Synthesis and Characterization of Alkaline-Soluble Triazine-Based Poly(phenylene sulfide)s with High Refractive Index and Low Birefringence

Mao-Chun Fu,¹ Yoshitaka Murakami,² Mitsuru Ueda,¹ Shinji Ando,³ Tomoya Higashihara ¹

¹Department of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

²JSR Corporation, 1-9-2, Higashi-Shinbashi, Minato-ku, Tokyo 105-8640, Japan

³Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan

Correspondence to: T. Higashihara (E-mail: thigashihara@yz.yamagata-u.ac.jp)

Received 27 November 2017; accepted 15 December 2017; published online 00 Month 2018 DOI: 10.1002/pola.28945

ABSTRACT: High-refractive-index (high-*n*) polymers (HRIPs) with a high optical transparency are highly needed in advanced optoelectronic devices. In this work, we report the synthesis and characterization of a series of high-*n*, transparent, totally colorless, and high-sulfur-containing poly(phenylene sulfide)s (PPSs) bearing a triazine unit. Two new triazine monomers **T1** and **T2** with hydroxyl and *tert*-butyl acetate side chains, respectively, were designed and synthesized to develop PPSs with high-*n* and high alkaline solubility. These PPSs were prepared by the single-phase polycondensation from **T1/T2** and

INTRODUCTION High-refractive-index (high-*n*) polymers (HRIPs) with a high optical transparency have been widely used in daily life. A very high-n over 1.7 or even 1.8 is frequently desired for advanced optical device applications (e.g., thermoplastic lenses, high-performance substrates for display devices, optical adhesives, encapsulates for light emitting diode (LED) and organic light emitting diode (OLED), antireflective coatings, or microlens components for CMOS or CCD image sensors).¹⁻⁷ Therefore, HRIPs with high-*n* values, high transparency and low birefringence have received considerable attention in the past few decades. The general approach to improve n values in polymers involves the introduction of substituents with high molar refraction and low molar volume according to the Lorentz-Lorenz equation.⁸ Thus, aromatic rings, heavy halogens (Cl, Br, and I, except for F), sulfur, and metallic elements have been introduced in polymers to enhance their n values.⁹ Therefore, many conventional sulfur-containing high-n polymers with high optical transparency have been reported for optical device applications, such as epoxy resins,¹⁰ polyurethanes,¹¹ polymethacrylates,¹² and poly(arylene sulfide)s.¹³

commercial aromatic dithiols such as 4,4'-thiobisbenzenethiol (**TBT**) and benzene-1,3-dithiol (**BDT**), achieving very high-*n* up to 1.7530 at 633 nm, a high optical transparency (T% > 90% @400 nm) and low birefringence ($\Delta n = 0.0014-0.0080$), and exhibiting high potential on the application of high-*n* photoresists. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

KEYWORDS: birefringence; optoelectronic; photoresist; poly(phenylene sulfide); refractive index

However, polymers have relatively low n values in the range of 1.5–1.7 at the sodium-D line (589 nm) or 633 nm.

In the past few decades, our group has developed a series of sulfur-containing aromatic polyimides (PIs) for optical applications because PIs have several advantages such as high thermal, oxidative, chemical, and mechanical stabilities.^{14–21} These PIs showed high-*n* values in the range of 1.74–1.77 and low birefringence values of less than 0.0093, but the optical transparency in approximately 400 nm of 10 μ m-thick films was lower than 80% due to the coloration originating from the inter/intra-charge transfer (CT) interactions between the electron-donating and electron-accepting moieties in the PIs. These problems limited the progress in optical applications of the aromatic PIs.

Alternatively, 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 well-known highperformance engineering thermoplastics. Such polymers have several advantages of not only high thermal, oxidative, and chemical stabilities but also high stiffness and

Additional Supporting Information may be found in the online version of this article.

© 2018 Wiley Periodicals, Inc.



