# Macromolecules

# Synthesis of Highly Refractive Poly(phenylene thioether) Derived from 2,4-Dichloro-6-alkylthio-1,3,5-triazines and Aromatic Dithiols

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Supporting Information

**ABSTRACT:** A highly refractive, transparent, and totally colorless poly(phenylene thioether) (PPT) containing a triazine unit has been developed. A new aromatic dithiol, thianthrene-2,7-dithiol, with a high sulfur content was designed and synthesized in order to develop PPTs with high refractive indices and high glass transition temperatures ( $T_{\rm g}$ s). These PPTs were prepared by the phase-transfer catalyzed polycondensation of 2,4-dichloro-6-alkylthio-1,3,5-triazines with aromatic dithiols such as 4,4'-thiobisbenzenethiol, benzene-1,3-dithiol, and thianthrene-2,7-dithiol. The PPTs obtained



• Low birefringence (~0.005)

from the 2,4-dichloro-6-methylthio-1,3,5-triazines and aromatic dithiols showed good thermal stabilities such as relatively high  $T_{\rm gs}$  over 120 °C and 5% weight-loss temperatures ( $T_{5\%}$ ) around 350 °C. The optical transmittance of the polymer films with a 1  $\mu$ m thickness is around 98% at 400 nm. The combination of the triazine and sulfur-containing thianthrene units provides PPTs with high refractive indices up to 1.7720 at 633 nm and low birefringences (<0.005).

# INTRODUCTION

A high refractive index (n) and low birefringence  $(\Delta n)$  combined with a good thermal stability and high optical transparency are the basic concerns in designing optical polymers for camera lens, antireflective coatings, and optical waveguide systems.<sup>1-6</sup> According to the Lorentz–Lorenz equation, the introduction of substituents with a high molar refraction and low molar volume efficiently increases the refractive indices of the polymers.<sup>7</sup> Among the various substituents, the sulfur atom with a high atomic refraction, is one of the most effective candidates, and many sulfur-containing polymers, such as epoxy,<sup>8</sup> polyurethane,<sup>9</sup> polymethacrylate,<sup>4</sup> and poly(arylene thioether)s,<sup>10</sup> have been reported to increase their refractive indices with a high transparency for optical device applications. However, the refractive indices of these polymers are relatively low in the range of 1.50–1.70 at 589 nm (sodium-D line) or 633 nm.

Recently, we have developed a series of sulfur-containing aromatic polyimides (PIs) for optical applications because the PIs have several merits, such as high thermal, oxidative, chemical, and mechanical stabilities.<sup>11–18</sup> These PIs showed very high refractive indices in the range of 1.74-1.77 and a low birefringence of less than 0.0093, but the optical transparency at around 400 nm of ca.10  $\mu$ m-thick films is lower than 80% due to the coloration originating from the charge transfer (CT) interactions between the electron-donating and electron-accepting moieties in the PIs. This may cause problems with the optical applications of the aromatic PIs.

To remedy this problem, well-known high performance engineering thermoplastics, such as poly(thioether ketone)s and poly(aryl thioether)s containing fluorene, sulfone, and oxadiazole substituents, have been developed for optical appli-cations.<sup>19–21</sup> Although these polymers showed a high thermal stability and excellent optical transparency with a low birefringence, the refractive indices of these polymers are still in the range of 1.66 - 1.72 at the sodium-*D* line (589 nm) because of the low sulfur content and the presence of sterically bulky substituents, such as fluorene and sulfone groups, which endow large free volumes among the polymer chains. To enhance the refractive index, heteroaromatic rings containing -C=N- bonding in place of the phenyl rings would be effective because the -C-N=C- bonds possess a higher molar refraction (4.10) as compared to the -C=C- bond (1.73).<sup>22</sup> On the basis of this finding, we were interested in triazine dichloride having an alkylsulfanyl side chain as a monomer, and briefly reported a highly refractive and transparent poly(phenylene thioether) (PPT) containing a triazine unit, which was obtained by the polycondensation of 4,4'-thiobisbenzenethiol (TBT) and 2,4dichloro-6-methylthio-1,3,5-triazine (DMT). The polymer exhibited a high refractive index of 1.7492 at 633 nm and excellent transmittance higher than 80% at 400 nm.<sup>23</sup> In order to clarify the potential of the triazine-containing PPTs as optical materials, 2,4-dichloro-6-butylthio-1,3,5-triazine (DBT) was chosen to improve the solubility of the polymers, and aromatic dithiols, such as benzene-1,3-dithiol (BDT) and thianthrene-2,7-dithiol (TDT), were chosen as monomers in addition to DMT and TBT to increase the sulfur content in the repeating unit.

