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Synthesis and characterization of thianthrene-based epoxy with high refractive index over 1.7

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ABSTRACT
A novel glycidyl resin 2,7-bis(β-epoxypropylthio)thianthrene (4SEP) with high refractive index was synthesized and characterized by ^{1}H NMR, FT IR and FD-MS analyses. The kinetics of 4SEP cured with methylhexahydrophthalic anhydride (MeHHPA) was investigated by nonisothermal differential scanning calorimetry. The results revealed that the reactivity of 4SEP was higher compared with that of diglycidyl ether of bisphenol A (DGEBA) due to the weakened electron-withdrawing effect of thioether on the epoxy group. The thermal properties and refractive index of 4SEP/MeHHPA were investigated with differential scanning calorimetry, thermogravimetric analyses, Abbe refractometer, prism coupler, and compared with those of the DGEBA/MeHHPA. Experimental results showed that, due to the introduction of thianthrene and thioether units, the glass transition temperature (T_g) was slightly enhanced, while the thermal stability was reduced. The refractive index of 4SEP was over 1.7000, and the refractive index of 4SEP/MeHHPA was up to 1.6808.

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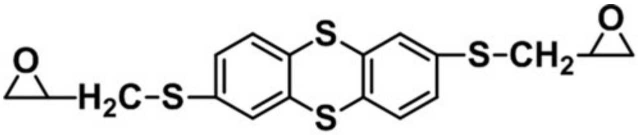
Epoxy resins; refractive index; thianthrene; thioether; sulfur

GRAPHICAL ABSTRACT



High refractive index at 632.8 nm (n>1.70)

Introduction

Epoxy resins, the most common and important thermosetting polymers, have been widely used in industry, as coating, adhesives, composite matrix, etc., due to their chemical resistance, small shrinkage, good processability and excellent mechanical properties. Light emitting diode (LED) encapsulation is one of the important applications of epoxy resins.[1] Gallium nitride chip of LED possesses high refractive index of about 2.2, while the refractive index of the ordinary epoxy-cured product is only about 1.57, the refractive index difference of these two mediums can cause total internal reflection when light travels from the die into the encapsulant at certain incident angles and can result in low light output (only 10% of the theoretical light extraction efficiency).[2–4] Moreover, the trapped light is converted into heat and brings problems to the LED. To effectively reduce the trapped light and improve the light-extraction efficiency, the refractive index of encapsulant materials should be as high as possible. Theoretical calculations show that the light extraction efficiency will be $>30\%$ when the refractive index of the encapsulant material is >1.7.[5]

According to the Lorentz-Lorenz equation, the introduction of substituents with high molar refractions, low molar volumes, or high density can increase the refractive indices of conventional polymers.[6] Among the substituents, the sulfur-containing groups might be one of the most promising candidates. Thioethers and thioalcohols are usually used to prepare epoxy resins with high refractive indexes.[7–9] Cui et al.[10] synthesized a thioether glycidyl resin bis[3-(2,3-epoxypropylthio)phenyl]-sulfone with high refractive index by condensation of bis(3-mercaptophenyl)sulfone with epichlorohydrin. The epoxy was cured with trimercaptothioethylamine to yield the cured resin with a high refractive index of 1.67. Luo et al.[11] synthesized a novel curing agent containing phosphorus and sulfur, the curing agent was mixed with triethylenetetramine and an epoxy prepolymer at a certain ratio to generate cured samples. The cured product yielded a refractive index as high as 1.593. Katsumasa et al.[12] patented a diglycidyl ether of thiodibenzenethiol epoxy resin with the refactive index of 1.669, which is the ever-reported highest refractive index of extant epoxy resins.

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The thianthrene group is a thermally stable heterocycle that has been incorporated into the backbones of several different types of polymers.[13,14] The thianthrene moiety has two sulfur atoms in the cyclic structure, which increases the sulfur content of the repeating unit. Moreover, the bent structures of the thianthrene ring may suppress packing between the polymer chains, which is required for high transparency. Recently, a series of thianthrene-containing polymers that exhibited high refractive indices were synthesized and characterized for optical applications, including polyimides,[15] poly(phenylene sulfide)s,[16–18] and acrylates.[19] Suzuki et al.[20] prepared a series of high refractive index poly(phenylene sulfide)s (PPSs) from 2,7-difluorothianthrene and dithiols. The PPSs showed excellent thermal stabilities and very high refractive indices reaching 1.8020. You et al.[19] prepared acrylate resins by photopolymerization under UV irradiation. The acrylate resin derived from 2,7-bis[(2-acryloylethyl)sulfanyl]thianthrene exhibited a very high-refractive index of 1.6645, which is one of the highest refractive photocurable polymer resins developed so far. However, the thianthrene-containing epoxy resins have not been reported to date.