1

toughness.²² Recently, poly(thioether ketones) and poly(aryl thioether)s containing fluorene, sulfone, and oxadiazole substituents have been developed for optical applications.^{13,23-26} Most of the polymers showed high thermal stability and excellent optical transparency with low birefringence. However, the n values of these polymers are in the range of 1.65-1.72 at the sodium-D line (589 nm). The relatively low refractive indices are mainly attributed to two factors. One is the low sulfur content because the n values of sulfur-containing polymers mainly depend on the sulfur content in the repeating unit.²⁷ The other is that the sterically bulky substituents such as fluorene and sulfone groups endow large free volumes among polymer chains, which lowers the n values. Therefore, a breakthrough in the tradeoff between the refractive index and optical transparency is an important topic. To enhance the n values, heteroaromatic rings containing -C=N- bonding in place of the phenyl rings can be effective because the -C-N=C- bonds possess a higher molar refraction (4.10) compared to the -C=C- bond (1.73).^{28,29} On the basis of this finding, we were interested in triazine dichloride with various alkylsulfanyl side chains as monomers and reported a highly refractive and transparent poly(phenylene sulfide)s (PPSs) containing a triazine unit, which were obtained by the polycondensation of the aromatic dithiols (4,4'-thiobisbenzenethiol (TBT), benzene-1,3-dithiol (BDT) and thianthrene-2,7dithiol (TDT)) and triazine dichloride derivatives (2,4dichloro-6-methylthio-1,3,5-triazine (DMT) and 2,4-dichloro-6-butylthio-1,3,5-triazine (DBT)). These polymers exhibited high-*n* values ($n_{av} = 1.7222 - 1.7720$ at 633 nm), excellent transmittance in the visible region (T > 80% @400 nm) and low birefringence values ($\Delta n = 0.0013 - 0.0051$).^{30,31} These results provide a new concept to develop HRIPs, prompting the development of a high-n polymer matrix for photoresists by employing sulfur-containing triazine-based poly(phenylene sulfide)s. In the application of positive-type photoresists, a dissolution inhibitor (DI) system employing diazonaphthoquinone (DNQ) has been widely used. In this system, an alkaline soluble polymer matrix is needed. After the exposure of UV light, DNQs changed structures generating carboxylic acid groups, working as dissolution promoters to increase the dissolution rate of the exposed area. However, the DNQs in the unexposed area could work as dissolution inhibitors to generate the dissolution contrast between the exposed and unexposed areas and the clear positive-tone patterns could be obtained. Therefore, the polymer matrices with a good alkaline solubility are highly desired in this area (e.g., Novolac® resin,³² poly (amic acid)s (PAAs),³³ and poly(hydroxyl amide)s (PHAs)³⁴).

Therefore, in this work, we focused on the development of alkaline-soluble high-*n* triazine-based poly(phenylene sulfide)s from triazine derivatives and aromatic dithiols. The triazine units together with sulfur atoms generally lead to a high transmittance in the visible region and high-*n* values. In addition, the chemoselectivity of each chloride toward the substitution reaction of cyanuric chloride facilitates the design of a monomer side chain,³⁵ providing the alkaline

solubility of the polymer by the introduction of a pendant phenolic and *tert*-butyl ester moieties. The obtained PPSs exhibited high-*n* values in the range of 1.6486–1.7530, low birefringence values in the range of 0.0014–0.0080, a high optical transparency over 400 nm and good solubility in 2.38 wt% tetramethylammonium hydroxide (TMAH)_(aq) after the deprotection of the *tert*-butyl ester groups in case of **PPS-3** and **PPS-4**.

EXPERIMENTAL

Materials

The materials were used without further purification unless otherwise noted. The thermal acid generator (TAG), isopropyl methanesulfonate (IMS), was prepared through a previous reference.³⁶ **TBT** and **BDT** were purified by recrystallization from toluene and a mixed solution of toluene/*n*-hexane, respectively.

Synthesis of tert-Butyl 2-((4-Hydroxyphenyl)sulfanyl)acetate

A 20 mL round flask was charged with 4-hydroxybenzenethiol (0.505 g, 4.00 mmol), *tert*-butyl bromoacetate (0.835 g, 4.28 mmol), potassium carbonate (0.354 g, 2.56 mmol), and *N*,*N*-dimethylformamide (DMF) (5 mL). The solution was stirred at room temperature for 24 h, extracted with ethyl acetate and then washed with deionized water. The organic fractions were combined, and the solvent was dried over MgSO₄. Then, the solvent was removed under reduced pressure. Further purification by flash column chromatography (silica gel, *n*-hexane/ ethyl acetate, 5/1, v/v) yielded 0.865 g (90%) of *tert*-butyl 2-((4-hydroxyphenyl)sulfanyl)acetate as a white solid. ¹H NMR (400 MHz, CDCl₃-d₁, δ , 25 °C): 7.40 (d, *J* = 9.20 Hz, 2H; ArH), 6.82 (d, *J* = 9.20 Hz, 2H; ArH), 4.48 (s, 1H; ArOH), 3.43 (s, 2H), 1.38 (s, 9H).

General Synthetic Procedures of the Triazine Monomer

Cyanuric chloride (30 mmol) was mixed with 100 mL of THF at different temperatures. The resulting solution was dropwise added to a solution of aromatic thiol or phenol derivatives (20 mmol) and triethylamine (TEA) (20 mmol) in 25 mL of tetrahydrofuran (THF). After stirring at -40 °C overnight, the reaction mixture was washed once with saturated NH₄Cl_(aq) and 3 times with NaCl_(aq). The organic fractions were combined and the solvent was dried over MgSO₄, then the solvent was further purified by flash column chromatography, yielding a white solid.