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#### Scheme 1. Synthesis of TDT



This article reports the synthesis and properties of the triazinecontaining PPTs prepared from 2,4-dichloro-6-alkylthio-1,3,5triazines and aromatic dithiols. The obtained PPTs exhibited high refractive indices in the range of 1.699-1.772, a low birefringence of less than 0.005, and a high optical transparency over 400 nm.

#### EXPERIMENTAL SECTION

**Materials.** TBT and BDT were purchased from Aldrich Japan. DMT and DBT were kindly donated by Sankyo Chemical Ltd. 2,7-Difluorothianthrene (DFT) was prepared according to a reported procedure.<sup>24</sup> Other commercially available reagents and solvents were used as received.

Synthesis of 2,7-Dibenzylthiothianthrene (DBTT). A 30 mL round flask was charged with potassium *tert*-butoxide (4.85 g, 43.0 mmol) and *N*,*N*-dimethylformamide (DMF) (15 mL) under a nitrogen atmosphere. Benzylmercaptan (5.1 mL, 42 mmol) and DFT (3.98 g, 15.8 mmol) were slowly added into the mixture cooled with an ice bath. The solution was stirred at 60 °C for 24 h and was poured into water. The precipitate was filtered and dried in vacuum. The crude product was recrystallized from 2-methoxyethanol to give 2,7-dibenzylthiothianthrene (DBTT) as a yellow crystal (65% yield). Mp: 116–117 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 4.10 (s, 4H), 7.13 (d, 2H), 7.27 (m, 12H), 7.39 (d, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 148.7, 148.6, 137.3, 137.1, 136.8, 133.5, 129.7, 129.3, 129.2, 129.0, 127.8, 39.4.

Anal. Calcd for  $C_{26}H_{20}S_4$ : C, 67.78; H, 4.38. Found: C, 67.59; H, 4.53.

Synthesis of Thianthrene-2,7-dithiol (TDT). A 50 mL twonecked round flask was charged with DBTT (1.38 g, 3.0 mmol),  $Cp_2TiCl_2$  (0.078 g, 0.31 mmol), and diglyme (10 mL) under a nitrogen atmosphere at 0 °C. Dibutylmagnesium (Bu<sub>2</sub>Mg, 20 mL, 2.5 M) was slowly added, and then the solution was stirred for 3 h. The aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (20 mL) was slowly added to the reaction mixture at 0 °C. The reaction mixture was extracted with dichloromethane and water. To the aqueous layer was added hydrochloric acid and the solution was stirred for 1 h. The precipitate was filtered and dried in vacuum to give TDT as an ivory-colored powder (0.517 g, 61% yield). Mp: 139 °C.

 $^1\rm H$  NMR (300 MHz, CDCl<sub>3</sub>, ppm): 3.48 (s, 2H), 7.13 (d, 2H), 7. 31 (d, 2H), 7.40 (s, 2H).  $^{13}\rm C$  NMR (CDCl<sub>3</sub>, ppm): 136.7, 132.3, 131.0, 129.1, 129.0, 128.5. Anal. Calcd for C<sub>12</sub>H\_8S<sub>2</sub>: C, 51.06; H, 2.96. Found: C, 51.39; H, 2.88.

**Synthesis of Poly(phenylene thioether) (PPT): PPT-4.** To a 5 mL round flask was charged with BDT (0.145 g, 1.02 mmol) and 2.1 mL of 1 M aqueous sodium hydroxide. CTMAB (30 mol %, 0.220 g) was added to the solution, and the mixture was stirred for 1 h. To the mixture was added a solution of BTD (0.243 g, 1.02 mmol) in chloroform (2 mL). The two-phase solution was vigorously stirred at room temperature for 24 h and poured into methanol. The precipitate was filtered and dried in vacuum. Then, the precipitate was dissolved in

chloroform and poured into hexane and dichloromethane (10:1 vol %). The precipitate was filtered and dried in vacuum. Yield: 0.220 g (71.5%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.54, 7.44, 2.78, 1.43, 1.26, 0.84. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 180.8, 180.7, 179.4, 141.5, 136.4, 129.5, 128.1, 30.8, 30.2, 21.8, 13.7. Anal. Calcd for C13H13N3S3 (1 mol % H<sub>2</sub>O): C, 50.78; H, 4.26; N, 13.67. Found: C, 50.75; H, 4.27; N, 13.66.

