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Synthesis of colorless and highly refractive Poly(phenylene thioether ether) derived from 2,7-(4,4′-diphenol)thiothianthrene

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HIGHLIGHTS

- Colorless, transparent, and highly refractive poly(phenylene thioether ether)s was prepared by polycondensation reaction.
- The polymer films exhibited a refractive index of in the range of 1.7188–1.7204 with low birefringence values.
- The poly(phenylene thioether ether)s showed a high thermal stability (> 360 °C).

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ABSTRACT

Totally colorless, transparent, and highly refractive poly(phenylene thioether ether)s (PPTEs) containing thianthrene-2,7-disulfanyl moiety were developed in this study. A new 4,4′-diol aromatic compound, 2,7-(4,4′-diphenol)thiothianthrene (DPTT), with a high sulfur content was designed and synthesized to develop polymers with high refractive indices and high thermal stabilities. The PPTEs were prepared by polycondensation of DPTT with organic dihalogen compounds, such as 2,6-difluorobenzonitrile (DFBN) and 4,6-dichloro-2-(methylthio)pyrimidine (DCMP). The obtained polymers showed good thermal stabilities such as relatively high glass transition temperatures (T_gs) in the range of 153–176 °C and 5% weight loss temperatures ($T_{5\%}$) over 344 °C. The cut-off wavelengths (λ_0) of the PPTE films are shorter than 343 nm, and they have a transmittance higher than 93% at 550 nm. The combination of the pyrimidine and high sulfur-containing thianthrene derivatives provides the PPTEs with a high refractive index of 1.7204 and a small birefringence of 0.0106 at 637 nm.

1. Introduction

Much attention has been given to high refractive index (high-*n*) polymers with low birefringence for optoelectronic applications such as camera lenses, mid-IR imaging devices, and components for organic light-emitting diode devices [1–6]. Many conventional polymers with high refractive indices and a high optical transparency have been developed for optical applications such as polymethacrylates (PMMAs) [7,8], epoxy (EP) resins [9], polyimides (PIs) [10,11], polyurethanes (PUs) [12], and poly(arylene sulfide)s (PASs) [13]. However, most of the polymers have a relatively low refractive index in the range of 1.5–1.7 at 633 nm. Recently, Ueda and coworkers developed highly refractive polyimides containing a sulfur atom for optical applications [14–16]. Most of them not only have high refractive indices over 1.7 but also have low birefringence values. Although the PIs have high-*n* values, the PI films have a deep coloration originating from the inter/intra charge transfer complex (CTC) [17,18]. Therefore, the balance between optical transparency and the refractive index is an important factor for optical applications. The general method to enhance the refractive indices of polymers is to incorporate substituents with a high molar refraction such as aromatic rings, heavy halogen (Cl, Br, and I) atoms, and a sulfur atom according to the Lorentz-Lorenz equation [19–22]. Other candidates to improve the refractive index are heteroaromatic rings and a benzonitrile group containing −C═N– and −C≡N bonds. This is because −C═N– and −C≡N bonds possess a high molar refraction compared to a C═C bond [23]. Therefore, the introduction of pyrimidine and benzonitrile units into a polymer backbone is an effective way to improve the refractive indices while maintaining a high optical transparency.

Quite recently, high refractive polymers with thianthrene unit have been developed for optoelectronic applications. Although the polymers showed high refractive indices in the range of 1.7–1.8 because of high

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sulfur contents and rigid structure, the polymers have relatively low solubility in common organic solvents, low transparency, and tedious synthetic steps [2,24–26].

In this work, we report the synthesis and characterization of new solution-processed polymers containing pyrimidine, benzonitrile units, and sulfur to achieve good optical properties such as a high refractive index and optical transparency and a low birefringence in the visible region. All of the poly(phenylene thioether ether)s (PPTEs) such as DPTT–DFBN and DPTT–DCMP have high refractive indices in the range of 1.7188–1.7204 with low birefringence values in the range of 0.0114–0.0106 and a high thermal stability (> 360 °C) and optical transparency. The effects of the structure on the optical and thermal properties of the polymers are discussed in detail.