Synthesis of 2,6-Dichloro-4-(4-hydroxyphenyl)sulfanyl-1,3,5-triazine (T1)

The general synthetic procedures for the triazine monomer were followed using 4-mercaptophenol as the aromatic thiol derivative. The reaction was carried out at -40 °C. The purification was performed by flash column chromatography (silica gel, *n*-hexane/ethyl acetate, 5/1, v/v), yielding a white solid (4.44 g, 80%). ¹H NMR (400 MHz, CDCl₃- d_1 , δ , 25 °C): 7.41 (d, *J* = 8.00 Hz, 2H; ArH), 6.91 (d, *J* = 8.00 Hz, 2H; ArH), 5.43 (s, 1H; ArOH). ¹³C NMR (100 MHz, CDCl₃- d_1 , δ , 25 °C): 187.18 (1 carbon), 170.60 (2 carbons),

ARTICLE

157.94 (1 carbon), 137.20 (1 carbon), 116.97 (2 carbons), 116.06 (2 carbons). Anal calcd. for $C_9H_5Cl_2N_3OS$: C, 39.44; H, 1.84; N, 15.33; S, 11.70. Found: C, 40.41; H, 1.95; N, 15.70; S, 11.75.

Synthesis of 4-[(4-(*tert*-Butoxycarbonyl)methylsulfanyl) phenoxyl]-2,6-dichloro-1,3,5-triazine (T2)

The general synthetic procedures for the triazine monomer were followed with *tert*-butyl 2-((4-hydroxyphenyl)sulfanyl)acetate as the aromatic thiol derivative. The reaction was carried out at 0 °C. The purification was performed by flash column chromatography (silica gel, *n*-hexane/ethyl acetate, 5/1, v/v), yielding a white solid (5.44 g, 70%). ¹H NMR (400 MHz, CDCl₃- d_1 , δ , 25 °C): 7.49 (d, J = 8.40 Hz, 2H; ArH), 7.11 (d, J = 8.40 Hz, 2H; ArH), 3.57 (s, 2H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃- d_1 , δ , 25 °C): 173.22 (1 carbon), 171.12 (2 carbons), 168.63 (1 carbon), 149.88 (1 carbon), 134.27 (1 carbon), 131.55 (2 carbons), 121.68 (2 carbons). 82.33 (1 carbon), 37.98 (1 carbon), 27.99 (3 carbons). Anal calcd. for C₁₅H₁₅Cl₂N₃O₃S: C, 46.40; H, 3.89; N, 10.82; S, 8.26. Found: C, 46.46; H, 3.91; N, 10.70; S, 7.71.

General Synthetic Procedures for Poly(phenylene Sulfide)s

The triazine monomer (1 mmol), aromatic dithiols (1 mmol), and 2 mL of THF were placed in a 10 mL round flask. TEA (2.2 mmol) was dropwise added to the solution at 0 °C with vigorous stirring. After stirring at room temperature overnight, the solution was poured into methanol. Then, the precipitate was filtered and dried under vacuum at 70 °C, yielding a white polymer.

PPS-1 (T1/TBT)

The general synthetic procedures for the poly(phenylene sulfide)s were followed, yielding **PPS-1** (0.36 g, 80%) as a white precipitate. ¹H NMR (400 MHz, THF- d_8 , δ , 25 °C): 8.81 (s, 1H; ArOH), 7.33 (d, J = 8.40 Hz, 4H; ArH), 7.24 (d, J = 8.40 Hz, 4H; ArH), 7.16 (d, J = 8.40 Hz, 2H; ArH), 6.69 (d, J = 8.40 Hz, 2H; ArH). ¹³C NMR (100 MHz, THF- d_8 , δ , 25 °C): 181.54 (2 carbon), 179.67 (1 carbon), 159.43 (1 carbon), 137.20 (1 carbon), 136.90 (1 carbon), 135.74 (1 carbon), 131.21 (4 carbons), 126.56 (4 carbons), 116.20 (2 carbon), 115.71 (2 carbons). Anal calcd. for C₂₁H₁₃N₃OS₄: C, 55.85; H, 2.90; N, 9.31; S, 28.40. Found: C, 55.36; H, 3.02; N, 8.46; S, 28.34.

