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Low birefringence and low dispersion aliphatic thermosets with a high and tunable refractive index†

Yujin Jeon,‡^a Jisung Choi,§‡^a Donghwa Seo,¶^a Soon Hwa Jung^b and Jeewoo Lim *^a

We herein present a new class of high refractive index polymers prepared through the reaction of bis(2,3-epithiopropyl)sulfide, a series of poly(alkyl polysulfide)s, and elemental sulfur. The addition of an amine catalyst leads to rapid polymerization, resulting in a series of thermosets with high transmittance over the entire visible range. The refractive index of the thermosets can be fine-tuned over the range of 1.700–1.745 ($\lambda = 589$ nm) by varying the feed ratios of elemental sulfur and the polysulfide polymers. A wide range of properties, including the birefringence (Δn), optical dispersion, temperature coefficient of refractive index (dn/dT), transmittance, and glass transition temperature (T_g), of the thermosets are presented. The polymers exhibited a very low birefringence ($\Delta n < 0.002$), which is attributed to the absence of aromatic functional groups, exceptionally low optical dispersion ($V_D > 30$), $T_g > 60$ °C, and dn/dT similar to that of PMMA.

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Introduction

Transparent and high refractive index polymers (HRIPs)^{1,2} constitute an integral class of materials for advanced optical components. Applications of HRIPs span from ophthalmic lenses, optical filters, and optical adhesives to high performance display substrates, encapsulants, microlens arrays for image sensors, high reflective/antireflective coatings, and beyond. The advantages, such as low cost, light weight, good impact resistance, and high processability, of HRIPs over their inorganic counterparts have been the major driving force behind the extensive research efforts for the development of novel HRIPs.

The Lorentz–Lorenz equation,^{3,4} which relates the refractive index of a material to its composition, is often used as the basis for designing HRIPs. One form of the equation is

$$n = \sqrt{((1 + 2[R]/V_0)/(1 - [R]/V_0))}$$

^aDepartment of Chemistry, College of Sciences, Kyung Hee University, 26 Kyungheedaero, Dongdaemun-gu, Seoul, 02447, Korea.

E-mail: jeewoo@khu.ac.kr

^bPlatform Technology Center, CTO, LG Chem, E7 Block, LG Science Park, 30, Magokjungang 10-ro, Gangseo-gu, Seoul, 07796, Korea

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‡ These authors contributed equally to this work.

§ Current address: Samsung Electro-Mechanics, 150, Maeyeong-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, Republic of Korea.

¶ Current address: Semiconductor R&D Center, DS Division, Samsung Electronics, 118 Sinwon-ro, Yeongtong-gu, Suwon, Gyeonggi-do, Republic of Korea.

where n is the refractive index, $[R]$ is the molar refraction, and V_0 is the molar volume of the repeating unit. While the precise refractive index cannot yet be modelled due to a wide range of factors influencing the molar volume and refraction of a polymer segment, the general design of HRIPs involves the employment of functional groups having high $[R]$ and low V_0 . The most widely utilized functional groups which meet such criteria include sulfur-containing motifs such as mono- and polysulfides, thiocarbonyls, sulfones, and aromatic groups such as phenyl and naphthyl units.^{1,2} Over the past few decades, a wide variety of HRIPs, both thermoplastics and thermosets, have been developed from the design principles based on the Lorentz–Lorenz equation. Notable HRIPs include acrylates,^{5–7} polysiloxanes,^{8,9} poly(arylene ether)s and poly(arylene thioethers),¹⁰ polyphosphazenes, and thermosets from thiol–ene crosslinking reactions.^{11–15}

While the refractive index (n) of an HRIP is its defining feature, there are other parameters crucial for its wide applicability. HRIPs need low optical dispersion (high Abbe number, V_D) and high optical isotropy (low birefringence, Δn).^{16,17} Both optical dispersion and optical isotropy are related to the polarizability of the repeating unit, with high polarizability leading to high optical dispersion and large anisotropy of the directional components of polarizability (of a repeating unit with respect to the polymer's main chain axis) leading to low optical isotropy. The temperature coefficient of refractive index (dn/dT), which is a measure of changes in a material's refractive index with temperature, is also crucial for the application

of HRIPs in advanced electronic applications. Despite the importance of the thermal and optical properties beyond the refractive index, reports presenting such properties are relatively rare.