2. Experiments

2.1. Materials

4-Fluoro-benzenthiol, 4-hdroxybenzenethiol, 2,6-difluorobenzonitrile, and 4,6-dichloro-2-(methylthio)pyrimidine, 2,6-difluoro-benzoic acid, and 2,6-difluoro-pyridine were purchased from Tokyo Chemical Industry Co. Ltd. N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were purified by a two-column solid-state purification system (Glass contour system, Joerg Meyer, Irvine, CA). All commercial reagents and organic solvents were used as received without further purification.

2.2. 2,7-(4,4′-diphenol)thiothianthrene (DPTT)

2,7-Difluorothianthrene was prepared as previously described [31]. 4-Hydroxybenzenethiol (2.20 g, 17.44 mmol) was added to a solution of 2,7-difluorothianthrene (2.00 g, 7.93 mmol) and K_2CO_3 (2.89 g, 20.91 mmol) in dehydrated DMF under a nitrogen atmosphere. The resulting solution was refluxed at 150 °C for a day. The excess K_2CO_3 was filtered. The filtrate was removed using a rotary evaporator. After the removal of the solvents, the product was separated by column chromatography using silica gel followed by recrystallization with ethyl acetate and hexane. The pale yellow powder was dried at 80 °C under a vacuum. Yield: 2.06 g (56%); pale yellow solid; mp 161–162 °C. ^{1}H NMR (600 MHz, DMSO-d_6) MS (–ESI): calculated for $C_{24}H_{16}O_2S_4$–H+: 463.63; found: 463.10. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.99 (s, 2H), δ = 7.44 (s, 1H), δ = 7.42 (s,1H) δ = 7.36–7.33 (m, 4H) δ = 7.15 (d, J = 2H) δ = 7.02–7.00 (dd, 2H) δ = 6.87–6.85 (m, 4H).

2.3. Synthesis of DPTT–DFBN

2,6-difluorobenzonitrile (0.15 g, 1.08 mmol) was added to a solution of **DPTT** (0.50 g, 1.08 mmol) K_2CO_3 (0.59 g, 4.30 mmol) in dehydrated NMP under a nitrogen atmosphere. The reaction solution was refluxed at 130 °C for a day. The resulting solution was poured into water/methanol to precipitate the product. The obtained polymer was collected by filtration and washed with methanol. The final product was dried at 150 °C under a vacuum. Yield: 0.501 g (82.4%). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) estimated by gel permeation chromatography (GPC) were 11.55×10^3 and 26.34×10^3, respectively, and the dispersity index (PDI = M_w/M_n) was 2.28.

2.4. Synthesis of DPTT–DCMP

4,6-dichloro-2-(methylthio)pyrimidine (0.21 g, 1.08 mmol) was added to a solution of **DPTT** (0.50 g, 1.08 mmol) K_2CO_3 (0.59 g, 4.30 mmol) in dehydrated NMP under a nitrogen atmosphere. The reaction solution was refluxed at 100 °C for a day. The resulting solution was poured into water/methanol to precipitate the product. The obtained polymer was collected by filtration and washed with methanol. The final product was dried at 150 °C under a vacuum. Yield: 0.510 g (80.6%). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) estimated by gel permeation chromatography (GPC) were 14.99×10^3 and 27.68×10^3, respectively, and the dispersity index (PDI = M_w/M_n) was 1.59.