*PPT-1*. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.38, 7.27, 2.21. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 180.0, 137.7, 136.3, 131.6, 126.8, 13.77

*PPT-2.* H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.41, 7.30, 2.77, 1.43, 1.26, 0.86. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 180.7, 179.6, 137.3, 136.0, 131.2, 126.5, 31.1, 30.1, 21.8, 13.7.

*PPT-3.* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.70, 7.56, 7.43, 7.27, 2.22. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 184.2, 182.5, 181.2, 179.8, 168.7, 148.5, 142.0, 137.6, 136.8, 130.2, 128.4, 14.1.

*PPT-5.* <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>, ppm):7.49 (2H), 7.21 (4H), 2.73 (2H), 1.35 (2H), 1.15 (2H), 0.76 (3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 179.8, 176.3, 148.8, 148.7, 135.1, 134.9, 129.5, 129.2, 31.2, 31.0, 22.1, 14.0.

*PPT-6.* <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>, ppm)): 7.48, 7.22, 7.18, 2.73, 2.22, 1.35, 1.14, 0.75.

<sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 181.1, 179.8, 160.0, 158.8, 157.6, 148.4, 137.4, 135.9, 135.1, 134.7, 129.2, 127.2, 31.2, 22.8, 22.1, 14.1, 13.9.

*Film Preparation.* All of the polymer films were prepared by solution casting in TCE, followed by heating on a hot plate from 25 to 250  $^{\circ}$ C in nitogen.

Measurements. The NMR spectra were recorded on a BRUKER DPX-300S spectrometer at the resonant frequencies at 300 MHz for <sup>1</sup>H and at 75 MHz for <sup>13</sup>C nuclei using CDCl<sub>3</sub> as the solvents. The <sup>13</sup>C DEPT sequence was used to detect and assign protonated carbons. The FT-IR spectra were obtained by a Horiba FT-120 Fourier transform spectrophotometer. The ultraviolet-visible (UV-vis) spectra were performed on a Hitachi U-3210 spectrophotometer. The optical transmittance of PPT films was evaluated in the wavelength range of 250-800 nm at 1  $\mu$ m film thickness. Elemental analyses were carried out on a Yanaco MT-6 CHN recorder elemental analysis instrument. Thermogravimetric analysis (TGA) was estimated by a Seiko TG/DTA 6300 under a nitrogen atmosphere at a heating rate of 10 °C/min. Differencial scanning calorimetry (DSC) was estimated by using a Seiko DSC 6300 at a heating rate of 20 °C/min. The in-plane  $(n_{\rm TE})$ and out-of-plane  $(n_{\rm TM})$  refractive indices of PPT films were carried out using a prism coupler (Metricon, model PC-2000) equipped with a He-Ne laser (wavelength: 633 nm) and a half-waveplate in the light-path. The in-plane/out-of-plane birefringences ( $\Delta n$ ) were estimated as a difference between  $n_{\text{TE}}$  and  $n_{\text{TM}}$ , and the average refractive indices were calculated according to the equation:  $n_{\rm av} = \left[\left(2n_{\rm TE}\right)^2 + \right]$  $n_{\rm TM}^{2})/3]^{1/2}$ .

**DFT Calculation.** The wavelength-dependent refractive indices of models for PPTs were calculated based on the Lorentz–Lorenz theory. The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) was used for the calculations of frequency-dependent linear polarizabilities. The three-parameter Beckestyle hybrid functional (B3LYP) was adopted as the functional and all



**Figure 1.** <sup>1</sup>H NMR spectrum of **TDT** in CDCl<sub>3</sub>.



the calculations were performed using the software package of Gaussian-09 (Rev.B01). A packing coefficient ( $K_p$ ) of 0.625 was used for evaluating the intrinsic molecular volumes of the models. The details of the calculation method were reported elsewhere.<sup>25</sup>

#### RESULTS AND DISCUSSION

As described in the Introduction, the refractive index (n) of a polymer generally increases with the increasing sulfur content in a repeating unit. Thus, a new aromatic dithiol, TDT, with the high sulfur content of 45.7% was designed and synthesized in order to develop novel PPTs with a high-*n* and high  $T_{g}$ .

