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Highly Refractive Poly(phenylene thioether) Containing Triazine Unit

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ABSTRACT: A highly refractive and transparent poly(phenylene thioether) containing a triazine unit has been developed. The polymer was prepared by a polycondensation procedure from 4,4′-thiobis(benzenethiol) and 2,4-dichloro-6-methylthio-1,3,5-triazine and showed good thermal stabilities such as a relatively high glass transition temperature at 116 °C and a 5% weight-loss temperature ($T_{5\%}$) at 367 °C. The optical transmittance of the polymer at 400 nm is higher than 80%. The triazine unit with sulfur atoms provides the polymer with a high refractive index of 1.7492 at 633 nm.

In recent years, much attention has been paid to high refractive index polymers with high transparency and low birefringence for optical applications such as camera lens, antireflective coatings, and telecommunication systems.[1−4] The general approach to improve refractive indices in polymers is the introduction of substituents with high molar refraction and low molar volume according to the Lorentz−Lorenz equation.[5] Thus, aromatic rings, heavy halogens (Cl, Br, and I) except for fluorine, sulfur, and metallic elements have been introduced in polymers to enhance their refractive indices.[6−8] Thus, many conventional sulfur-containing polymers characterized by high optical transparency and a high refractive index have been reported for optical device applications such as epoxy resins,[9] polyurethanes,[10] polymethacrylates,[4] and poly(arylene sulfide)s.[11] However, the polymers have relatively low refractive indices in the range 1.5−1.7 at the sodium-D line (589 nm) or 633 nm. Recently, we have developed sulfur containing aromatic polyimides (PIs) for optical applications because the PIs have several merits such as high thermal, oxidative, chemical, and mechanical stabilities.[12−18] Although most of them exhibit very high refractive indices in the range 1.74−1.77, the films have coloration, which is a problem of aromatic PIs. Poly(aryl ether)s and poly(aryl thioether)s, such as poly(arylene ether ketone)s, poly(arylene ether sulfone)s, and poly(phenylene sulfide)s, are of the well-known high performance engineering thermoplastics. Such polymers have several advantages: not only high thermal, oxidative, and chemical stabilities but also high stiffness and toughness.[19] Recently, poly(thioether ketones) and poly(aryl thioether)s containing fluorene, sulfone, and oxadiazole substituents have been developed for optical applications.[20−22] Most of the polymers showed high thermal stability and excellent optical transparency with low birefringence. However, the refractive indices of these polymers are still in the range of 1.66−1.72 at the sodium-D line (589 nm). The relatively low refractive indices are mainly attributable to two factors. One is the low sulfur content because the refractive indices of sulfur containing polymers mainly depends on the sulfur content in the repeating unit.[23] The other is that the sterically bulky substituents such as fluorene and sulfone groups would endow large free volumes among polymer chains, which lowers the refractive index. Therefore, the breakthrough of the trade-off between the refractive index and optical transparency is an important topic.

There are other candidates as effective substituents to enhance refractive index such as heteroaromatic rings containing −C═N− bonding for a high refractive polymer. It has been reported that −C−N═C− bonds possess relatively high molar refraction (4.10) as compared to a −C═C− bond (1.73).[24] In fact, heterocyclic rings such as pyridazine and pyrimidine units in place of phenyl units could be effective to increase the refractive indices of polymers while maintaining high optical transparency.[17] The triazine unit containing sulfur atom and dichlorides would be an effective substituent for high refractive polymers because triazine unit contains three −C═N− bond to improve the refractive index and the dichloride in the triazine unit is also very reactive with thiol and hydroxyl groups to produce polymers under mild conditions.

In this paper, we report the design and synthesis of a new polymer containing sulfur atom and triazine unit to achieve high refractive index and high optical transparency in the visible region at the same time.

As a sulfur-containing trazine monomer, 2,4-dichloro-6-methylthio-1,3,5-triazine (**1**), which can be easily prepared from cyanuric chloride and methanethiol (Scheme 1),[25] was selected.

As triazine dichloride is generally very reactive for aromatic substitution reactions, the phase-transfer catalyzed polycondensation of **1** with 4,4′-thiobisbenzenethiol **2** was carried out in a nitrobenzene-aqueous alkaline solution system at room temperature (see Supporting Information). The phase-catalyzed polycondensation with several kinds of phase-transfer catalyst such as benzyl triethylammonium chloride (BTEAC), benzyl triphenyl phosphonium chloride, and cetyltrimethyl ammonium bromide (CTMAB) has widely been used for the synthesis of polysulfide.[26,27] In this synthesis, CTMAB was employed as a quaternary onium salt (Scheme 2).