To further increase the refractive index of epoxy resins, in this study, we introduced both thianthrene and thioether groups into the backbone of the epoxy resin. Firstly, the thianthrene group has high sulfur content, its rigid structure facilitates the close packing of the polymer chains, increasing the refractive index and thermal properties of the resulting resins. Secondly, the introduction of thioether groups can simultaneously increase the refractive index and toughness of the resins. The synthesis and characterization of the novel epoxy was reported. The thermal properties and refractive indices of the cured resins were investigated with those of DGEBA for comparison.

Results and discussion

Synthesis and characterization

The epoxy resin 4SEP was synthesized through a five-step procedure, as shown in Scheme 1. In the experiments, thianthrene-2,7-dithiol (TDT) reacted with epichlorohydrin (ECH) by ring-opening polyaddition reaction in the presence of ethanol and NaOH, then a ring-closure reaction gave rise to 4SEP with a yield >68%. This procedure has been proven to be an efficient pathway for the preparation of thioether glycidyl resin.[10]

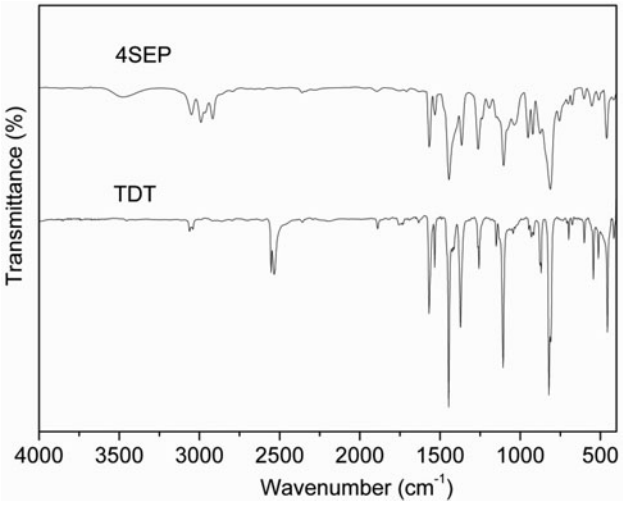
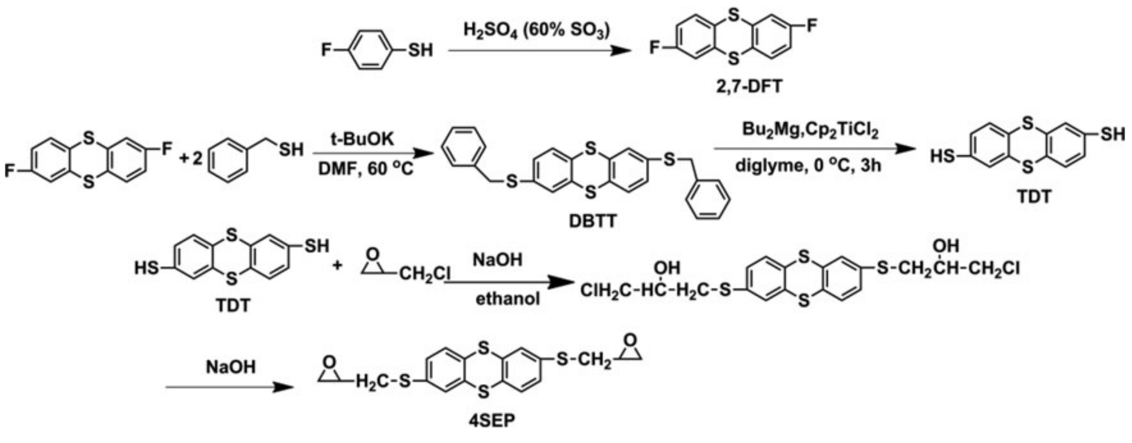


Figure 1. FT IR spectra of TDT and 4SEP.