**Synthesis of TDT.** TDT was synthesized by a two-step procedure with DFT as the starting material (Scheme 1). In the first step, DFT was reacted with benzylmercaptan in the presence of potassium *tert*-butoxide in DMF to afford DBTT. The deprotection of the benzyl thioether was then attempted using general reagents, such as strong acids or bases (alkali metals or stannyl hydride). All these trials, however, did not produce TDT.

Recently, Akao et al. reported a highly effective and mild deprotection method of the benzyl thioethers using Bu<sub>2</sub>Mg in the presence of a catalytic amount of titanocene dichloride.<sup>26</sup> Thus, DBTT was treated with Cp<sub>2</sub>TiCl<sub>2</sub> and Bu<sub>2</sub>Mg in diglyme at 0 °C. This reaction smoothly proceeded to give TDT in 65% yield.

The structure of TDT was characterized by FT-IR and NMR spectroscopy. The IR spectrum of TDT showed the characteristic absorption at 2534 cm<sup>-1</sup> due to the S–H stretching of a thiol group (Supporting Information, Figure S1). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of TDT are shown in Figures 1 and 2 along with assignments of all the signals. The characteristic proton of the thiol group is observed at 3.47 ppm. In the <sup>13</sup>C NMR spectrum, the six carbon signals, which are consistent with the expected structure, are observed. The structure of TDT was further confirmed by elemental analysis, in which the measured C and H composition agreed well with the calculated values.

Synthesis and Characterization of Triazine-Containing PPTs. The synthetic route for the triazine-containing PPTs is

## Scheme 2. Synthesis of PPTs



	Table 1.	Molecular	Weights and	Thermal	Properties	of PPTs
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	dichloride-dithiol	$M_{ m w}^{\ a}$	$M_{\rm w}/M_{\rm n}$	$T_{g}^{\ b}$	$T_{5\%}{}^{c}$	
PPT-1	DMT-TBT	37 000	2.2	127	367	
PPT-2	DBT-TBT	29 000	4.1	77.0	335	
PPT-3	DMT-BDT	24 500	2.2	129	377	
PPT-4 DBT-BDT 27 000 2.8 75.0 342						
PPT-5 DBT-TDT 26 000 5.2 93.1 327					327	
PPT-6	DMT (70%) DBT (30%) -TDT	7300	3.7	185	343	
PPT-7	DMT (50%) DBT (50%) -TDT	16 000	2.8	170	364	
<sup><i>a</i></sup> PSt standard. <sup><i>b</i></sup> Glass transition temperature measured by DSC. <sup><i>c</i></sup> 5% weigh loss temperature.						

shown in Scheme 2. All the triazine-containing PPTs were prepared by the phase-transfer catalyzed polycondensation of the 2,4-dichloro-6-akylthio-1,3,5-triazines, DMT and DBT with aromatic dithiols, such as TBT, BDT, and TDT. The phasetransfer-catalyzed polycondensation was carried out in a chloroform/aqueous alkaline solution system in the presence of cetyltrimethylammonium bromide (CTMAB) as a quaternary ammonium salt at room temperature. The results are summarized in Table 1.

The polymerizations of the 2,4-dichloro-6-akylthio-1,3,5-triazines with TBT or BDT afforded the PPTs with the weightaverage molecular weights  $(M_w s)$  of around 25000 (PSt standard). On the other hand, the PPT prepared from DMT and TDT has a limited molecular weight due to the low solubility of the resulting PPT. The polycondensation of DBT with TDT smoothly proceeded to give PPT-5 with the  $M_{\rm w}$  of 26000, indicating that a butyl group in DBT effectively to improves the solubility of the resulting PPT. To obtain PPTs with a higher sulfur content, PPT-6 and PPT-7 were prepared by the polycondensation of TDT with the mixture of DMT and DBT (7:3 and 1:1 respectively, mol %). The solubilities of the PPTs are listed in Table 2. The PPTs prepared from TBT and BDT, except for TDT, are soluble in chloroform, 1,1,2,2-tetrachloroethane (TCE), and N,N'-dimethylpropyleneurea (DMPU) at room temperature. In particular, PPT-4 and PPT-5 are soluble in cyclohexanone (CHO) at room temperature and upon heating,

 Table 2. Solubility of PPTs<sup>a</sup>

	CHO	CHCl <sub>3</sub>	TCE	DMPU		
PPT-1	_	++	++	++		
PPT-2	+	++	++	++		
PPT-3	+	++	++	++		
PPT-4	++	++	++	++		
PPT-5	_	++	++	++		
PPT-6 – + + +						
PPT-7	_	+	++	++		
<sup><i>a</i></sup> Key: $(-)$ p	artially dissolv	ed; (+) dissolved	on heating; (-	++) dissolved		

at room temperature.

respectively. Furthermore, PPT-6 and PPT-7 are soluble in chloroform, TCE, and DMPU upon heating.

