

## Development of Novel High Refractive Index and Low Birefringence Triazine-based Poly(phenylene sulfide)s

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### Abstract

In the applications of advanced optoelectronic devices, the high-refractive-index (high- $n$ ) polymers (HRIPs) with a high optical transparency and low birefringence ( $\Delta n$ ) are highly required. However, the high- $n$  and low- $\Delta n$  values suffer from a trade-off relationship which remains a challenge nowadays. Herein, we report the synthesis and characterization of a novel series of high- $n$ , low- $\Delta n$ , highly transparent and colorless triazine-containing poly(phenylene sulfide)s (PPSs). Four new triazine monomers, **T1–T4**, with various pendant groups *via* different linkers ( $-O-$  and  $-NH-$ ) were designed and synthesized for developing PPSs with high- $n$  and low  $\Delta n$  values. These PPSs (**P1–P4**) were prepared by the single-phase polycondensation from **T1–T4** and commercial aromatic dithiol, 4,4'-thiobisbenzenethiol (**TBT**), respectively, showing very high- $n$  values ( $n_{av}$ : 1.6902-1.7169 at 633 nm), high optical transparency ( $T\% > 90\%$  @400 nm) and low birefringence ( $\Delta n = 0.0015-0.0042$ ). All the PPSs exhibited high  $n_{\infty}$  values (1.6340–1.6654), providing valuable information for the development of high- $n$  triazine-based PPS materials accessible for applications not only in the visible region but also in the NIR region.

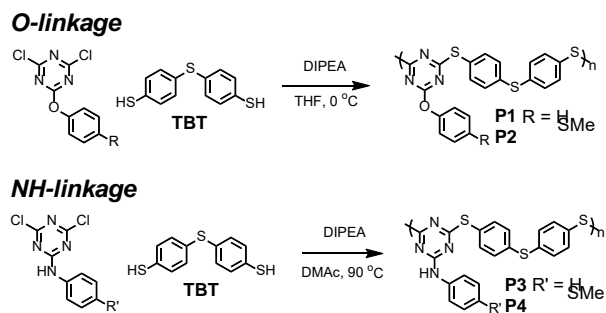
### Introduction

High-refractive-index (high- $n$ ) polymers (HRIPs) with a high optical transparency and low birefringence (low  $\Delta n$ ) are highly required in the applications of advanced optoelectronic devices due to the significant improvement in the device performance. However, the types of high- $n$  polymers with all the desired and balanced optical properties are still limited. Previously, Oishi and coworkers reported that the hyperbranched poly(guanamine)s, which were prepared from cyanuric chloride and aromatic diamines, showed high- $n$  values ( $n_D > 1.70$ ).<sup>1</sup> In our previous work, the linear poly(phenylene sulfide)s (PPSs) were synthesized by triazine derivatives and aromatic dithiols, also exhibiting high- $n$  values ( $n_{633nm}$ : 1.64-1.75).<sup>2</sup> Based on these results, the polymers with the triazine unit showed high- $n$  values and high transparency in the visible region. On the other hand, the chemoselectivity of cyanuric chloride gives the flexibility to design the various triazine monomers overcoming the trade-off relationship between high  $n$  and low  $\Delta n$  values. In this study, a novel series of high- $n$ , low- $\Delta n$ , highly transparent and colorless triazine-containing PPSs were reported, showing a high potential in the optical applications.<sup>4</sup>

## Experiments

Four different triazine monomers (**T1-T4**) were prepared from cyanuric chloride and aniline or phenol derivatives by the substitution reaction in acetone in good yields (> 90%). The triazine monomers could be divided into two series of *O*-linkage and *NH*-linkage, (**T1/T2** and **T3/T4**, respectively), and these monomers

were polymerized with aromatic dithiol, 4,4'-thiobisbenzenethiol (**TBT**), through the typical solution polycondensation, affording **P1 - P4** without problems (**Scheme 1**).



**Scheme 1.** Synthesis of triazine-based PPSs (**P1-P4**).<sup>4</sup>

## Results and Discussion

**Table 1** summarized the basic properties of PPSs. All the PPSs show an outstanding thermal stability, such as a 5% weight-loss temperature ( $T_{5\%}$ ) above 350 °C under a nitrogen atmosphere, and high  $T_g$  over 140 °C, probably due to high aromatic ring contents. It should be mentioned that **P3** and **P4** derived from *NH*-linkage-triazine monomers exhibited a higher  $T_g$  value (165 °C and 175 °C, respectively) compared with **P1** and **P2** (145 °C and 140 °C, respectively) with *O*-linkages. This might be explained by the contribution of three-dimensional H-bonding formation between *-NH-* and the lone pair of electrons on the sulfur or nitrogen atoms.