2.5. Measurements

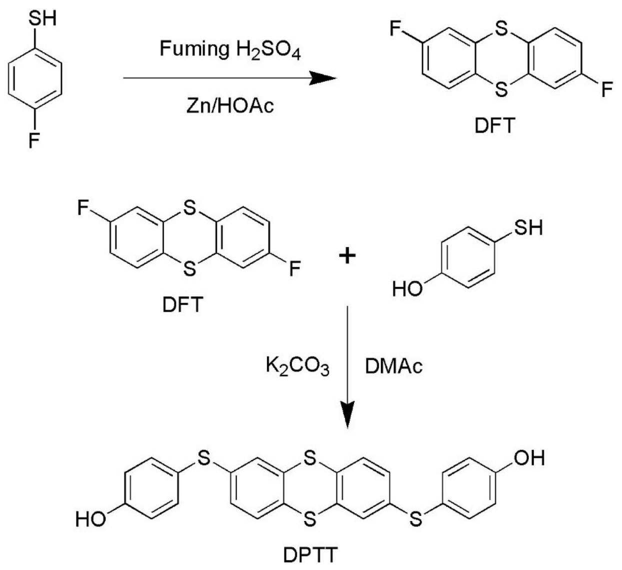
The ^{1}H (600 MHz) and ^{13}C (150 MHz) nuclear magnetic resonance (NMR) spectra were measured on an Agilent 600 MHz Premium COMPACT in dimethyl sulfoxide-d_6 (DMSO-d_6) or chloroform-d ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC, Tosoh HLC-8320GPC EcoSEC) measured the number-average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersities (M_w/M_n) with tetrahydrofuran (preservative-free HPLC grade, Fisher or Daejung Chemical Company) at 40 °C at 1.0 mL/min and were calibrated with 14 monodisperse polystyrene standards (purchased from Alfa Aesar). Fourier transform-infrared (FT-IR) spectra were obtained with a Nicolet IS10 with 32 scans per spectrum at a 2 cm^{-1} resolution. Thermogravimetric analysis (TGA) was carried out with a Q50 TA Instruments at a heating rate of 20 °C/min under a nitrogen gas flow. The glass transition temperature (T_g) was taken by differential scanning calorimetry (DSC) analysis with a Q10 (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere. Dynamic mechanical thermal analysis (DMA) was examined using a Q800 (TA Instruments) at a scanning rate of 3 °C/min with a load frequency of 1 Hz in air. The specimens were prepared in film form (30 mm length, 5 mm width, and *ca.* 20 μm thickness). Thermogravimetric analysis (TGA) was performed under a nitrogen gas flow using a Q50 (TA Instruments) at a heating rate of 10 °C/min. Ultraviolet–visible (UV–vis) spectra were recorded on a JASCO V-670 spectrometer in transmittance mode at a wavelength range of 250–800 nm, a resolution of 1 nm, and a scanning rate of 400 nm/min. The refractive indices of the samples such as in-plane (n_{TE}) and out-of-plane (n_{TM}) were measured by a prism coupler (Metricon PC-2000), and the wavelength was a 637 nm He—Ne laser light source. The birefringence (Δn) was calculated between the n_{TE} and n_{TM}, and the average refractive index (n_{av}) was calculated by the following equation: $n_{av} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$.

3. Results and discussion

3.1. Synthesis of DPTT

The novel 4,4′-diol aromatic monomer, 2,7-(4,4′-diphenol)thiothianthrene (**DPTT**), which contains a thianthrene unit with 4 sulfur atoms, was synthesized by a two-step procedure with 2,7-difluorothianthrene as the starting material (Scheme 1). First, the intermediate 2,7-difluorothianthrene (**DFT**) was synthesized as previously described [26]. Then, **DFT** was reacted with 4-hydroxybenzenethiol to give the final compound **DPTT** with a yield of 56%. The thermal properties of the synthesized compound **DPTT** were measured by TGA and DSC shown in Fig. S1. The onset decomposition temperature (T_d) of **DPTT** in a nitrogen flow was 203 °C, and its melting temperature (T_m) was about 159 °C.

The chemical structure of **DPTT** was characterized by FT-IR and NMR spectroscopy. In the FT-IR spectrum (Fig. 1), the band from the O—H of both terminal hydroxyl groups of **DPTT** appears at around 3550–3200 cm^{-1}. The characteristic absorption from the C—S—C bond of the thioether group was observed at 817 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of the model compound **DPTT** are presented in Fig. 2 along with the assignments of all the signals. In the ^{1}H NMR spectrum (Fig. 2(a)), the characteristic proton of the hydroxyl group was observed at 9.88 ppm. In the ^{13}C NMR spectrum (Fig. 2(b)), 9 carbon signals were observed in the range of 39–160 ppm which are consistent with the expected molecular structure of **DPTT**.



