent sulfur-containing semi-alicyclic polyimide (SAPI) with a high refractive index as an organic matrix. The SAPIs were prepared by the Michael polyaddition of sulfur-containing bismaleimides (SBMIs) with 4,4'-thiobis(benzenethiol) (TBT) because bismaleimide as a monomer can add more sulfur content in a repeating unit compared to alicyclic dianhydrides such as CBDA or CHDA.

As a monomer having a high sulfur content with an alicyclic ring structure, an SBMI was selected, and two SBMIs were prepared via two steps from maleic anhydride with 3SDA and APTT, as shown in Scheme 1.

The structures of SBMIs were characterized on the basis of elemental analysis, as well as FT-IR and ¹H NMR spectroscopy (Supporting Information²⁰).

TBT was chosen as the counter monomer. The Michael polyaddition is a useful method for preparing polymers with high molecular weights from dithiols and bismaleimides. The polymerization of SBMI and TBT was carried out at 100 °C for SBMI-1 and at room temperature for SBMI-2, respectively, for several hours in the presence of a catalytic amount of pyridine as a basic catalyst, as shown in Scheme 2.

The polymerization proceeded in the homogeneous state and provided SAPIs with number and weight average molecular weights (M_n , M_w) of (12000, 30000) (SAPI-1), and (23000, 64000) (SAPI-2), respectively. The polymers thus obtained were

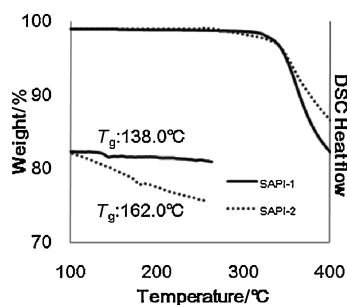


Figure 1. TGA and DSC curves of SAPIs (solid line: SAPI-1, dashed line: SAPI-2).

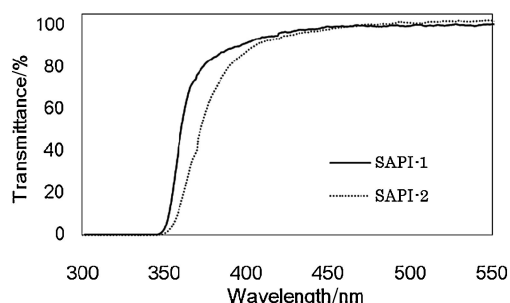


Figure 2. UV-vis spectra of SAPI films (thickness: 13.0 μm (SAPI-1), 10.6 μm (SAPI-2)).

white solids and soluble in chloroform, cyclohexanone, DMF, 1-methyl-2-pyrrolidinone, and heated γ -butyrolactone. A tough and flexible film was readily obtained by casting a cyclohexanone solution of the polymers onto a fused silica substrate followed by drying in vacuo.

The structures of SAPIs were characterized by FT-IR and ^1H NMR spectroscopy. The IR spectra of the polymers demonstrated characteristic absorptions of an imide moiety located at ca. 1781 and 1716 cm^{-1} (asymmetric and symmetric stretching vibrations of the carbonyl group, see Figure S1 in Supporting Information²⁰). The resonances observed by ^1H NMR spectra of SAPIs were all assigned (Supporting Information,²⁰ Figure S2). Signals at 2.8, 3.4, and 4.6 ppm, assignable to the methine and methylene (cis and trans) groups of succinimide, respectively, and those at 7.2 ppm, assignable to the vinylene group were not observed. Furthermore, the atomic composition of the polymer was confirmed by elemental analysis.

The thermal properties of SAPI were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). As shown in Figure 1 (TG and DSC), SAPI-1 and SAPI-2 exhibit 5% weight loss temperatures at 349 and 348 $^{\circ}\text{C}$ under nitrogen, and glass transition temperatures (T_g s) at 138 and 162 $^{\circ}\text{C}$, respectively.

Optical transparency of the PI films is a crucial factor for their use in optical applications. Figure 2 displays the optical transmission spectra of SAPIs. Both SAPIs films exhibit very high transparency (>87%) in the visible region (wavelengths: 400–800 nm).

As shown in Table 1, the refractive index (n_{av}) at 632.8 nm increases from a minimum of 1.7112 (SAPI-1) to a maximum of 1.7272 (SAPI-2) by increasing the sulfur content. These values

Table 1. Optical properties of the SAPI films

	Sc /wt % ^a	n_{TE}^{b}	n_{TM}^{c}	Δn^{d}	n_{av}^{e}
SAPI-1	22.82	1.7124	1.7088	0.00361	1.7112
SAPI-2	25.71	1.7288	1.7240	0.00478	1.7272

^aSulfur content. ^bIn-plane refractive index. ^cOut-of-plane refractive index. ^dSee Measurement section in Supporting Information.²⁰ ^eAverage refractive index: $n_{\text{av}} = [(2n_{\text{TE}}^2 + n_{\text{TM}}^2)/3]^{1/2}$.

are all higher than the n_{av} value of previously reported SAPI derived from CHDA and APTT (1.6994).¹⁶ The Δn of the PI films ranges from 0.00361 to 0.00478, which is suitable for optoelectronic applications.

In summary, the SAPIs were successfully prepared by the Michael polyaddition of SBMIs with TBT, and exhibited high refractive indices in the range of 1.7112–1.7272 with high thermal stability (up to 340 $^{\circ}\text{C}$), high transparency (>400 nm), and low Δn in the range of 0.00361–0.00478. These SAPIs can be good candidates as an organic matrix for sulfur-containing PI-TiO₂ nanocomposite film with a high refractive index.

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- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.