The vast majority of HRIPs exhibit a n_D (refractive index at $\lambda = 589.3$ nm) of over 1.6, and the attention has recently shifted to those that have a n_D of over 1.7.¹⁸ Such HRIPs are yet very scarce and are largely limited to materials with high aromatic group contents.^{10,14,15,19,20} The presence of conjugated π -systems in HRIPs, however, usually leads to large Δn and low V_D .²¹ Careful monomer design to force aromatic groups into an orthogonal orientation is required to prevent the alignment and π - π interactions of aromatic groups.^{22,23} Despite such efforts, achieving HRIPs featuring a combination of high n_D (>1.70), high V_D (>30), and low Δn (<0.002) still remains a formidable challenge.

Polysulfide polymers,²⁴ the structure of which consists of alternating polysulfide and aliphatic chains, are among the polymers with the highest sulfur contents known to date. While the excellent thermal stability, weatherability, and chemical resistance of these elastomeric materials led to their widespread application as sealants, their low T_g and T_m ,²⁵ along with their low transparency, make them unsuitable for direct application as HRIPs.

Based on previous reports on linear polymers from sulfur and thiaranes,^{26,27} along with our recent studies towards the development of functional polysulfide latexes,^{28,29} we envisioned that fully aliphatic polysulfide polymers and their analogues could be used as starting materials in the preparation of high sulfur content HRIPs under suitable polymerization conditions. Herein, we report a new class of HRIPs, **p(PS-BEPS)**, prepared through the copolymerization of polysulfide polymers, bis(2,3-epithiopropyl)sulfide (BEPS), and elemental sulfur (Scheme 1). Unlike previous HRIPs from episulfides,^{19,30,31} no thiols are used for the reaction with episulfides. This is potentially advantageous since thiols have relatively poor shelf lives.³² The resulting polymers exhibit high transparency over the visible range and into the NIR region (up to 2200 nm) and, under optimized conditions, a n_D of 1.7448, a Δn of 0.0013, and a V_D of 30.8. The temperature coefficient of refractive index is $-1.52 \times 10^{-4} \text{ K}^{-1}$, which is similar to that of a widely used optical polymer, PMMA. Interestingly, the refractive index could be tuned over the range of 1.7000–1.7448 in a modular fashion, simply by varying the feed ratio of the polysulfide prepolymer and elemental sulfur.

Experimental

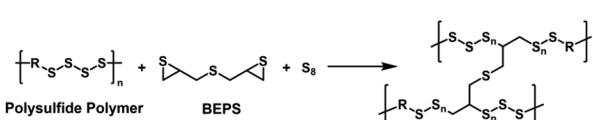
Materials and methods

All reagents were commercially available from Alfa Aesar, Sigma-Aldrich, and TCI. Bis(2,3-epithiopropyl) sulfide was provided by LG Chem. Divinyl sulfone was purified by directly passing through a short column of neutral alumina prior to use. Other chemicals were used as received unless otherwise noted. The preparation of polysulfide stock solutions and polysulfide polymers therefrom was carried out under a dry argon atmosphere using standard Schlenk techniques. S-DIB films were prepared using previously reported methods.³³ Films (thickness = 1 mm) of p(PS-BEPS) were prepared by conducting the polymerization in a mold pre-treated with a releasing agent. Fourier transform infrared (FT-IR) spectra from 3500 cm^{-1} to 400 cm^{-1} were obtained using a Bruker Invenio-R instrument. The transmittance of the thermosets was measured using a Shimadzu UV-1800 spectrophotometer in the wavelength range of 200–800 nm. Differential scanning calorimetry (DSC) was conducted using a TA Instruments DSC 250. Thermogravimetric analysis was carried out on a TA Instruments SDT Q600 TGA. Elemental analyses (CHNS) of the prepolymers were conducted on a CE Instruments Flash EA1112. The refractive index, birefringence, thermo-optic coefficient, and film thickness were measured on a Sairon Technology SPA-4000 prism coupler using a 632.8 nm He-Ne laser light source. Both GGG and high refractive index rutile prisms were used. Abbe number was obtained using an ATAGO DR-M4 multi-wavelength Abbe refractometer.