Scheme 1. Synthesis of DPTT.

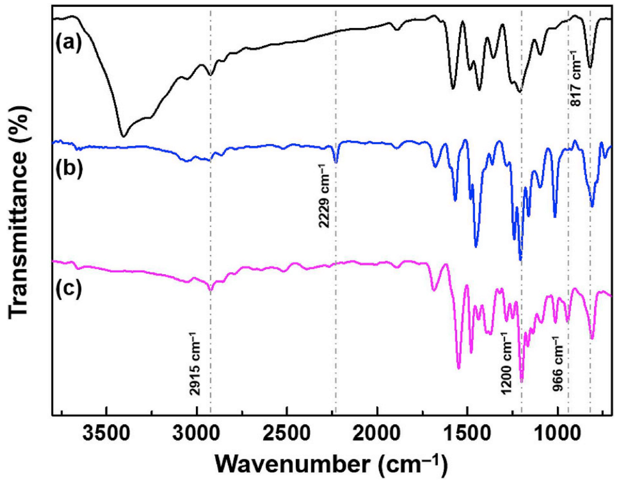


Fig. 1. FT-IR spectra of DPTT (a), DPTT–DFBN (b), and DPTT–DCMP (c).

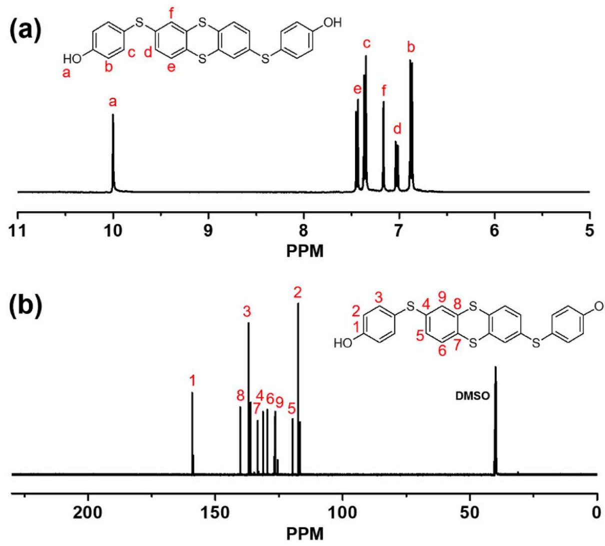


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of DPTT.

3.2. Synthesis of the PPTEs

The synthetic procedure for the thianthrene-containing poly(phenylene thioether ether)s (PPTEs) is depicted in Scheme 2. All the PPTEs were synthesized by the polycondensation of **DPTT** with organic dihalogen compounds, such as **DFBN**, **DCMP**, **DFBA**, and **DFP**. The polycondensation was carried out for 24 h in the presence of K_2CO_3 at various temperatures.

The molecular weights of the resulting polymers were determined by GPC, and the results are listed in Table 1. The polymerizations of **DPTT** with **DFBN** or **DCMP** yielded PPTEs with a M_ns of around 11,000 and a M_ws of around 26,000 (polystyrene standard), respectively. However, the attempt to prepare PPTEs from **DFBA** and **DFP** had limited success. The molecular weights of **DPTT–DFBA** and **DPTT–DFP** were very low (less than 1600 for the M_ns and 1800 for the M_ws), and much more solvent had to be used because of the low solubility of **DFBA** and **DFP**. Therefore, two types of colorless PPTEs with high molecular weights were successfully synthesized by the facile aromatic nucleophilic substitution polycondensation.

