Synthesis of Highly Refractive and Transparent Polyimides Derived from 4,4’-Thiobis[2”’,6”’-dimethyl-4”’-(p-phenylenesulfanyl)aniline]

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In recent years, much attention has been paid to high-refractive-index polymers for their practical application in advanced optoelectronic fabrications, such as encapsulants for organic light-emitting diode devices (OLED), charge-coupled devices (CCDs), and complementary metal oxide semiconductor (CMOS) image sensors (CISs). According to the Lorentz-Lorenz equation, the refractive index of polymers depends on several factors such as the molar refraction, molar volume, or density. Thus, the introduction of heavy halogen atoms, sulfur atoms, and metal atoms with high molar refractions is effective to increase the refractive indices of polymers. Aromatic polyimides (PIs) are one of the most important classes of advanced polymers which possess various outstanding properties, such as excellent thermal and chemical resistance, low dielectric constants, high mechanical properties, and inherently high refractive indices. Therefore, much attention has been devoted to optical device applications of PIs.

Recently, we have developed highly refractive and transparent polyimides derived from aromatic dianhydrides and aromatic diamines containing sulfur atoms with thioether linkages. All PIs showed high refractive indices, high transparency and low birefringence. Although the refractive index of polymers can be effectively improved by using the aforementioned methods, optical polymers require several other functions, such as low in-plane/out-of-plane birefringence (Δn) and high transparency in the visible light region for optical device applications. In this study, new aromatic diamines with methyl groups at the ortho position of amino groups were prepared to develop high transparent aromatic.

RESULTS AND DISCUSSION
Synthesis of Diamines 2 and 5

Diamines 2 and 5 were prepared by a two- and three-step procedure, respectively, as shown in Scheme 1. Compound 3 was prepared by nitration of 3,5-dimethylbromobenzene with fuming nitric acid. Then, a mixture of ortho- and para-substituted nitro compounds was separated by column chromatography. Nucleophilic aromatic substitution of 3 with 4,4’-thiobisbenzenethiol in the presence of cesium carbonate produced 4, which was converted to diamine 5 by catalytic reduction. On the other hand, diamine 2 was prepared by similar procedure according to the literature. The structures of 2 and 5 were characterized by FT-IR and NMR spectroscopy.

Scheme 1. Synthesis of diamine (2) and diamine (5)

Synthesis and Characterization of Polyimides (PIs)

All PIs were synthesized by a two-step polycondensation of diamines such as 2 and 5 with 6 via soluble poly(amic acid) (PAA) precursors, followed by thermal imidization at elevated temperatures (Scheme 2). The
inherent viscosities of the PAA solutions are in the range of 0.32-0.68 g/dL. Flexible PI films were prepared by thermal imidization of the corresponding PAA films cast onto glass substrates and fused silica under nitrogen. After thermal conversion from PAA to PI, the characteristic IR absorption peaks of the imide moiety, such as 1774 (as, C=O), 1727 (s, C=O), and 1365 cm⁻¹ (C-N) are observed. In addition, an absorption peak of aromatic thioether groups (Ar-S-Ar) is observed at 1099 cm⁻¹. Furthermore, the elemental analysis also supported the formation of the expected PIs.

Thermal Properties of PIs

The thermal properties of the PIs, such as 10% weight loss temperatures (T_d,10) and glass transition temperatures (T_g), were evaluated by TGA, DSC, and DMA measurements. The results are summarized. All PIs exhibit good thermal stability, such as the T_d,10 values at 460–505°C. The T_gS of the PIs estimated by DSC and DMA show similar values. All PIs show high T_gS in the range of 179–218 in the order of PI-2 > PI-1 > PI-3. This trend is related to the structural effects of the diamines. The results indicate that the introduction of methyl groups at the ortho position of amino groups is effective to increase the T_gS due to the increase in the chain rigidity of PI-1 and PI-2, that is, the methyl groups significantly restrict the bond rotation at the C-N imide bond. Figure 6 illustrates the variations in the storage modulus (E'), loss modulus (E'') and loss factor (tan δ) measured by DMA at a heating rate of 2°C/min under air. The modulus remains constant or slightly decreased on heating over a wide temperature range below the T_gS. Above the T_gS, the modulus dramatically decreases. The T_gS determined from the peak temperatures of E'' were close to the T_gS estimated from DSC.

Optical Properties

Figure 1 shows the optical transmission spectra of PI films with PMDA-ODA as the reference PI (~10 μm thick). All PIs show much better transparency with the cutoff wavelengths (λ_cutoff) at 402–375 nm compared with PMDA-ODA. The transmittances of PI-1 and PI-2 measured at 425 nm are significantly higher than that of PI-3 derived from 6 and 4,4'-thiobis[p-phenylenesulfanyl]aniline. This is attributable to the ortho methyl groups in the aromatic diamines which induce significant steric hindrance around the C-N imide bond. This is supported by the fact that the dihedral angles at the C-N bonds in the optimized geometry of the models are 66°, 73°, and 42° for PI-1, PI-2, and PI-3, respectively, as shown in Figure 1. The significantly distorted conformations in PI-1 and PI-2 effectively reduce the formation of intramolecular and intermolecular CTCs in the main chains. The πυv.
of PI films is in the range of 1.7135–1.7482 in the order of PI-3 > PI-1 > PI-2. The highest $n_w$ observed for PI-3 could have originated from two factors. Firstly, the introduction of methyl groups into the diamines reduces the sulfur content, which is the primary factor of the high refractive indices of sulfur-containing PIs. Secondly, the distorted conformation around the C-N imide bond lowers the inter-molecular packing of PIs, which increases the molar volumes of PIs. All of the PIs show low birefringence ($\Delta n$) in the range of 0.0066–0.0076 compared with PMDA-ODA as reference PI. The relatively low $\Delta n$ value is related to the highly flexible and phenyl-sulfanyl-phenyl linkages in the main chains. The results indicate that aromatic diamines with ortho methyl groups are effective to improve the optical transparency of the resulting PIs while maintaining high refractive indices and low birefringences of the PIs.

![Figure 1. UV-vis spectra of PI films (film thickness: ~10 µm)](image)

**SUMMARY**

Aromatic diamines containing methyl groups at the ortho positions of amino groups were newly synthesized to enhance the optical transparency of the resulting PIs. The PIs derived from 2 and 5 showed higher transparency compared to 6-3SDA, while maintaining relatively high refractive indices. At the same time, the glass transition temperatures of the PI films were increased and exhibited low birefringences. The experimental results indicate that the introduction of methyl groups at the ortho position of aromatic diamines is an effective way to improve the optical transparency of PIs. These high optical transparency, high refractive index, and high thermal stability factors make the resulting PIs promising candidates for advanced optical device applications.

References and Notes