The structures of the PPTs were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and FT-IR spectroscopies. The characteristic IR peaks were observed at 1473 and 1245 cm<sup>-1</sup>, which are attributable to the -C=N- groups in the triazine and thioether units, respectively. In the <sup>1</sup>H NMR spectrum of PPT-4 (Figure 3), the signals that resonated at 7.54, 7.44, 2.78, 1.43, 1.26, and 0.84 ppm are assignable to the aromatic and butyl protons. Additionally, in the <sup>13</sup>C NMR spectrum (Figure 4), 11 carbon signals, which agree well with the expected structure, are observed. Among these signals, three quaternary carbon signals are assigned based on the DEPT-90 <sup>13</sup>C NMR experiment (Supporting Information, Figure S2).

**Thermal Properties.** The thermal stability, i.e., the glass transition temperatures ( $T_g$ ) and thermal decomposition temperatures of the high-*n* polymers, plays a critical role in the optical device fabrication. The thermal requirement mainly comes from the consideration of the servicing circumstance of the optical devices and the thermal-releasing problem caused by the miniaturization of the opto-integrated assembly.<sup>27,28</sup> The thermal stabilities of the PPTs investigated by TGA and DSC are summarized in Table 1. As shown in Figure 5 (TG curves for PPT-2, PPT-4, PPT-5, and PPT-7), PPTs show a good thermal stability, such as a 5% weight loss temperature ( $T_{5\%}$ ) above 325 °C in a nitrogen atmosphere. Figure 6 shows the DSC thermograms of the PPTs. The PPTs prepared using DMT show high  $T_gs$  in the range of 127–185 °C. On the other hand, the



Figure 3. <sup>1</sup>H NMR spectrum of PPT-4 in CDCl<sub>3</sub>.





Figure 5. TG curves of PPTs.



Figure 6. DSC curves of PPTs.

 Table 3. Optical Properties of PPTs

	$S (wt \%)^a$	$d^{b}\left(\mu\mathrm{m} ight)$	$n_{\rm TE}^{c}$	$n_{\rm TM}^{\ \ d}$	$n_{\rm av}^{\ \ e}$	$\Delta n^{f}$	$n_{\rm calc}^{\ \ g}$	$\lambda_{\mathrm{off}}^{h}$ (nm)
PPT-1	34.2	5.2	1.7535	1.7486	1.7518	0.0049	1.762	345
PPT-2	30.8	22.3	1.7223	1.7207	1.7222	0.0023	1.733	350
PPT-3	36.3	13.5	1.7391	1.7371	1.7384	0.0020	1.714	330
PPT-4	31.3	33.5	1.6999	1.6972	1.6990	0.0027	1.683	325
PPT-5	36.0	12.5	1.7533	1.7482	1.7516	0.0051	1.749	350
PPT-6	38.4	7.0	1.7724	1.7711	1.7720	0.0013	_	345
PPT-7	37.7	25.8	1.7604	1.7591	1.7600	0.0013	1.762	340

<sup>*a*</sup> Sulfur content. <sup>*b*</sup> Film thickness. <sup>*c*</sup> The in-plane refractive index. <sup>*d*</sup> The out-of-plane refractive index. <sup>*e*</sup> Average refractive index at 633 nm. <sup>*f*</sup> Birefringence. <sup>*g*</sup> Calculated refractive index at 633 nm. <sup>*h*</sup> Cut-off wavelength.



Figure 7. UV-vis spectra of PPTs.

PPTs derived from DBT exhibit lower  $T_{gs}$ , which are derived from the flexible long alkyl chains.

**Optical Properties.** The optical properties of the PPT films are summarized in Table 3. Figure 7 displays the representative UV–visible transmission spectra of the PPT films (PPT-2, PPT-4,



Figure 8. Wavelength dispersion of calculated refractive indices of PPTs.



Figure 9. Relation between calculated and experimental refractive indices of PPTs.