Synthetic procedures

Sodium polysulfide solution. Sodium sulfide nonahydrate (2.401 g, 10 mmol) and elemental sulfur (0.962 g, 30 mmol of S, for sodium polysulfide solution) were added to a 20 mL scintillation vial containing 6 mL of degassed, deionized water under an argon atmosphere. The mixture was stirred overnight at 30 °C. No residual, undissolved elemental sulfur remained. Additional degassed, deionized water was added until the volume of the solution reached 10 mL to give a clear, orange sodium tetrasulfide solution.

Polysulfide polymers from DVS. Divinylsulfone (1 mL, 10 mmol) was charged into a 500 mL round bottom flask containing degassed, deionized water (200 mL) under argon. The mixture was stirred at 30 °C until complete dissolution of DVS was observed (30 minutes). Sodium sulfide solution (9 mL, 9 mmol) was subsequently added dropwise over 45 seconds. The pale yellow reaction mixture gradually turned into a cloudy white dispersion. The reaction mixture was stirred further at 30 °C for 15 minutes and then neutralized by slow addition of aqueous HCl (2 M). The neutralization was monitored using pH paper. The polysulfide polymer was obtained by centrifugation followed by three cycles of dispersion and centrifugation in water and three cycles of dispersion and centrifugation in methanol. The solid product was dried *in vacuo* to yield the desired polysulfide polymer as ivory solids.



Scheme 1 Synthesis of high sulfur content, fully aliphatic HRIPs under thiol-free conditions involving the polysulfide polymer, bis(episulfide) (BEPS), and elemental sulfur.

($\text{PS}_4\text{-DVS}$, 1.29 g, 58%). Anal. Calcd for $(\text{C}_4\text{H}_8\text{O}_2\text{S}_5)_n$ ($\text{PS}_4\text{-DVS}$): C, 19.34; H, 3.25; S, 64.53. Found: C, 18.10; H, 2.84; S, 65.90.

Polysulfide polymers from DCE. Sodium sulfide solution (9 mL, 9 mmol) was added to a vigorously stirred mixture of dichloroethane (0.79 mL, 10 mmol) and degassed, deionized water (200 mL) under argon at 60 °C. The reaction mixture was further stirred at 60 °C for 12 hours. Off-white solids deposited at the bottom of the flask were isolated and purified following the procedures identical to those used for polysulfide polymers from DVS described above. The polysulfide polymer was obtained as rubbery yellow solids ($\text{PS}_4\text{-DCE}$, 1.20 g, 85%). Anal. Calcd for $(\text{C}_2\text{H}_4\text{S}_4)_n$ ($\text{PS}_4\text{-DCE}$): C, 15.37; H, 2.58; S, 82.05. Found: C, 14.41; H, 2.42; S, 83.92.

p(PS-BEPS). Representative procedures are given here for p(PS-BEPS) containing 15 wt% $\text{PS}_4\text{-DCE}$ and 15 wt% elemental sulfur. Other p(PS-BEPS) thermosets were prepared using an identical set of procedures using appropriate types and amounts of polysulfide polymers and additives. A 5 mL scintillation vial equipped with a stirring bar was charged with $\text{PS}_4\text{-DCE}$ (0.6 g), elemental sulfur (0.6 g), and BEPS (0.8 g). The mixture was stirred vigorously at room temperature for 3 hours, at which point a homogeneous solution was obtained. In a separate 5 mL scintillation vial containing BEPS (2.0 g), a catalytic amount of dicyclohexyl methyl amine was added. The mixture was stirred at room temperature for 15 minutes. The catalyst solution was subsequently added in one portion to the BEPS solution of $\text{PS}_4\text{-DCE}$ and elemental sulfur and the reaction mixture was stirred briefly before being transferred to a glass mold pre-treated with a releasing agent. The mold containing the reaction mixture was transferred to an oven pre-heated to 60 °C and cured for 12 hours to yield a glassy, transparent film having a thickness of 1 mm.

Results and discussion

Polysulfide polymers were prepared by the reaction of aqueous sodium polysulfides with divinyl sulfone (DVS) and dichloroethane (DCE) (Fig. 1a). DVS was chosen since it readily undergoes a polysulfide-ene²⁹ precipitation polymerization in the aqueous phase to give the corresponding polysulfide polymers under mild conditions and contains the sulfone group, which, while having a slightly smaller molar refraction than functional groups with sulfur atoms in lower oxidation states,² features very low molar dispersion.¹⁷ DCE was chosen to maximize the sulfur content of the polysulfide polymers. An aqueous polysulfide solution was prepared by dissolving elemental sulfur in a solution of sodium sulfide. The stoichiometry was controlled to provide polysulfide solutions having an average sulfur rank of 4. A slight excess of DVS and DCE was used to prevent the formation of thiol chain ends which are prone to chain extension through oxidation.