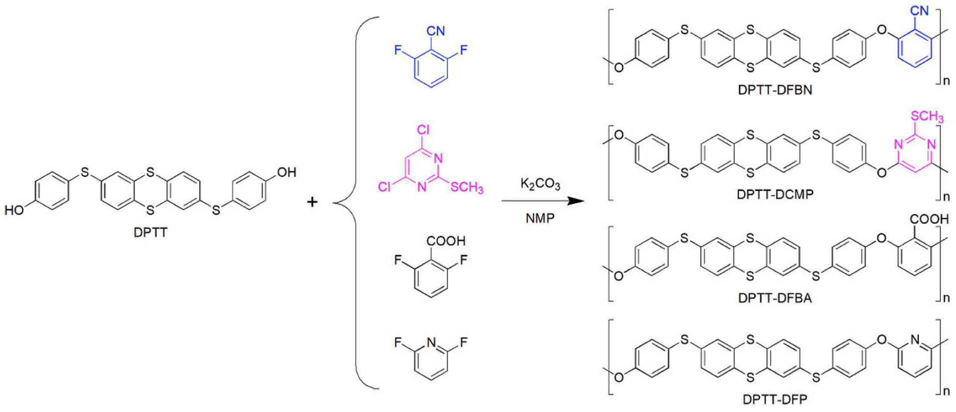
The chemical structure of the PPTEs originating from the **DFBN** and **DCMP** was investigated by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. As seen in Fig. 1, characteristic IR peaks were observed at 2229 cm^{-1} and 1549 cm^{-1}, which is attributable to the $-C{\equiv}N$ in the benzonitrile and $-C{=}N-$ group in the pyrimidine ring, respectively. Furthermore, the absorption peak of the ether (C—O—C) stretching vibration was observed at 1200 cm^{-1}. As seen in Fig. 1, characteristic IR peaks were observed at 1200 cm^{-1} and 2229 cm^{-1}, which is attributable to the ether (C—O—C) stretching vibration and the $-C{\equiv}N$ in the benzonitrile. Furthermore, the absorption peaks of the $-SCH_3$ group were observed at 2915 cm^{-1} and 966 cm^{-1}. In the ^{1}H NMR spectrum of **DPTT–DFBN** (Fig. S2(a)), the signals that resonated at 7.37, 7.15, 7.08, and 6.57 ppm were assigned to the aromatic protons, respectively. Additionally, in the ^{13}C NMR spectrum (Fig. S2(b)), the aromatic carbons of the benzene ring were observed near 90–160 ppm, and the carbon of the $-C{\equiv}N$ group was observed at 130.52 ppm. In Fig. S3(a), the methyl protons of **DPTT–DCMP** were observed at 2.28 ppm. In the ^{13}C NMR spectrum (Fig. S3(b)), the signals that resonated at 172.407, 170.465, and 87.119 ppm were assigned to the pyrimidine carbon. In addition, the signal that resonated at 14.09 ppm was assigned to the methyl carbon.

3.3. Solubility

The qualitative solubility of the PPTEs was evaluated in common organic solvents, and the results are listed in Table S1. Those polymers derived from **DFBN** and **DCMP** showed good solubility in several organic solvents. This was attributed to the recognized noncoplanarity of the thianthrene ring in addition to the flexible thioether (—S—) and ether linkages in their backbone structure. The **DPTT–DFBN** dissolves in chloroform upon heating, whereas the **DPTT–DCMP** is soluble in THF, NMP, and chloroform at room temperature probably due to the introduction of the pyrimidine unit with $-SCH_3$ substitution.

3.4. Thermal properties

The thermal properties of the PPTEs evaluated by TGA, DSC, and DMA are summarized in Table 1. Fig. 3(a) shows the weight-temperature curves of the PPTEs in a nitrogen atmosphere obtained by TGA. The derivative curves of the weigh-decrease to temperature are also shown. The TGA thermograms show that all the PPTEs were stable up to around 250 °C. The temperatures at 5% weight loss ($T_{5\%}$) of the **DPTT–DFBN** and **DPTT–DCMP** were 389 and 344 °C, respectively. The significantly higher thermal decomposition temperature of the PPTEs derived from **DFBN** than from **DCMP** could be interpreted by the fact that it has a relatively linear, rigid, and ordered molecular structure which increases the intermolecular interactions between the chains [27,28]. In addition, the carbonized residues after heating up to 600 °C



Scheme 2. Synthesis of PPTEs.