This series of PPSs showed high- $n$  values ( $n_{633\text{nm}}$ : 1.6902-1.7169), high transmittance in visible region ( $T\%_{400\text{nm}} \sim 90\%$ ) and low birefringence ( $\Delta n$ : 0.0015-0.0042) as summarized in **Table 2**. In **Figure 1(a)**, all the films show a short cut-off wavelength ( $\lambda_{\text{off}}$ ) around 350-380 nm, and a high optical transmittance of approximately 90% is observed at 400 nm for a film thickness of approximately 10-50  $\mu\text{m}$ . Such excellent transparency and colorlessness are probably due to the employment of triazine units with metasubstituted geometry, i.e., bulky substituted pendant groups and flexible thiol linkages efficiently suppress the localization of the  $\pi$ -electrons and charge-transfer interactions in PPSs and thus prevent the interchain packing.

Thus, the results clearly indicate that the combination of the triazine unit and thiol linkage brings about a promising level of high optical transparency in the visible region.

On the other hand, the in-plane ( $n_{\text{TE}}$ ) and out-of-plane ( $n_{\text{TM}}$ ) refractive indices for the PPS films at 633 nm were

**Table 1** Synthesis and characterization of **P1-P4**.<sup>4</sup>

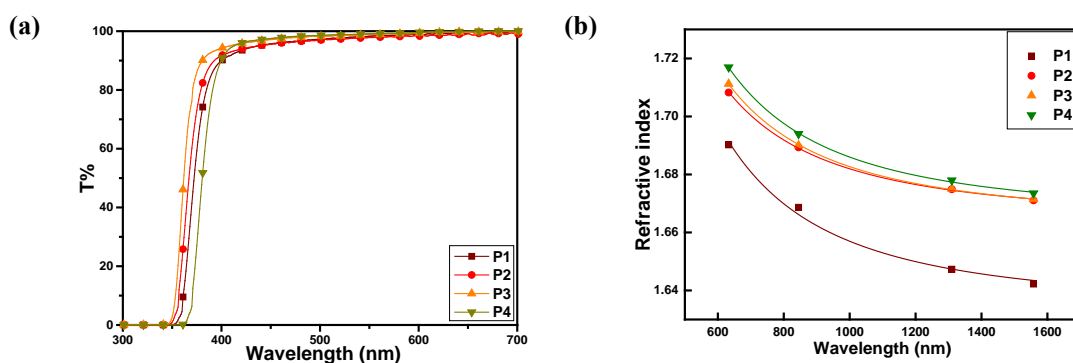
	$M_n^a$	$\bar{M}_w^a$	Yield (%)	$T_g^b$ (°C)	$T_{d5\%}^c$ (°C)
<b>P1</b>	67,000	2.06	80	145	400
<b>P2</b>	32,000	1.63	75	140	375
<b>P3</b>	12,000	1.56	70	165	350
<b>P4</b>	67,000	1.76	85	175	355

<sup>a</sup> Determined by SEC eluted with THF using polystyrene standards. <sup>b</sup> Determined by TGA at a heating rate of 10 °C/min. <sup>c</sup> Determined by DSC in the second heating scan at a heating rate of 10 °C/min.

**Table 2** Optical properties of **P1-P4**.<sup>a</sup>

	S (wt%) <sup>b</sup>	$n_{TE}$ <sup>c</sup>	$n_{TM}$ <sup>d</sup>	$n_{av}$ <sup>e</sup>	$\Delta n$ <sup>f</sup>	$\lambda_{off}$ <sup>g</sup>
<b>P1</b>	22.93	1.6916	1.6874	1.6902	0.0042	359
<b>P2</b>	27.54	1.7093	1.7062	1.7082	0.0031	352
<b>P3</b>	22.98	1.7118	1.7100	1.7112	0.0018	355
<b>P4</b>	27.60	1.7174	1.7159	1.7169	0.0015	373

<sup>a</sup> Characterized by a prism coupler method. The data were taken from ref. 4. <sup>b</sup> Sulfur content <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> Cut-off wavelength.

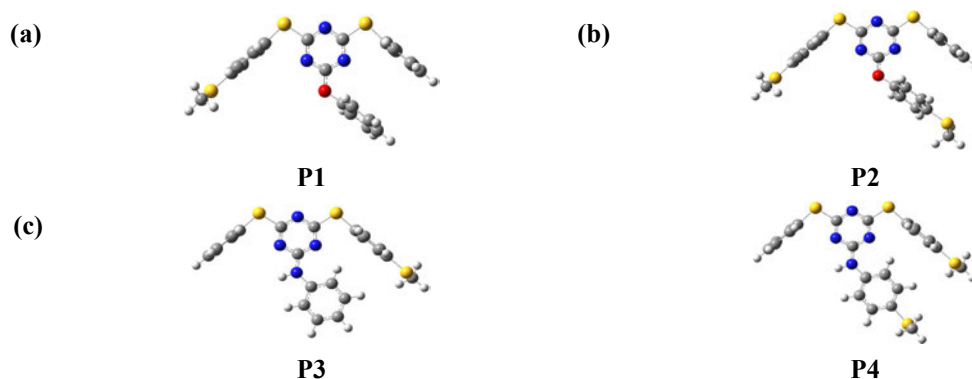


**Figure 1.** (a) UV-Vis transmittance spectra of **P1-P4** and (b) wavelength-dependent experimental refractive indices of **P1-P4** films.<sup>4</sup>