The two polysulfide polymers, $\text{PS}_4\text{-DVS}$ and $\text{PS}_4\text{-DCE}$, showed extremely low solubility in water and in common organic solvents, making characterization through common solution-based methods difficult. FT-IR spectroscopy revealed,

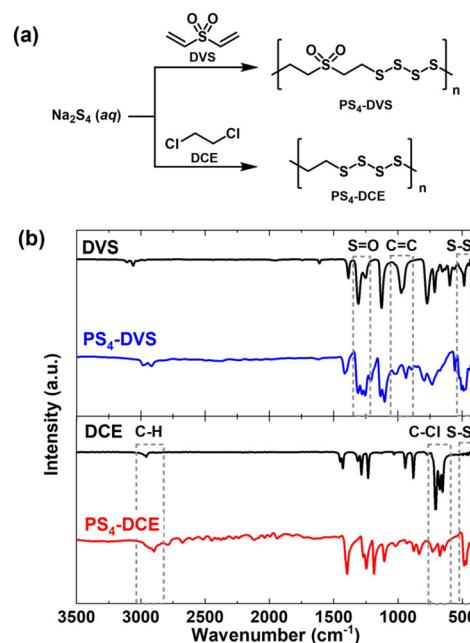


Fig. 1 (a) Synthesis of polysulfide polymers used in this work and (b) FT-IR spectra of polysulfide polymers obtained from DVS (top) and DCE (bottom).

along with the emergence of S-S bond vibrations³⁴ in the 450–500 cm^{-1} region, nearly complete consumption of vinyl groups (for $\text{PS}_4\text{-DVS}$) and C-Cl bonds (for $\text{PS}_4\text{-DCE}$) (Fig. 1b). The results of thermogravimetric analysis of $\text{PS}_4\text{-DCE}$ and $\text{PS}_4\text{-DVS}$ (Fig. S1†) were consistent with those of previously reported polysulfide rubbers.²⁵ The differential scanning calorimetry of the two polysulfide polymers (Fig. S2†) indicated melting transition at 67 °C, also consistent with the thermal transitions previously reported for polysulfide rubbers.

Despite their lack of solubility in common organic solvents, the prepolymers exhibited solubilities of over 15 wt% in BEPS. While the solutions of polysulfide polymers in BEPS did not undergo spontaneous vitrification under ambient conditions, the introduction of a catalytic amount of dicyclohexyl methyl amine led to the vitrification of the solutions to give transparent, glassy polymers (p(PS-BEPS), Fig. 2a). Interestingly, the yellow color of $\text{PS}_4\text{-DCE}$ faded to give a reaction mixture with a pale-yellow tint upon the addition of dicyclohexyl methyl amine. Organic tri- and tetrasulfides have been reported to undergo facile desulfurization by amines³⁵ and phosphines³⁶ through a process initiated by the nucleophilic attack of the S-S bond. The observation that the characteristic yellow color³⁷ of long polysulfides fades upon the addition of the amine suggests that the catalyst reacts with the polysulfide unit of the polysulfide polymer, which would then initiate curing through a proposed mechanism shown in Fig. 2b. Similar curing behavior was observed with other polysulfide polymers. The thermogravimetric analyses of p(PS-BEPS) showed a single stage weight loss, along with a significantly enhanced onset temperature of degradation (Fig. S3†). This observation