Table 1
Molecular weights and thermal properties of the PPTEs.

Polymer	M_w	M_n	M_w/M_n [a]	T_g (°C)		$T_{5\%}$ [c] (°C)	$T_{10\%}$ [c] (°C)
				DSC [b]	DMA		
DPTT–DFBN	26,338	11,553	2.28	175.87	189.48	389.20	399.57
DPTT–DCMP	27,680	14,989	1.59	153.05	177.85	343.63	360.65
DPTT–DFP	1763	1525	1.156	–	–	–	–
DPTT–DFBA	1552	1087	1.427	–	–	–	–

[a] Determined by GPC in THF with respect to polystyrene standard at 40 °C.
[b] Glass transition temperature (T_g) reported second heating thermograms.
[c] Decomposition temperatures at 5% and 10% weight loss, respectively.

were in the range of 57–62%. This is the attributed to the presence of the high content of sulfur atoms and the aromatic backbone structure of the PPTEs.

In the DSC profiles (Fig. 3(b)), the PPTEs derived from **DFBN** have glass transition temperature (T_g) values of 176 °C. On the other hand, the PPTEs prepared using **DCMP** have lower T_gs, which are derived from the flexible −S− group [15,29]. The high T_g of the **DPTT–DFBN** is achieved by a rigid −C≡N group on the organic dihalogen compound that reduces the flexibility of the main chain and increases the chain stiffness in the crystalline state.

The viscoelastic behaviors were analyzed by DMA measurement. The temperature dependence of the dynamic storage modulus (E'), loss modulus (E''), and tan δ (where tan δ is the loss factor that is equal to E''/E') of the PPTE films are shown in Fig. 3(c). The PPTE films have a tan δ in the range of 178–189 °C which decreased with increasing −S− segments in the PPTE main chain. The onset temperature at which the storage modulus decreased rapidly was 133 °C for **DPTT–DFBN**, which was 15 °C higher than that for **DPTT–DCMP** (118 °C), implying that the thermal properties of the **DPTT–DFBN** was improved by the presence of the −C≡N segments in their backbones.

3.5. Optical properties

Fig. 4(a) shows the representative UV–vis transmission spectra of the **DPTT–DFBN** and **DPTT–DCMP** films at a wavelength from 250 to 800 nm, in which the absorbance was normalized to a 10 μm thickness. The cut-off wavelengths (λ_0) of the PPTE films are around 343 nm and 352 nm, and transmittance is as high as 93.2% at 550 nm. In particular, **DPTT–DCMP** has almost complete visual transparency ($T_{550} > 93.4\%$) in the visible region. The excellent optical transparency and colorlessness are probably due to the *meta*-substituted pyrimidine and $-SCH_3$ substitution in the pyrimidine unit, which efficiently inhibits the localization of the π–electrons and charge transfer interactions in the PPTEs as well as prevents intermolecular chain packing [30,31].

The polarization-dependent refractive indices of the PPTE films were measured by a prism coupler at several laser beam wavelengths: 637, 1306.5, and 1549.5 nm. As shown in Table 2, the in-plane refractive index (n_{TE}) and out-of-plane refractive index (n_{TM}) of the PPTE films are in the range of 1.7226–1.7239 and 1.7112–1.7133, respectively. The fact that the value of n_{TE} is slightly higher than the value of n_{TM} for all the PPTE films reflects the preferential alignment of the molecular chains parallel to the film plane. The average refractive index (n_{av}) estimated from the n_{TE} and n_{TM} values increases from a minimum of 1.7188 (**DPTT–DFBN**) to a maximum of 1.7204 (**DPTT–DCMP**). The n_{av} depends on several factors, such as the polarizability per atomic volume and molecular chain flexibility [10,18,32]. Initially, the introduction of the nonplanar thianthrene moiety was expected to increase the molecular free volume of the PPTEs, thus decreasing the n_{av} value according to the Lorentz–Lorenz equation. However, all the synthesized PPTE films have high n_{av} values above 1.71. This might be a result of the competition between the molecular free volumes and the number of polarizable groups in a unit volume. Therefore, the high n_{av} values of **DPTT–DFBN** and **DPTT–DCMP** originate from the plural polarizable sulfur atoms. The **DPTT–DCMP** has a slightly higher n_{av} than