The polymerization proceeded smoothly, giving poly(phenylene thioether) **3** with the number- and weight-average molecular weights of 13000 and 21900 (PSt standard), respectively. The white solids of **3** were soluble in chloroform, tetrahydrofuran, and tetrachloroethane. The structure of **3** was characterized by ^{1}H NMR and FT-IR spectroscopy. The characteristic IR peaks were observed at 1473, 1245 cm^{-1} and which are attributable

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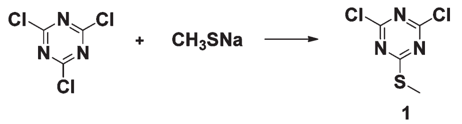
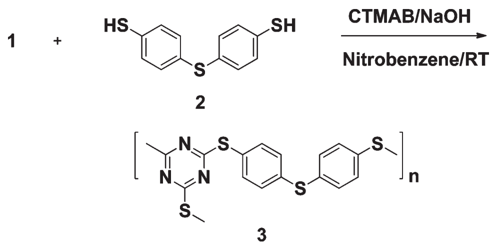
to the −C=N− groups in triazine unit and thiol(-SH) group (see Supporting Information). In the ^{1}H NMR spectrum, the signals resonated at 7.38, 7.27, and 2.21 ppm are assignable to the aromatic and methyl protons, respectively. Additionally, in the ^{13}C NMR spectrum, six carbon signals, which accord well with the expected structure, are observed. Among these peaks, three quaternary carbon signals are assigned by DEPT-135 measurement as shown in Figure 1. Furthermore, the elemental analysis also supported the formation of the expected polymer **3**.

The thermal properties of **3** were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). **3** shows thermal stability such as 5% weigh loss temperature ($T_{5\%}$) of 367 °C in a nitrogen atmosphere as shown in Figure 2. The glass transition temperature (T_g) measured by DSC is 116 °C.

Scheme 1. Synthesis of 1



Scheme 2. Synthesis of 3



The temperature dependence of the dynamic storage modulus (E'), loss modulus (E''), and tan δ of **3** are shown in Figure 3. The initial values of E' (30 °C) are in the range of 3.7 GPa, which remains constant up to approximately 90 °C before its T_g. After T_g, which is determined as the peak temperature of E'', the modulus decreases. The T_g value of 95 °C is lower than that measured by DSC. The difference is attributed to the different testing techniques, and the different responses of the polymer between DSC and DMA measurements.[28]

Figure 4 displays the UV−vis spectrum of **3** film with thickness of approximately 10 μm. The cutoff wavelength (λ_{cutoff}) is 348 nm. The optical transmittance of 400 nm is higher than 80% because the meta-substituted triazine group and thiomethyl group in the triazine unit would effectively prevent interchain molecular packing. These results indicate that the optical transparency is not deteriorated by the introduction of triazine unit

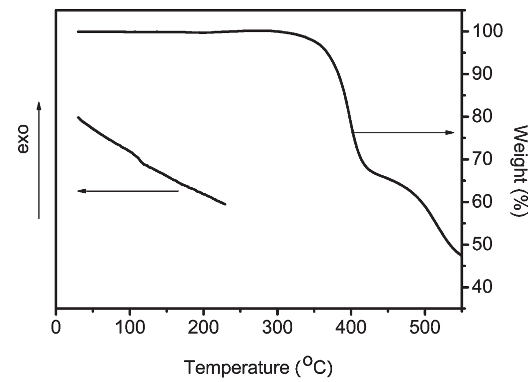


Figure 2. TGA and DSC (second scan) traces of the polymer (10 °C/min under nitrogen).