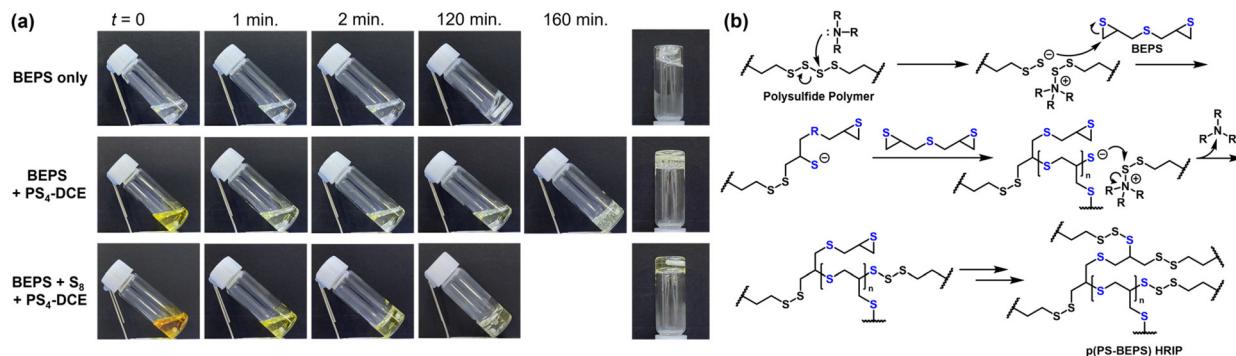


Fig. 2 (a) Digital photographs of the amine-catalyzed polymerization of BEPS, BEPS containing PS₄-DCE (15 wt%), and BEPS containing 15 wt% each of PS₄-DCE and elemental sulfur (S₈) at 60 °C, with *t* = 0 indicating the time at which the dicyclohexyl methyl amine catalyst was added, and (b) the proposed mechanism of the polymerization of BEPS and PS₄-DCE giving a high refractive index thermoset.

suggests that the thermosets and homogeneous polymers have high degrees of crosslinking.

With the sulfur contents of **BEPS**, PS₄-DVS, and PS₄-DCE at 53.9, 64.5, and 82.1%, respectively, we expected that the refractive indices of p(PS-BEPS)s would be above 1.70. To investigate the possibility, p(PS-BEPS)s were prepared by curing the solutions of polysulfide polymers in **BEPS** at various concentrations and their refractive index ($n_{632.8\text{nm}}$), birefringence (Δn , measured at 632.8 nm), and optical transmittance were studied (Table S1†).

The $n_{632.8\text{nm}}$ values of the thermosets prepared from the polymerization of polysulfide polymers and **BEPS** were shown to increase with increasing polysulfide polymer content (Fig. 3a). Polysulfide polymers bearing DVS units demonstrated a lower degree of enhancement than those bearing DCE units, an observation consistent with the higher sulfur content of PS₄-DCE.

The $n_{632.8\text{nm}}$ increase was found to show a linear relationship with the polysulfide polymer content, allowing for the slope of the linear fit to be used for quantitative comparison of the impact of each polysulfide polymer on the resulting polymers' optical properties. This analysis showed that, for PS₄-DVS, a 1 wt% increase resulted in a $n_{632.8\text{nm}}$ increase of 2.7×10^{-4} . At 15 wt% loading, the p(PS-BEPS) polymer from PS₄-DVS exhibited a $n_{632.8\text{nm}}$ value of 1.7030. The polysulfide

polymer from DCE has a stronger impact on $n_{632.8\text{nm}}$ increase, with a 1 wt% increase in the PS₄-DCE content giving a $n_{632.8\text{nm}}$ increase of 9.0×10^{-4} . A $n_{632.8\text{nm}}$ of 1.712 was measured at a PS₄-DCE content of 15 wt%.

Glassy polymers could also be obtained by replacing polysulfide polymers with elemental sulfur (S₈) (Table S2† and Fig. 3b). Per wt.% increase in the $n_{632.8\text{nm}}$ values of 15.8×10^{-4} was obtained from S₈. The $n_{632.8\text{nm}}$ value obtained at 15 wt% loading was 1.722 for S₈. While all thermosets exhibited high transmittance over the visible range (Fig. 3c and Fig. S4†), p(PS-BEPS), obtained from the reaction of elemental sulfur and BEPS, showed lower transmittance along with a window of transparency starting at a longer wavelength compared to those from polysulfide polymers. This observation is attributed to the presence of longer polysulfide chains in p(PS-BEPS) from sulfur due to higher sulfur contents compared to the polysulfide polymer counterparts.³⁷ In all polymers, extremely low Δn values of below 0.002 were obtained, which is attributed to the absence of highly polarizable functional groups, such as aromatic moieties and halogens (excluding F and Cl), in p(PS-BEPS)s.