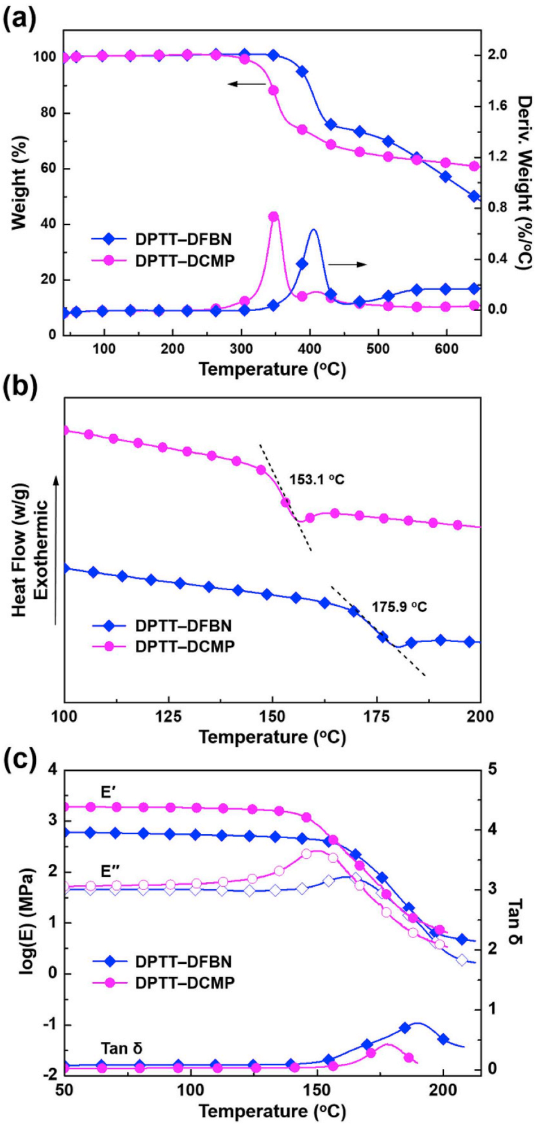


Fig. 3. TGA thermograms and derivative weight (a), DSC (b), and DMA (temperature dependence of the dynamic storage modulus (E'), loss modulus (E''), and tan δ) curves (c) of the PPTE films.

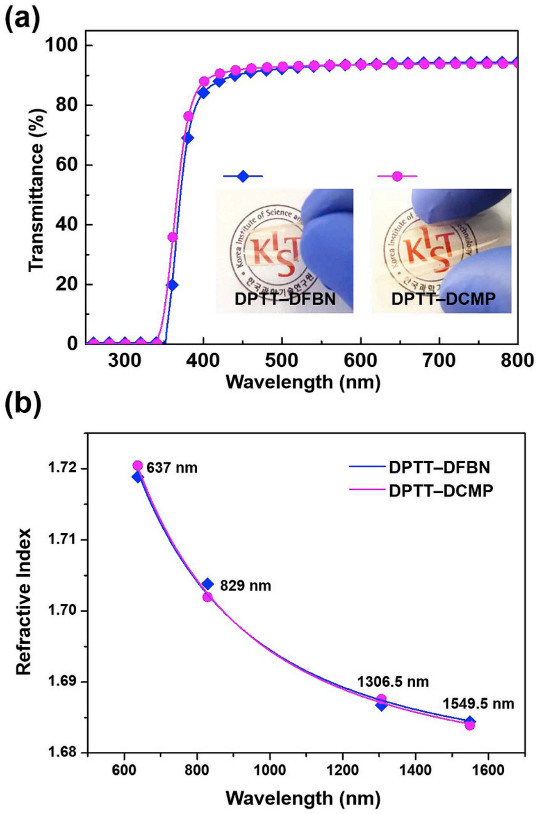


Fig. 4. Wavelength dependent transmittance (a) and wavelength dispersions of the refractive indices (b) of the PPTE films. The insert shows the physical appearance of the PPTE films.