PPS-2 (T1/BDT)

The general synthetic procedures for poly(phenylene sulfide)s were followed, yielding **PPS-2** (0.24 g, 70%) as a white precipitate. ¹H NMR (400 MHz, THF- d_8 , δ , 25 °C): 10.00 (s, 1H; ArOH), 7.40 (d, J = 8.00 Hz, 2H; ArH), 7.35 (s, 1H; ArH), 7.10 (t, J = 8.40 Hz, 1H; ArH), 6.83 (d, J = 8.40 Hz, 2H; ArH), 6.65 (d, J = 8.40 Hz, 2H; ArH). ¹³C NMR (100 MHz, THF- d_8 , δ , 25 °C): 181.54 (2 carbons), 179.71 (1 carbon), 159.15 (1 carbon), 140.77 (1 carbon), 136.73 (2 carbons), 136.14 (1 carbon), 129.67 (1 carbon), 127.88 (2 carbons), 116.22 (2 carbons), 115.41 (2 carbons). Anal calcd. for



 $C_{15}H_{11}N_3OS_3{:}$ C, 52.46; H, 2.64; N, 12.24; S, 28.01. Found: C, 53.28; H, 3.04; N, 11.33; S, 26.17.

PPS-3 (T2/TBT)

The general synthetic procedures for poly(phenylene sulfide)s were followed, yielding **PPS-3** (0.47 g, 85%) as a white fiber. ¹H NMR (400 MHz, $CDCl_3-d_1$, δ , 25 °C): 7.31 (d, J = 8.00 Hz, 4H; ArH), 7.28 (d, J = 8.40 Hz, 2H; ArH), 7.24 (d, J = 8.00 Hz, 4H; ArH), 6.91 (d, J = 8.40 Hz, 2H; ArH), 3.54 (s, 2H), 1.37 (s, 9H). ¹³C NMR (100 MHz, $CDCl_3-d_1$, δ , 25 °C): 183.40 (2 carbons), 168.72 (1 carbon), 168.06 (1 carbon), 150.47 (1 carbon), 137.49 (2 carbons), 135.79 (2 carbons), 132.76 (1 carbons), 131.34 (4 carbons), 130.66 (4 carbons), 126.08 (2 carbons), 122.04 (2 carbons), 82.11 (1 carbon), 38.20 (1 carbon), 28.02 (3 carbons). Anal calcd. for $C_{27}H_{23}N_3O_3S_4$: C, 57.32; H, 4.10; N, 7.43; S, 22.67. Found: C, 57.21; H, 3.87; N, 7.34; S, 22.38.

PPS-4 (T2/BDT)

The general synthetic procedures for poly(phenylene sulfide)s were followed, yielding **PPS-4** (0.38 g, 84%) as a white fiber. ¹H NMR (400 MHz, $CDCl_3-d_1$, δ , 25 °C): 7.34 (d, J = 8.00 Hz, 2H; ArH), 7.33 (s, 1H; ArH), 7.25 (d, J = 8.40 Hz, 2H; ArH), 7.14 (t, J = 8.00 Hz, 1H; ArH), 6.84 (d, J = 8.40 Hz, 2H; ArH) 3.53 (s, 2H), 1.40 (s, 9H). ¹³C NMR (100 MHz, $CDCl_3-d_1$, δ , 25 °C): 183.26 (2 carbons), 168.70 (1 carbon), 168.08 (1 carbon), 150.38 (1 carbon), 141.40 (2 carbons), 136.59 (1 carbon), 132.73 (1 carbon), 131.08 (2 carbons), 129.81 (2 carbons), 127.71 (1 carbon), 122.00 (2 carbons), 82.16 (1 carbon), 38.12 (1 carbon), 28.02 (3 carbons). Anal calcd. for $C_{21}H_{19}N_3O_3S_3$: C, 55.12; H, 4.19; N, 9.18; S, 21.02. Found: C, 54.77; H, 3.95; N, 9.03; S, 21.21.

Film Preparation

All of the polymer films were prepared by solution casting in DMAc, followed by heating on a hot plate from 25 to 100 °C under a nitrogen atmosphere. Films with a thickness of 20–60 μ m were obtained.

Solubility Tests

The solubility tests using organic solvents are carried out in the bulk samples at the concentration of 10 mg/mL. The alkaline solubility is checked by the film samples that were prepared from DMAc solutions through spin coating on silicon wafers. For **PPS-3** and **PPS-4**, 10 wt% of the thermal acid generator (TAG) was first blended with PPSs after spin coating on the silicon substrates. The resulting films were heated on a hot plate at 150 °C for 2 min to catalyze the deprotection reactions of *t*-butyl ester groups.