To probe the possibility of increasing the $n_{632.8\text{nm}}$ beyond 1.720 while maintaining high optical transmittance and low birefringence, polymerization was conducted using a neat mixture of **BEPS** and equal amounts of PS₄-DCE and S₈ to yield p(PS-BEPS)s having a combined PS₄-DCE/S₈ content of 5.0 to

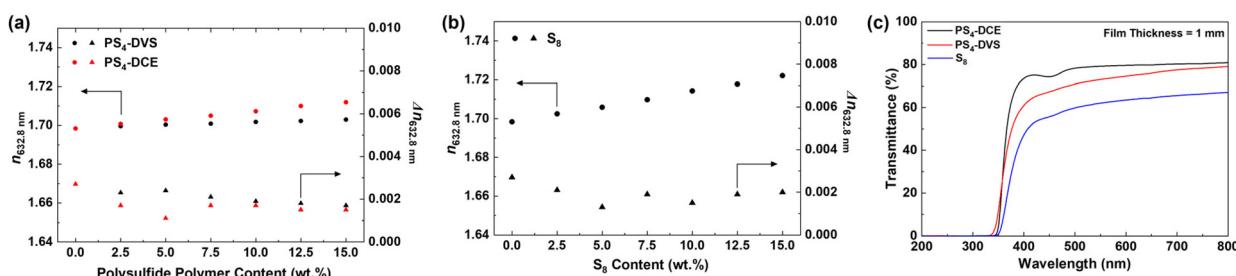


Fig. 3 Relationship between the refractive indices at 632.8 nm ($n_{632.8\text{nm}}$), birefringence ($\Delta n_{632.8\text{nm}}$), and the composition of thermosets prepared from BEPS and (a) polysulfide polymers from DVS and DCE and (b) elemental sulfur; (c) UV-Vis transmittance of 1 mm-thick polymer films prepared using 15 wt% of various polysulfide polymers or elemental sulfur.

30.0 wt%. Glassy, transparent polymers (**P1–P6**) could be obtained, the refractive indices of which increased linearly upon increasing the combined content of $\text{PS}_4\text{-DCE}$ and S_8 over the range of 1.71–1.74 (Fig. 4). While attempts to increase the loading of $\text{PS}_4\text{-DCE}$ or S_8 each beyond 15 wt% in BEPS led to cloudy reaction mixtures yielding polymers with low transmittance, a glassy, transparent polymer having a $n_{632.8\text{nm}}$ approaching 1.74 and a birefringence of below 0.0015 could be obtained at a combined content of 30 wt% (**P6**).

With a simple, solvent- and thiol-free method for preparing high n , low Δn polymers free of conjugated π -systems in hand, the wavelength-dependent dispersion in the refractive index of the materials was investigated. The trade-off between refractive index and optical dispersion, where materials with high refractive index also exhibit high optical dispersion,³⁸ is well established. The optical dispersion was evaluated by measuring refractive indices at 486, 589, and 656 nm using a multiangle Abbe refractometer and deriving Abbe numbers following the equation

$$V_D = ((n_d - 1)/(n_f - n_c))$$

where n_f , n_d , and n_c are the refractive index values at 486, 589, and 656 nm, respectively. The calculated refractive index at infinite wavelength (n_∞) and the dispersion coefficient of refractive index were obtained by fitting the measured n_f , n_d , and n_c values to the simplified Cauchy equation

$$n_\lambda = n_\infty + D\lambda^{-2}$$

where n_λ is the refractive index at the wavelength of λ and D is the coefficient of dispersion.

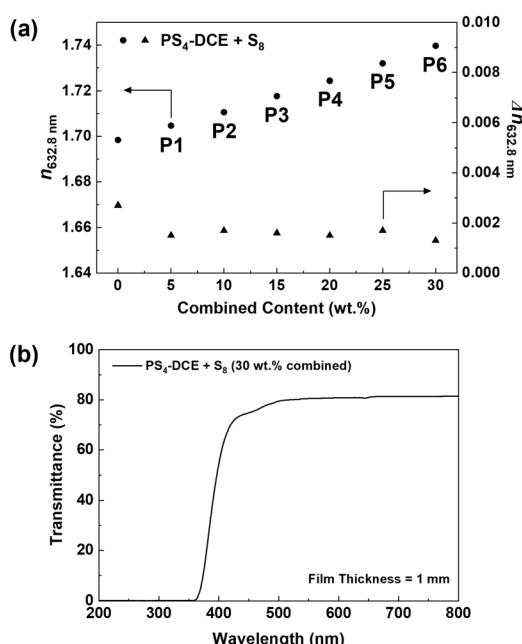


Fig. 4 Relationship between the refractive indices at 632.8 nm ($n_{632.8\text{nm}}$), birefringence ($\Delta n_{632.8\text{nm}}$), and the composition of thermosets prepared from BEPS and equal amounts of $\text{PS}_4\text{-DCE}$ and S_8 (a) and (b) UV-Vis transmittance of a 1 mm-thick polymer film obtained from 15 wt% each of $\text{PS}_4\text{-DCE}$ and S_8 in BEPS.