that of the analogous **DPTT–DFBN**. This result clearly indicates that the pyrimidine ring endows a high molecular polarizability compared to a phenyl ring. Moreover, all the PPTEs show a positive and low in-plain/out-of-plane birefringence (Δn) in the range of 0.0106–0.0114 [33]. The low Δn might be due to the flexible —S— and —O— bridges in their molecular chains, which increase the chain mobility.

A graph showing the relation between the n_{av} and each wavelength is provided in Fig. 4(b). In Fig. 4(b), the solid lines are fitted with the simplified Cauchy formula [$n_\lambda = n_\infty + D\lambda^{-2}$], where n_λ is the refractive index at the wavelength; n_∞ is the calculated refractive index at the infinite wavelength, and (D) is the coefficient of dispersion [34]. The n_∞ and D of the PPTE films are in the range of 1.6768–1.6770 and 1.6944–1.7710, respectively. The high n_∞ values of the PPTEs are considered to be an inherent refractive index that exclude the effect of light absorption which can be obtained with a high sulfur content. These results indicate that the introduction of the pyrimidine moiety together with multiple sulfur atoms is an effective way to yield PPTEs that are colorless with a high optical transparency and refractive index and a low birefringence.

4. Conclusion

Thianthrene and thioether containing a 4,4′-diol aromatic compound were readily synthesized by nucleophilic aromatic substitution of 2,7-difluorothianthrene with 4-hydroxybenzenethiol to develop thermally stable high-*n* polymers. The PPTEs were prepared by polycondensation of **DPTT** with organic dihalogen compounds, such as **DFBN** and **DCMP**. The PPTEs derived from **DFBN** exhibited high thermal stabilities, *i.e.,* T_g (> 175 °C) and $T_{5\%}$ (> 390 °C). All the PPTEs exhibited excellent optical properties, in particular, the **DPTT–DCMP** is colorless and visually transparent (T_{550} > 93%), and has the highest n_{av} of 1.7204 and a small birefringence of 0.0106 at 637 nm. It can be concluded that the high refractive indices of the PPTEs are caused by the high content of polarizable groups including the sulfur atoms and pyrimidine ring and the minimal presence of alkyl chains. Thus, the PPTEs have high potential as a target material that is colorless and transparent and has a high refractive index, a low birefringence, and a high thermal stability, simultaneously.

Table 2
Refractive indices of the PPTEs.

Polymer	λ_0[a]	T_{550}[b] (%)	Refractive Index and Birefringence at 637 nm[c]			Δn[e]	n_∞[f]	D[g] (× 10^4)	V_{NIR}[h]
			n_{TE}	n_{TM}	n_{av}[d]				
DPTT–DFBN	352	93.2	1.7227	1.7113	1.7188	0.01141	1.6774	1.7119	21.91
DPTT–DCMP	343	93.4	1.7239	1.7134	1.7204	0.01060	1.6767	1.7654	21.36

[a] λ_0 defined as the point at which the transmittance becomes less than 1%.
[b] UV-transmittance at 550 nm.
[c] Measured by prism coupler at 637 nm.
[d] Average refractive index was calculated by formula: $n_{av} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$.
[e] The birefringence (Δn) was calculated by the equation: $\Delta n = n_{TE} - n_{TM}$.
[f] Refractive index at the infinite wavelength.
[g] Dispersion coefficient of refractive index fit by the Cauchy formula ($n_\lambda = n_\infty + D\lambda^{-2}$).
[h] Abbe's number is given by as $V_{NIR} = (n_{829} - 1)/(n_{637} - n_{1306})$ [35].

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.01.033.

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