Figure 1 shows the FTIR spectrum of 4SEP and TDT. It can be seen that the –SH group appearing at 2530 cm^{-1} in TDT disappeared in 4SEP, and the characteristic band of the oxirane rings was detected at 920 cm^{-1} in 4SEP. Furthermore, the symmetric stretching vibration and asymmetric stretching vibration absorptions of the saturated C-H bond of oxirane rings were also observed at 2983 cm^{-1} and 2915 cm^{-1}, respectively. The absorption in the range of 3600–3300 cm^{-1} was assigned to the hydroxyl groups which existed in the oligomers. The absorptions of the thioether (C-S-C) was observed at 1102 cm^{-1}.[15] Figure 2(A) is the ^{1}H NMR spectra of 4SEP. The peaks at 2.92 ppm, 2.70 ppm and 2.47 ppm were assigned to the protons in the oxirane ring. The signal at 3.06 ppm was assigned to the protons of methylene connected the thioether group and the oxirane ring, the peaks at 7.42 ppm, 7.26 ppm and 7.19 ppm were specified to the protons of benzene ring. Figure 2(B) is the ^{13}C NMR spectra of 4SEP. Signals at 136.5, 135.7, 133.4, 129.6, 129.3 and 129.0 ppm were ascribed to the carbons in the aromatic rings, e.g. C_9, C_8, C_7, C_6, C_5 and C_4, respectively. The



Scheme 1. Synthesis of epoxy resin 4SEP.

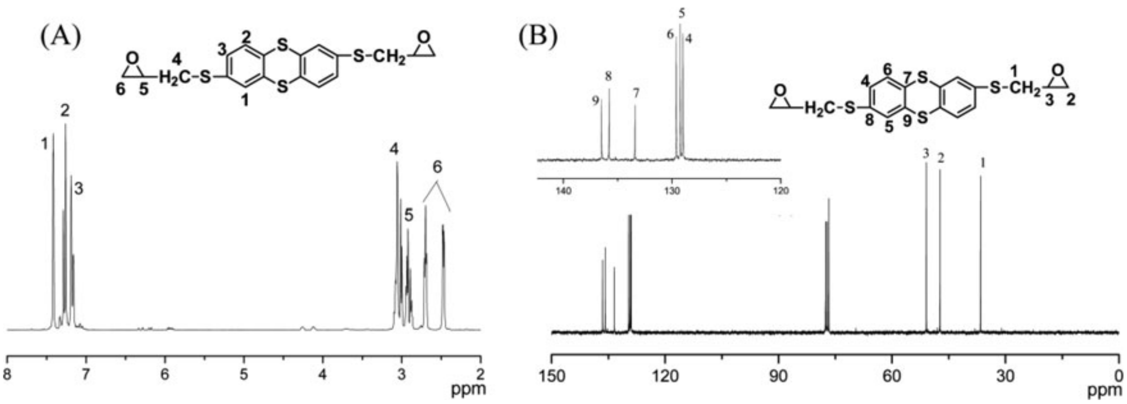


Figure 2. ^1H-NMR (400MHz, $CDCl_3$) (A) and ^{13}C-NMR (400MHz, $CDCl_3$) (B) spectra of 4SEP epoxy resin.

aliphatic carbons (C_3, C_2, and C_1) were observed at 50.9, 47.5 and 36.6 ppm. The FD-MS spectra of 4SEP is shown in Figure 3. The molecular ions peak was at m/z = 392.25, which was the molecular weight of 4SEP. The purity of 4SEP, determined by the relative abundance, was 88.8%. The product also contained a small amount of oligomers, its molecular weight was 728.51, which was in agreement with the results of FTIR.

Curing of epoxy resins

The curing kinetics of the epoxy resins was studied using non-isothermal differential scanning (DSC) calorimeter at various heating rates (β) 5, 10, 15 and 20 °C/min (Figure 4). The curing of the two epoxy resin systems exhibited only one exothermic peak during the non-isothermal DSC analysis. Table 1 lists the exothermic peak temperature (T_p), which increase with increasing heating rate. Based on the DSC data, activation energies (E_a) were calculated using Ozawa's equation[21,22] and the reaction orders were determined with Crane equation.[23] The plots are shown in Figure 5 and the results are summarized in Table 1. As seen in Table 1, 4SEP/MeHHPA and DGEBA/MeHHPA show the same reaction order of 1.1. The apparent activation energy of 4SEP/MeHHPA was 61.38 kJ/mol, about 6 kJ/mol less than that of DGEBA/MeHHPA, indicating the higher reactivity of 4SEP.