PPT-5, and PPT-7), in which the absorbance was normalized to a 1  $\mu$ m thickness. All films exhibit the cutoff wavelengths ( $\lambda_{off}$ ) of 325–350 nm, and the values of the optical transmittance are as high as 98% at 400 nm. The excellent colorlessness is probably due to the meta-substituted triazine and thioalkyl groups in the triazine unit, which efficiently suppresses the localization of the  $\pi$ -electrons and CT interactions in PPTs in addition to the prevention of interchain packing. These results clearly indicate that the optical transparency is not reduced by the introduction of a triazine unit into the polymer chains. Moreover, the colorlessness of the films maintained after thermal treatment up to 250 °C.

The in-plane  $(n_{\text{TE}})$  and out-of-plane  $(n_{\text{TM}})$  refractive indices of the PPT films range from 1.6999-1.7724 and 1.6972-1.7711, respectively. The facts that the values of  $n_{\rm TE}$  are slightly higher than those of  $n_{\rm TM}$  for all the PPT films reflect the preferential orientation of the main chains parallel to the film plane. The average refractive indices  $(n_{av})$  range between 1.699 and 1.772. Figure 8 shows the wavelength-dependent calculated refractive indices  $(n_{calc})$  of monomeric models for PPTs, and Figure 9 shows the relation between the calculated and refractive indices at 633 nm. As shown in Figure 9 and Table 3, the DFT calculations well reproduce the experimental trend of  $n_{av}$ , in which the refractive indices increase with increasing the sulfur content. In particular, the replacement of the  $-CH_3$  side chain with  $-C_4H_9$  lowers the refractive indices of PPT-1 and PPT-3 to those of PPT-2 and PPT-4, respectively, by ca. 0.03. The notably higher experimental  $n_{av}$  of PPT-3 and PPT-4 compared to their  $n_{\text{calc}}$  values could be due to the dense molecular packing of these polymers. Since the rotational barrier around the thioether (-S-) linkage in diphenylsulfide  $(0.44 \text{ kJ/mol})^{29}$  is lower than that of the freely rotatable ether (-O-) linkage of diphenylether (0.67 kJ/mol),<sup>30</sup> the smaller number (two) of *meta*-linked -Slinkages in the main chains of PPT-3 and PPT-4 can generate more compact aggregation structure compared with PPT-1 and PPT-2 having two para- and one meta-linked -S- linkages. Although PPT-5 possesses four -S- linkages, two of them in the thianthrene unit are not rotatable. Moreover, the molecular polarizability per unit volume, which corresponds to 'molar refraction', and the sulfur content of thianthrene (0.146, 29.6 wt %) are significantly higher than those of diphenylsulfide (0.138, 17.2 wt %). As a consequence, the PPT-6 which contains one thianthrene unit and two rotatable -S- linkages with the highest sulfur content (38.5 wt %) showed the highest  $n_{av}$  of 1.7720. These  $n_{av}$  values are much higher than those of the already reported poly(arylene sulfide)s ( $n_{\rm D} < 1.72$ ).<sup>19–21,31</sup> Furthermore, the flexible thioether linkages in the PPT chains endow a birefringence ( $\Delta n$ ) lower than 0.005. All these results indicate that the introduction of the triazine moiety together with multiple sulfur atoms is an effective way to afford PPTs with a high refractive index and high transparency in the visible region.

#### CONCLUSIONS

A new aromatic dithiol, TDT, with a high sulfur content was designed and synthesized in order to develop high-n PPTs with a high thermal stability. The PPTs were prepared by the phasetransfer-catalyzed polycondensation of 2,4-dichloro-6-alkylthio-1,3,5-triazines, DMT and DBT with aromatic dithiols, such as TBT, BDT, and TDT. The PPTs obtained from the DMT and aromatic dithiols showed good thermal stabilities, such as  $T_{gs}$ higher than 110 °C and a  $T_{5\%}$  around 350 °C. All the PPTs exhibited refractive indices higher than 1.69, in particular, the PPT-6 derived from TDT showed the highest  $n_{\rm av}$  of 1.772 at 633 nm. It can be concluded that the high refractive indices are caused by high sulfur contents and minimal alkyl chains, while keeping the solubility of polymers in organic solvents. Moreover, the optical transmittance of the PPT films with a 1  $\mu$ m thickness is around 98% at 400 nm. The synthesis of the TTPs is more facile than the other monomers reported for sulfur-containing polymers. Thus, the TTPs are promising candidate polymers for optical applications, such as optical wave guides for CMOS image sensor.

### ASSOCIATED CONTENT

**Supporting Information.** IR spectra of DBTT and TDT and NMR spectra of the polymers, This material is available free of charge via the Internet at http://pubs.acs.org.

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