Measurements

The ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer at resonant frequencies of 400 MHz for ¹H and 100 MHz for ¹³C nuclei using CDCl₃ and THF- d_8 as the solvents and tetramethylsilane as the reference. FTIR spectra were measured by a Nicolet iS5 Fourier transform spectrophotometer. M_n and M_w values were measured by SEC on a JASCO GULLIVER 1500 system equipped with two polystyrene gel columns (Plegel 5 μ m MIXED-C) that were

3



SCHEME 1 Synthesis of the triazine monomers T1 and T2.

eluted with chloroform at a flow rate of 1.0 mL/min and calibrated by polystyrene standard samples. Thermogravimetry (TG) measurements were performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analysis system at a heating rate of 10 °C/min. DSC analysis was conducted on a DSC 6200 at a heating rate of 10 °C/min under nitrogen. The inplane ($n_{\rm TE}$) and out-of-plane ($n_{\rm TM}$) refractive indices of PPS films were measured 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 inplane/out-of-plane birefringences (Δn) were estimated as the difference between $n_{\rm TE}$ and $n_{\rm TM}$, and the average refractive indices were calculated according to the following equation: $n_{\rm av} = [(2n_{\rm TE}^2 + n_{\rm TM}^2)/3]^{1/2}$.

The refractive indices of PPSs synthesized in this study were calculated based on the Lorentz–Lorenz theory using the corresponding model compounds (see Fig. S11 in supporting information) as reported previously.⁹ One-electron transition energies and the corresponding oscillator strengths of the PI models were also calculated using the time-dependent density functional theory (TD-DFT) to predict the optical absorption in the UV-vis region.⁸ The 6–311G(d) basis set was used for geometry optimizations under no constraints, and the 6–311++G(d,p) was used for calculating linear polarizabilities, transition energies, and oscillator strengths. The three-parameter Becke-style hybrid functional (B3LYP) was adopted as a function and all the calculations were

$CI \prod_{N \neq CI} TEA \qquad TEA \qquad TEA \qquad N \neq N \\ S \downarrow OH T1 \qquad THF, 0 °C, overnight \qquad S \downarrow OH PPS-1,2 \\ CI \prod_{N \neq CI} TEA \qquad S \downarrow OH PPS-1,2 \\ S \downarrow OH T1 \qquad S \downarrow OH PPS-1,2 \\ THF, 0 °C, overnight \qquad S \downarrow OH PPS-1,2 \\ THF, 0 °C, overnight \qquad S \downarrow OH PPS-1,2 \\ S \downarrow OH PPS-1,2 \qquad S \downarrow OH PPS-1,2 \\ S \downarrow OH PPS-1,3 \qquad PPS-2,4 \\ S \downarrow OH PS-1,3 \qquad PPS-2,4 \qquad PP$

SCHEME 2 Synthesis of triazine-containing PPSs.



	<i>M</i> _n ^a	D^{a}	Yield (%)	Т _g ^b (°С)	<i>T</i> d5% ^c (°C)
PPS-1	30,000	2.55	80	180	265
PPS-2	11,000	2.43	70	185	255
PPS-3	21,000	1.80	85	150	220
PPS-4	20,800	1.88	84	140	210

^a Determined by SEC eluted with chloroform using polystyrene standards. ^b Determined by TGA at a heating rate of 10 °C/min.

^c Determined by DSC in the first heating scan at a heating rate of 10 °C/min.

Determined by DSC in the first heating scan at a heating rate of 10°C/min.

performed using the software package of Gaussian-03 (Rev. C02 and D01). A typical packing coefficient (K_p) of 0.60 was used for evaluating the intrinsic molecular volumes of models to predict the refractive indices.⁹

RESULTS AND DISCUSSION

Synthesis of the Triazine Monomer

In the synthesis of the triazine monomer, the chemoselectivity of each chloride toward the substitution reaction of cyanuric chloride generally facilitates the design of a monomer side chain.³⁵ In the synthesis of **T1**, due to the strong electron-donating effect of a hydroxyl group on the para position, the nucleophilic property of thiol group increased. This situation caused a multisubstitution reaction to occur; therefore, an optimization of the reaction conditions (dropwise-addition method, low concentration, and temperature $(-40 \ ^{\circ}C)$) was required to obtain the monosubstituted target compound **T1**. However, this is not the case for **T2** due to the lower nucleophilicity of the phenol group compared with the thiol group. Therefore, the reaction was carried out at 0 $^{\circ}C$ and the mono-substituted target compound **T2** could be obtained. After optimizing the conditions, both monomers



FIGURE 1 FTIR spectra of PPSs.



Polymer

JOURNAL OF POLYMER SCIENCE Chemistry

FIGURE 2 ¹HNMR spectra of PPS-1 and PPS-4.