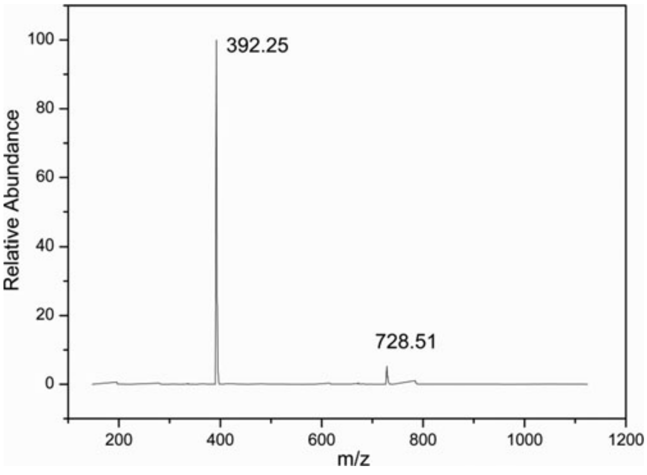


Figure 3. FD-MS spectrum of 4SEP.

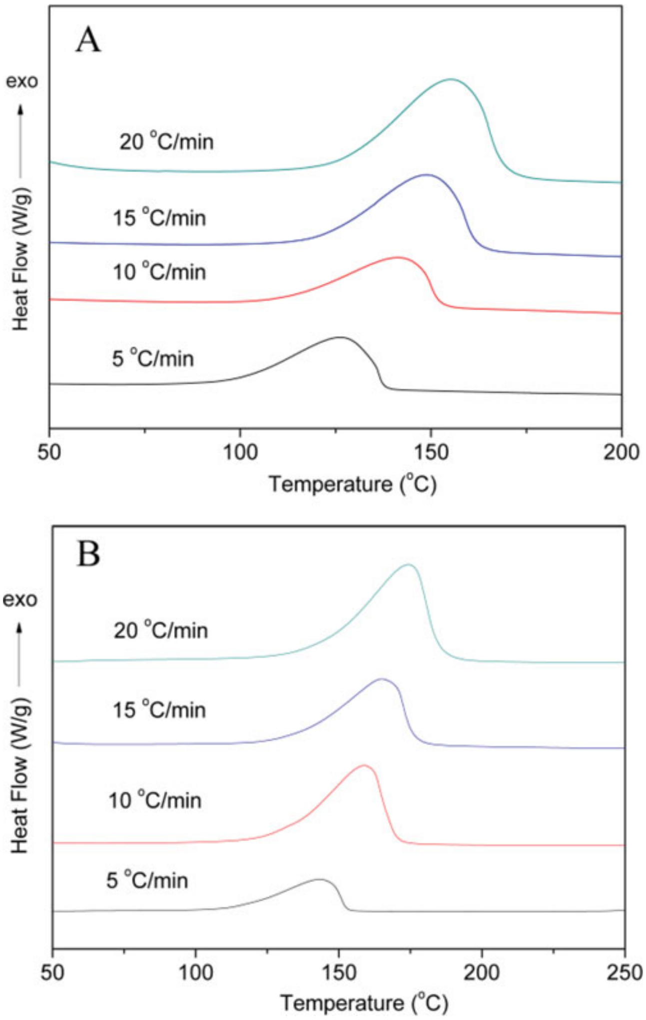


Figure 4. DSC thermograms of 4SEP/MeHHPA (A) and DGEBA/ MeHHPA (B) at 5, 10, 15, 20 °C/min heating rates in N_2 atmosphere.

Table 1. DSC data for DGEBA/MeHHPA and 4SEP/MeHHPA.