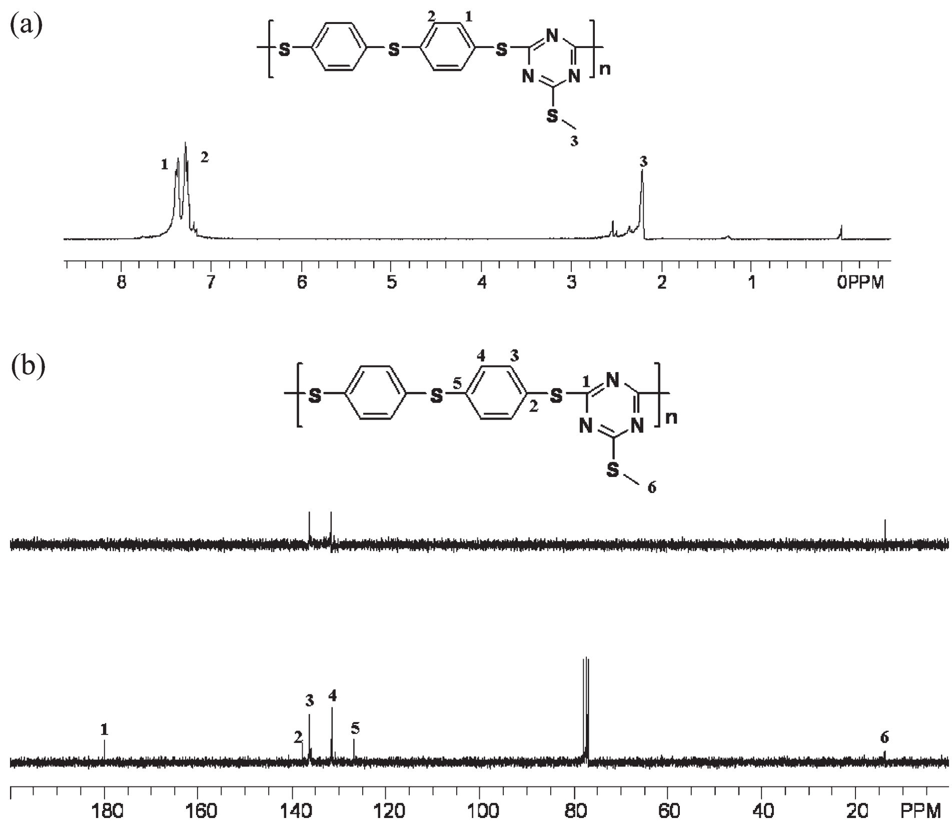


Figure 1. NMR spectra of the polymer: (a) ^{1}H NMR; (b) ^{13}C NMR (bottom) and DEPT-135 (top).

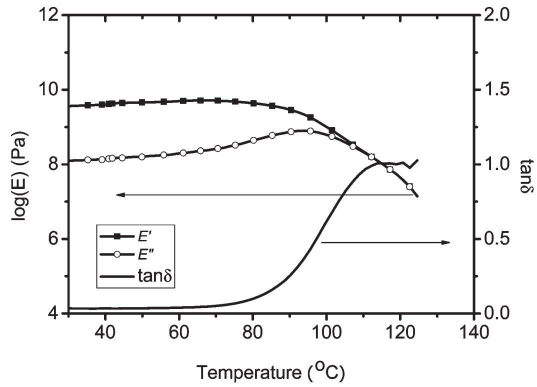


Figure 3. DMA curves of the polymer (1 Hz, 2 °C/min): modulus and tan δ.

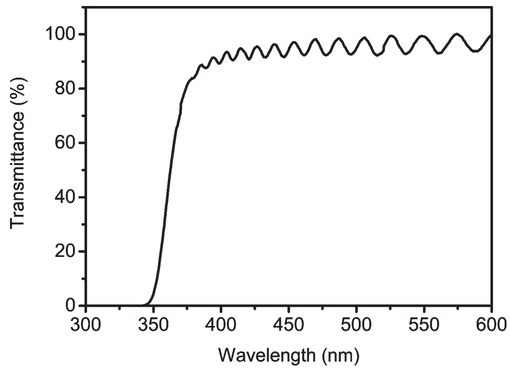


Figure 4. UV−vis spectrum of **3** (film thickness: ~10 μm).

Table 1. Optical Properties of 3 Film

		refractive indices and birefringence at 633 nm			
S (%)[a]	d[b] (μm)	n_{TE}[c]	n_{TM}[d]	n_{av}[e]	Δn[f]
34.2	3.5	1.7506	1.7464	1.7492	0.0041

[a] Sulfur content. [b] Film thickness of the polymer. [c] n_{TE}: the in-plan refractive index. [d] n_{TM}: out-of-plan refractive index. [e] n_{av}: average refractive index. [f] *see Measurements* in Supporting Information.

into the polymer. Moreover, no coloration of films was observed during thermal treatment up to 200 °C.

The optical properties of **3** film such as in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, average refractive index (n_{av}), and birefringence (Δn) are listed in Table 1.

The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the polymer at 633 nm are 1.7506 and 1.7464, respectively. The n_{av} value of the polymer at 633 nm is 1.7492, which is much higher than those ($n_D < 1.72$) of already reported poly(arylene sulfide)s.[11,20−22] The high refractive index of the polymer is obviously attributed to the introduction of sulfur atom and triazine unit into the polymer without bulky substituents. Moreover, thioether linkages in the molecular chain of the polymer endow with the low Δn of 0.0041.

All the results suggest that the introduction of triazine moiety together with sulfur atom is an effective way to produce **3** with high refractive index and high transparency in the visible region.

In conclusion, a new polymer **3** containing triazine unit with sulfur atom was synthesized to improve the refractive index and optical transparency in the visible region. As expected, **3** containing a high sulfur content (34.2%) and a triazine unit in the repeating unit showed excellent optical properties such as the high refractive index (1.7492) at 633 nm with a low birefringence (0.0041) and good optical transparency in the visible region. At the same time, **3** exhibited good thermal properties such as the 5% weigh loss temperature ($T_{5\%}$) of 367 °C and the glass transition temperature (116 °C). Moreover, **3** can easily be prepared by the phase-transfer catalyzed polycondensation of **1** with **2** at room temperature. The synthesis of **1** is also easier than those of other monomers for reported sulfur-containing polymers. This polymer will thus be a good candidate for optical applications.

Supporting Information Available: Text giving the experimental details and the figures showing the NMR and IR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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