Synthesis and Characterization of Triazine-Containing **PPSs**

The synthetic route for the triazine-containing PPSs is shown in Scheme 2. All the triazine-containing PPSs were prepared by the single-phase polycondensation of T1 and T2 with aromatic dithiols TBT and BDT. A single-phase polycondensation was carried out in THF in the presence of TEA as an HCl scavenger at 0 °C to room temperature. The polycondensation proceeded smoothly to give PPSs with M_n values from 11,000 to 30,000. The results are summarized in Table 1. The structures of the PPSs were characterized by ¹H, ¹³C NMR, and FTIR spectroscopies. The characteristic IR absorption peaks were observed at 1473 and 1245 cm⁻¹, which are attributable to the -C=N- groups in the triazine and thioether units, respectively. For PPS-1 and 2, the broad Ph-OH peaks were observed at $3500-3000 \text{ cm}^{-1}$ (Fig. 1). In the ¹H NMR spectrum of **PPS-1** (Fig. 2), the signals that resonated at 7.33, 7.24, 7.16, and 6.69 ppm are assigned to the aromatic and Ph-OH protons (8.81 ppm). In the ¹H NMR spectrum of PPS-4 (Fig. 2), the signals that resonated at 3.51 and 1.38 ppm are assigned to the methylene and tertbutyl protons, respectively. Other ¹H and ¹³C NMR spectra of PPSs are shown in supporting information (Figs. S5-S10).

TABLE 2 Optical Properties of PPSs

	<i>S</i> (wt%) ^a	n _{TE} b	n _™ °	n _{av} d	$\Delta n^{\rm e}$	λ_{off}^{f}
PPS-1	28.27	1.7550	1.7480	1.7530	0.0080	363
PPS-2	27.84	1.7430	1.7390	1.7420	0.0040	357
PPS-3	22.59	1.6784	1.6741	1.6769	0.0043	350
PPS-4	20.93	1.6490	1.6476	1.6486	0.0014	329

^a Sulfur content.

^b In-plane refractive index.

^c Out-of-plane refractive index.

^d Average refractive index at 633 nm.

^e Birefringence ($=n_{TE}-n_{TM}$).

^f Cut-off wavelength.





FIGURE 5 UV-vis spectra of PPSs.



FIGURE 6 Calculated refractive indices of PPSs.

Thermal Properties

The thermal stability, that is, the glass transition temperatures (T_g) and thermal decomposition temperatures of the high-n polymers, plays a critical role in optical device fabrication. The thermal requirement mainly comes from a consideration of the servicing circumstance of the optical devices and the thermal-releasing problem caused by the miniaturization of the opto-integrated assembly. The thermal stabilities of the PPSs investigated by TGA and DSC are summarized in Table 1. In Figure 3, PPSs show a relatively good thermal stability, such as a 5% weight loss temperature $(T_{5\%})$ above 250 °C for both **PPS-1** and **PPS-2** in a nitrogen atmosphere. For PPS-3 and PPS-4, due to the tbutyl ester side-chain as the carboxyl acid protection group, the first degradation stages were observed at approximately 200 °C, and the first-stage weight losses were 9% and 14%, respectively, which were in a good agreement with the weight percentage of departing t-butyl ester groups in **PPS-3** and **PPS-4**. Therefore, these first-stage weight losses can be assigned as the elimination of *t*-butyl ester groups. Figure 4 shows the DSC thermograms of the PPSs. The PPSs derived from T1 (PPS-1 and PPS-2) show high T_{σ} over 180 °C. However, the PPSs prepared from T2 (PPS-3 and **PPS-4**) exhibit lower T_{g} , which are derived from the flexible t-butyl ester groups.

TABLE	3	Solubility	∕ of	PPSs
-------	---	------------	------	------

Optical Properties

The optical properties of the PPS films are summarized in Table 2. Figure 5 displays representative UV-visible transmission spectra of the PPS films. All films exhibit short cutoff wavelengths (λ_{off}) of 320–370 nm, and the optical transmittance are as high as 90% at 400 nm. The high optical transparency is consistent with the calculated absorption spectra as shown in Figure S12, in which all PPSs show no absorption peaks in the visible region (400–800 nm). The excellent colorlessness is probably due to the meta-substituted triazine and thio groups in the triazine unit, which efficiently suppresses the localization of the π -electrons and CT interactions in PPSs as well as 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.