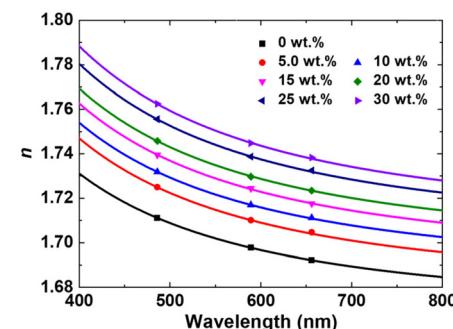


Fig. 5 Wavelength-dependent refractive indices of BEPS copolymers prepared with various $\text{PS}_4\text{-DCE}/\text{S}_8$ loadings.

The plots of n_f , n_d , and n_c , along with the respective Cauchy fitting, are shown in Fig. 5, and the relevant optical properties are summarized in Table 1.

The results show that the polymers obtained from the amine-catalyzed polymerization of BEPS with $\text{PS}_4\text{-DCE}$ and elemental sulfur, **P1–P6**, exhibit high refractive indices of above 1.7, extremely low birefringence values of below 0.0017, and very low optical dispersion as indicated by the V_D value of over 30 even at a n_d of 1.7448. Reported optical polymers that exhibit a combination of $n > 1.7$ and $V_D > 30$ are extremely scarce, with thermosets containing polarizable $\text{P}=\text{Se}$ moieties¹⁴ and thin films from vapor deposition polymerization involving elemental sulfur being representative examples.³⁹ Variations in the composition of the polymer allowed for a precise control of the refractive index without significant alterations in Δn , suggesting that the results could be utilized as a platform for producing high- n index matching materials.

The n_∞ values are the materials' inherent refractive indexes which exclude contributions from absorptions. The n_∞ values for **P5** and **P6**, with the combined $\text{PS}_4\text{-DCE}$ and S_8 contents of 25 wt% and 30 wt%, were 1.7032 and 1.7079, respectively, which are higher than those of high-index, amorphous polyimides from thiophene-bearing aromatic diamines.⁴⁰ The higher n_∞ values of p(PS-BEPS) than those of high-index polyimides despite the latter having higher n_d values (in the range of 1.748–1.761) are attributed to the low D values resulting

Table 1 Optical properties of polymers prepared from BEPS and various amounts of $\text{PS}_4\text{-DCE}$ and S_8

Content ^a (wt%)	n_d	Δn^b	n_∞	$D (\mu\text{m}^2)$	V_D
0	1.6978	0.0027	1.6691	0.0099	36.7
5.0 (P1)	1.7101	0.0015	1.6786	0.0110	34.9
10.0 (P2)	1.7170	0.0017	1.6853	0.0106	34.7
15.0 (P3)	1.7244	0.0016	1.6910	0.0115	33.1
20.0 (P4)	1.7297	0.0015	1.6962	0.0121	32.6
25.0 (P5)	1.7387	0.0017	1.7032	0.0110	32.1
30.0 (P6)	1.7448	0.0013	1.7079	0.0127	30.8

^a Total content of $\text{PS}_4\text{-DCE}$ and S_8 , each added in equal weights, in BEPS. ^b Measured at 632.8 nm from n_{TE} and n_{TM} measurements.

Table 2 Thermo-optical properties of p(PS-BEPS) from various feed ratios of PS₄-DCE and S₈

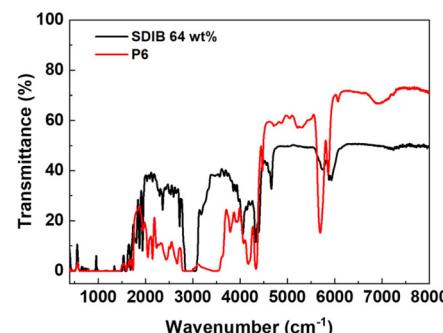
Content ^a (wt%)	$dn/dT^b \times 10^4 \text{ K}^{-1}$	$T_g^c (\text{°C})$
0	-1.58	61
5.0 (P1)	-1.49	64
10.0 (P2)	-1.62	64
15.0 (P3)	-1.21	62
20.0 (P4)	-1.56	61
25.0 (P5)	-1.64	62
30.0 (P6)	-1.52	61

^a Total content of PS₄-DCE and S₈, each added in equal weights, in BEPS. ^b Measured at 632.8 nm. ^c Measured from dn/dT curves.

from the absence of conjugated π -systems which have high molar dispersion.