determined to lie in the range of 1.6916-1.7174 and 1.6874-1.7159, respectively (**Table 2**). The fact that  $n_{TE}$  shows slightly higher than  $n_{TM}$  for all the PPS films reflects the favored orientation of the main chains parallel to the substrates. The average refractive indices ( $n_{av}$ s) ranged between 1.6902 and 1.7169 at 633 nm. In fact, **P4** with the highest sulfur content (27.60 wt %) showed the highest  $n_{av}$  value of 1.7169, as expected. It should be mentioned that the formation of H-bonding in **P3-P4** can be proven by the broad absorption peaks observed in the IR spectra ( $3000\text{ cm}^{-1}$  -  $3400\text{ cm}^{-1}$ )<sup>3</sup>. It can be also suggested from the DSC results which showed that **P3** and **P4** with *NH*-linkages exhibited higher  $T_g$  values compared to **P1** and **P2** with *O*-linkages (**Table 1**). Such an H-bonding effect also leads to the higher  $n$  values obtained for **P3** and **P4** (1.7112 and 1.7169, respectively) compared to **P1** and **P2** (1.6902 and 1.7082, respectively), probably due to the H-bonding-induced denser packing structures.<sup>1</sup>

In **Figure 1(b)**, the experimental  $n_{av}$  values as a function of wavelength are showed and the solid lines are fitted with the simplified Cauchy formula [ $n_\lambda = n_\infty + D\lambda^{-2}$ ], where  $n_\lambda$  is the refractive index at wavelength  $\lambda$ ,  $n_\infty$  is the calculated refractive index at infinite wavelength, and  $D$  is the coefficient of dispersion. The  $n_\infty$  and  $D$  values for the PPS films determined from the experimental  $n_{av}$  values are found to range from 1.6340–1.6654 and 0.0164–0.0230, respectively. The high  $n_\infty$  values (inherent refractive indices that exclude the effect of optical absorption in the UV region) for the PPSs essentially originate from the high sulfur content. Additionally, the small  $D$  values (wavelength dispersion of the refractive indices) also originate from the UV absorption observed in the relatively shorter UV region (< 360 nm).

Moreover, the meta-linkages and flexible thioether units in the PPS chains might also lead to the



**Figure 2.** Optimized geometries of model compounds for **P1-P4**.

very small  $\Delta n$  values in the range of 0.0015-0.0042 for triazine-based PPSs which eventually show a good balance of high  $n$  and low  $\Delta n$  values. Furthermore, the intramolecular conformational effect as well as the H-bonding effect in the PPS chains might result in the lower  $\Delta n$  for **P3** and **P4** (0.0018 and 0.0015, respectively) compared with **P1** and **P2** (0.0042 and 0.0031, respectively). As shown in **Figures 2(c)** and **2(d)**, the energetically stable conformations predicted by DFT between the triazine and pendant phenyl ring for the PPSs with *NH*-linkages are coplanar, which might effectively reduce the  $\Delta n$  value by compensating the anisotropies in the polarizability of the main chain with that for the side chain.

## Conclusion

Four types of new poly(phenylene sulfide)s (PPSs) (**P1-P4**) were successfully synthesized through the single-phase polycondensation between triazine monomers with *O*- and *NH*- linkages (**T1/T2** and **T3/T4**, respectively) and dithiol monomers. **P1-P4** possessing high sulfur contents (22.93-27.60 wt%) exhibited high- $n$  values (1.6902-1.7169) at 633 nm, high transparency ( $T\% \sim 90\%$  @400 nm) and low birefringence values ( $\Delta n = 0.0015$ -0.0042). **P1-P4** also exhibited a good thermal stability ( $T_{d5\%} > 330$  °C and  $T_g$ : 140-175 °C), which can facilitate most of device manufacturing processes. All the PPSs exhibited high  $n_{\infty}$  values (1.6340–1.6654), providing valuable information for the development of high- $n$  triazine-based PPS materials for applications not only in the visible region but also in the NIR region. Especially for **P3** and **P4**, very low  $\Delta n$  values (0.0018 and 0.0015, respectively) were accomplished, probably due to the intermolecular H-bonding formation and the highly isotropic structures originating from the energetically stable coplanar conformations between the triazine and pendant phenyl rings, as expected by DFT calculation. In summary, the newly-developed PPSs are promising candidates as advanced materials for optical applications in the future.

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