The in-plane ($n_{\rm TE}$) and out-of-plane ($n_{\rm TM}$) refractive indices of the PPS films show the range of 1.649–1.755 and 1.648– 1.748, respectively. The fact that the values of $n_{\rm TE}$ are slightly higher than those of $n_{\rm TM}$ for all the PPS films might reflect the preferential orientation of the main chains parallel to the film plane. The average refractive indices ($n_{\rm av}$) range between 1.649 and 1.753. Therefore, **PPS-1** with the highest sulfur content (28.3 wt%) showed the highest $n_{\rm av}$ of 1.753. This trend is also consistent with the calculated refractive indices by TD-DFT as shown in Figure 6. The lower $n_{\rm av}$ of

	THF	CHCl₃	TCE	DMAc	DMSO	PGME ^c	PGMEA ^d	MMP ^e	EDM ^f	2.38 wt% TMAH(aq)
PPS-1	++			++	+	-	_	-	-	-
PPS-2	++			++	++	++	+	++	++	_
PPS-3	++	++	++	++	++	++	++	++	++	$+^{b}$
PPS-4	++	++	++	++	++	++	++	++	++	$++^{b}$

^a Key: (-) partially dissolved, (+) dissolved after heating, (++) dissolved at room temperature, Conc. 10 mg / 1 mL.

^b Measured after deprotection by TAG.

^c Propylene glycol monomethyl ether.

^d Propylene glycol monomethyl ether acetate.

^e Methyl 3-methoxypropionate.
^f Ethylene glycol dimethyl ether.

Etr

PPS-3 compared with PPS-1 is explainable by the lower sulfur content (22.6 wt%), and the substitution of tert-butyl ester moieties lower the refractive indices of PPS-2 and **PPS-4**. The calculated Abbe numbers for **PPS-2**-4 are 15.7, 17.7, 18.5, 21.2, respectively, which are relatively high, indicating lower wavelength dispersion of refractive indices, as high-n polymers. Furthermore, the flexible thioether and meta-linkages in the PPS chains provide very small birefringence (Δn) values in the range of 0.0014–0.0080. Moreover, the PPSs prepared from BDT (PPS-2 and PPS-4) exhibited lower Δn compared with those of **PPS-1** and **PPS-3** derived from TBT due to the meta-linkage of BDT allowing more three-dimensional and isotropic structures of the main chains. All these results indicate that the introduction of the triazine moiety together with multiple sulfur atoms is an effective way to provide PPSs with high-n values, low birefringence, and high transparency in the visible region.

Solubility Tests

The solubilities of PPSs are summarized in Table 3. PPS-2 and PPS-4 with BDT units showed a higher solubility in green solvents or alkaline solution compared to PPS-1 and PPS-3 with TBT units. The meta-linkage structure in the BDT may provide the main-chain flexibility and thereby increasing the solubility. However, PPS-3 and PPS-4 showed better solubility in common solvents and therefore preferred processability due to the ester protection groups. To achieve a highly photosensitive system, a polymer matrix with high alkaline solubility is needed. The hydroxyl groups were introduced in the side chain of PPS-1 and PPS-2 to increase the alkaline solubility; however, PPS-1 and PPS-2 were insoluble in 2.38 wt% TMAH_(aq), even after heating, which is probably due to the highly hydrophobic main-chain structure. In contrast, the blended films of PPS-3 and PPS-4 with 10 wt% of the thermal base generator (TAG) after deprotection at 150 °C for 2 min could be dissolved after heating and at room temperature, respectively. The TAG could catalyze the deprotection reaction from the ester to the carboxyl acid group, resulting in a balanced solubility between common, green, and alkaline solutions.

CONCLUSIONS

Two new triazine monomers (**T1** and **T2**) and corresponding poly(phenylene sulfide)s (PPSs) have been successfully synthesized. PPSs with high sulfur contents and the combination of triazine groups exhibited high-*n* values (1.6448–1.7530), high transparency (T% > 90% @400 nm), and low birefringence ($\Delta n = 0.0014-0.0080$). PPSs exhibited relatively good thermal stabilities ($T_{d5\%}$: 210–265 °C and T_g : 140–180 °C), which could facilitate opto-electrical device manufacturing processes. For **PPS-3** and **PPS-4**, after deprotection by TAG, the blended polymer films were soluble in 2.38 wt% TMA-H_(aq). All results produced valuable information to develop high-*n* and alkaline-soluble photosensitive triazine-based poly(phenylene sulfide) materials. The investigation of photolithographic applications is ongoing.

ACKNOWLEDGMENTS

This work was mainly supported by JSR Corporation. M. C., Fu thanks Innovative Flex Course for Frontier Organic Material Systems (iFront) at Yamagata University for financial support.