The thermo-optical properties of **P1–P6** were accessed using variable-temperature prism coupler measurements (Fig. S5† and Table 2). In all cases, dn/dT values in the range of -1.21 to $-1.62 \times 10^4 \text{ K}^{-1}$ were observed, similar to those of PMMA⁴¹ and amorphous polyimides.⁴² The linear fit of n vs. T relations revealed a change in the slope between 62 and 64 °C, suggesting a more rapid expansion of the specific volume above the temperature range due to glass transition. The T_g values of **P1–P6** were obtained from the intersection of the slopes and were found to be similar regardless of polymer composition. Evaluation of T_g values using differential scanning calorimetry (DSC) was difficult due to weak and broad change in heat flows over the range of 60–90 °C. While we are currently investigating methods for increasing the T_g values of HRIPs obtained using polymerization methods described herein, the current results represent a very simple, solvent-free method of preparing HRIPs with $n > 1.7$ and $V_D > 30$ wherein the refractive index could be varied over a wide range without significant alterations in the materials' birefringence, dn/dT , and T_g .

Finally, with a high sulfur content and the lack of aromatic moieties in p(PS-BEPS)s, it was expected that the material could show high transparency beyond the visible range and into the NIR region. This was of interest since transparency at 1310 and 1550 nm (7634 and 6452 cm^{-1}) is important for telecommunication applications and significant research effort has recently been dedicated to the development of HRIPs with high transmittance at the relevant wavelengths.⁴³ The FT-IR transmittance spectra of a 1 mm-thick sample of P6 was obtained using transmission mode and compared to those of the inverse vulcanization polymer (SDIB), obtained from elemental sulfur and diisopropenyl benzene (DIB), having an identical sulfur content (Fig. 6). The results show that P6 has high transmittance, similar to that of SDIB, in the NIR region with a cut-off wavelength at approximately 2200 nm (4500 cm^{-1}). While the inverse vulcanization product has additional windows of transparency at longer wavelengths, the advantage of p(PS-BEPS) is in the large transparency window in the range of 400 nm–2200 nm, conducive to applications

**Fig. 6** FT-IR transmittance spectra of 1 mm-thick samples of S-DIB prepared from inverse vulcanization and p(PS-BEPS) with 15 wt% each of PS₄-DCE and S₈.

requiring transparency both in the visible and short-wave-length NIR regions.

Conclusions

We have demonstrated a solvent-free method of preparing HRIPs with a high transparency window spanning from 400 to 2200 nm wherein the refractive index (n_d) could be systematically varied from 1.700 to over 1.745 without changes in the polymers' birefringence, T_g , or dn/dT . This simple, thiol-free polymerization method involves the copolymerization of a bis (episulfide), BEPS, with various polysulfide polymers and chalcogenide additives, resulting in HRIPs with a very low optical dispersion (chromatic aberration) with V_D exceeding 30 even at a n_d of 1.745. The very low birefringence ($\Delta n < 0.0020$) and the high intrinsic refractive index (n_∞) values, which exceed those reported from high-index polyimides, were observed and attributed to the lack of highly polarizable groups such as aromatic moieties and halides (-Br and -I) in the newly developed HRIPs. The combination of optical properties ($n > 1.7$, $\Delta n < 0.0020$, and $V_D > 30$), along with the modular controllability of n , make the p(PS-BEPS) suitable not only for applications requiring advanced HRIPs but also for applications requiring precise index matching at high- n ranges.

Author contributions

JL and SHJ devised the project and the main conceptual ideas. YJ, JC, and DS designed and carried out the synthesis of polysulfide polymers and the thermosets therefrom. YJ and JC carried out the thermal and optical analyses of the materials. YJ, JC, and JL drafted the manuscript and designed the figures. The initial draft was edited and developed through the contribution of all authors.

Conflicts of interest

There are no conflicts to declare.

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