REFERENCES AND NOTES

1 H. Dislich, Angew. Chem. Int. Ed. Engl. 1979, 18, 49.

2 T. Matsuda, Y. Funae, M. Yoshida, T. Yamamoto, T. Takaya, *J. Appl. Polym. Sci.* **2000**, *76*, 50.

3 A. Nebioglu, J. A. Leon, I. V. Khudyakov, *Ind. Eng. Chem. Res.* **2008**, *47*, 2155.

4 J-g. Liu, M. Ueda, J. Mater. Chem. 2009, 19, 8907.

5 J.-P. Kim, W.-Y. Lee, J.-W. Kang, S.-K. Kwon, J.-J. Kim, J.-S. Lee, *Macromolecules* **2001**, *34*, 7817.

6 K.-S. Lee, J.-S. Lee, Chem. Mater. 2006, 18, 4519.

7 T. Higashihara, M. Ueda, *Macromolecules* 2015, 48, 1915.

8 S. Ando, T. Fujigaya, M. Ueda, Jpn. J. Appl. Phys. 2 2002, 41, L105.

9 J-g. Liu, Y. Nakamura, T. Ogura, Y. Shibasaki, S. Ando, M. Ueda, *Chem. Mater.* 2008, *20*, 273.

10 C. Lü, Z. Cui, Y. Wang, B. Yang, J. Shen, *J. Appl. Polym. Sci.* **2003**, *89*, 2426.

11 C. Lü, Z. Cui, Y. Wang, Z. Li, C. Guan, B. Yang, J. Shen, *J. Mater. Chem.* **2003**, *13*, 526.

12 L.-H. Lee, W.-C. Chen, Chem. Mater. 2001, 13, 1137.

13 S. Seesukphronrarak, S. Kawasaki, K. Kobori, T. Takata, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3073.

14 J-g. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, M. Ueda, *Polym. J.* **2007**, *39*, 543.

15 J-g. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, M. Ueda, *Macromolecules* 2007, *40*, 4614.

16 C. A. Terraza, J.-G. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* 2008, *46*, 1510.

17 N.-H. You, Y. Suzuki, D. Yorifuji, S. Ando, M. Ueda, *Macro-molecules* 2008, *41*, 6361.

18 N.-H. You, Y. Suzuki, T. Higashihara, S. Ando, M. Ueda, *Polymer* **2009**, *50*, 789.

19 N.-H. You, N. Fukuzaki, Y. Suzuki, Y. Nakamura, T. Higashihara, S. Ando, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 4428.

20 N.-H. You, Y. Nakamura, Y. Suzuki, T. Higashihara, S. Ando, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* 2009, 47, 4886.

21 N.-H. You, T. Higashihara, S. Ando, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 656.

22 P. M. Hergenrother, B. J. Jensen, S. J. Havens, *Polymer* 1988, *29*, 358.

23 S. Matsumura, N. Kihara, T. Takata, *J. Appl. Polym. Sci.* 2004, *92*, 1869.

24 S. Kawasaki, M. Yamada, K. Kobori, F. Jin, Y. Kondo, H. Hayashi, Y. Suzuki, T. Takata, *Macromolecules* 2007, *40*, 5284.

25 K. Nakabayashi, T. Imai, M.-C. Fu, S. Ando, T. Higashihara, M. Ueda, *J. Mater. Chem. C* **2015**, *3*, 7081.

26 K. Nakabayashi, T. Imai, M.-C. Fu, S. Ando, T. Higashihara, M. Ueda, *Macromolecules* 2016, *49*, 5849.

27 C. Paquet, P. W. Cyr, E. Kumacheva, I. Manners, *Chem. Mater.* 2004, *16*, 5205.

28 Chemical Handbook Basic II, 1979, 520

29 N. Nishimura, Y. Shibasaki, M. Ozawa, Y. Oishi, J. Photopolym. Sci. Technol. 2012, 25, 355.



30 N.-H. You, T. Higashihara, Y. Oishi, S. Ando, M. Ueda, *Macromolecules* **2010**, *43*, 4613.

31 Y. Nakagawa, Y. Suzuki, T. Higashihara, S. Ando, M. Ueda, *Macromolecules* **2011**, *44*, 9180.

32 C. G. Willson, In *Introduction to Microlithography*; L. F., Thompson, C. G., Willson, M. J., Bowden, Eds.; ACS: Washington, DC, **1983**; p 87.

33 Y. Inoue, Y. Saito, T. Higashihara, M. Ueda, *J. Mater. Chem. C* **2013**, *1*, 2553.

34 K. Ebara, Y. Shibasaki, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 3399.

35 P. Gamez, J. Reedijk, Eur. J. Inorg. Chem. 2006, 2006, 29.

36 P. N. Culshaw, J. C. Walton, *Tetrahedron Lett.* **1990**, *31*, 2457.