	Exothermic peak temperature (°C) at different heating rate (°C/min)					
Samples	5	10	15	20	Ozawa E_a(kJ/mol)	Reaction order
DGEBA/MeHHPA	143.3	158.9	165.1	174.3	67.43	1.05
4SEP/MeHHPA	126.2	141.5	148.9	155.2	61.38	1.11

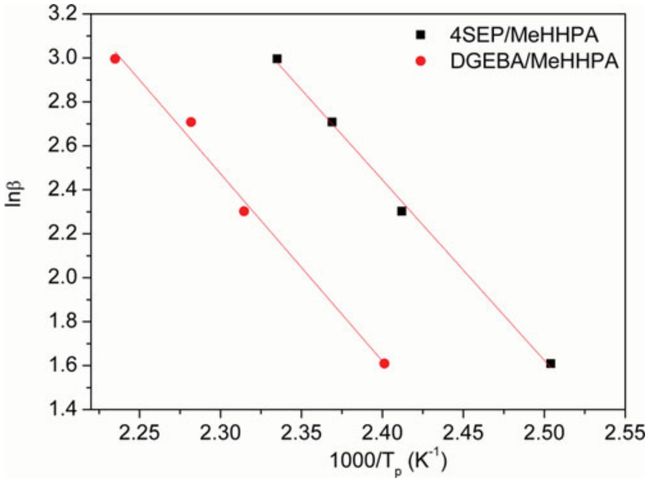


Figure 5. The plots of Ozawa of 4SEP/MeHHPA and DGEBA/ MeHHPA.

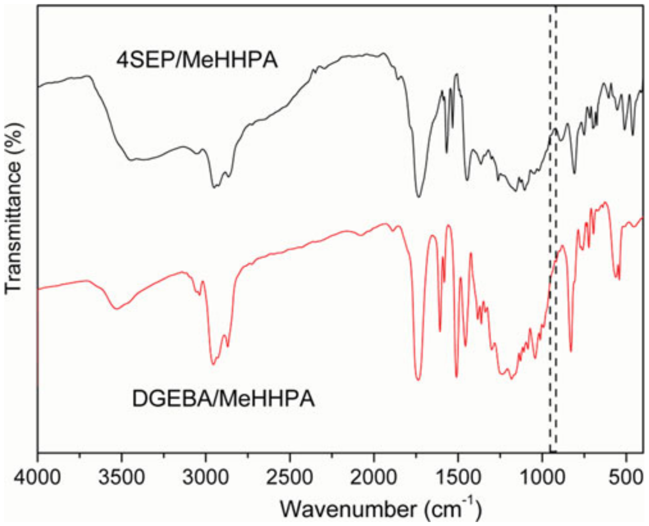


Figure 7. FTIR spectra of cured 4SEP/MeHHPA and DGEBA/ MeHHPA.

The reaction mechanism for epoxy anhydride curing with phosphonium salts by Smith dates back to 1973.[24] The curing mechanism of 4SEP and MeHHPA with BPP is shown in Figure 6. The acidic protons of the methylene group attatched to the phosphine phosphorus atom would be available for bonding with nucleophiles such as an epoxy oxygen. Thus, the epoxy-phosphonium salt adduct is formed, which is vulnerable to attack by another epoxy molecule resulting in the formation of an oxonium ion. Also, reaction of this epoxy-phosphonium salt adduct with MeHHPA is likely to form active hydroxyl compounds.

As the electronegativity of sulfur is less than that of oxygen, the electron-withdrawing effect of thioether on the epoxy group of 4SEP is weakened compared with that of DGEBA, so the epoxy-phosphonium salt adduct is more easily formed in the case of 4SEP, thus the activation energy of 4SEP/MeHHPA is less than that of DGEBA/MeHHPA.

Figure 7 shows the FT IR spectra of the cured epoxy resins. The absorptions at 3400∼3600 cm^{-1} were attributed to the secondary hydroxyl groups generated by the ring-opening reaction of epoxy groups. The characteristic epoxy absorptions at 920 cm^{-1} in 4SEP and 915 cm^{-1} in DGEBA disappeared, indicating the complete cure of the epoxy resins.

The X-ray diffractograms of the cured epoxy resins (Figure 8) indicated that all the resins were amorphous polymers, in which no absorption attributed to the crystal structure was detected.[25] The intermolecular distance of epoxy resins can be calculated from the peaks of the halo using Bragg's equation and the results are listed in Table 2. It can be seen that the intermolecular distance of 4SEP/MeHHPA was 4.79 A°, 0.3 A° less than that of DGEBA/MeHHPA. This is inconsistent with the reduced level of crystallinity of thianthrene-containing polymers reported in the literature.[26,27] The possible reason might be that the bent structures of thianthrene ring suppressed packing between the

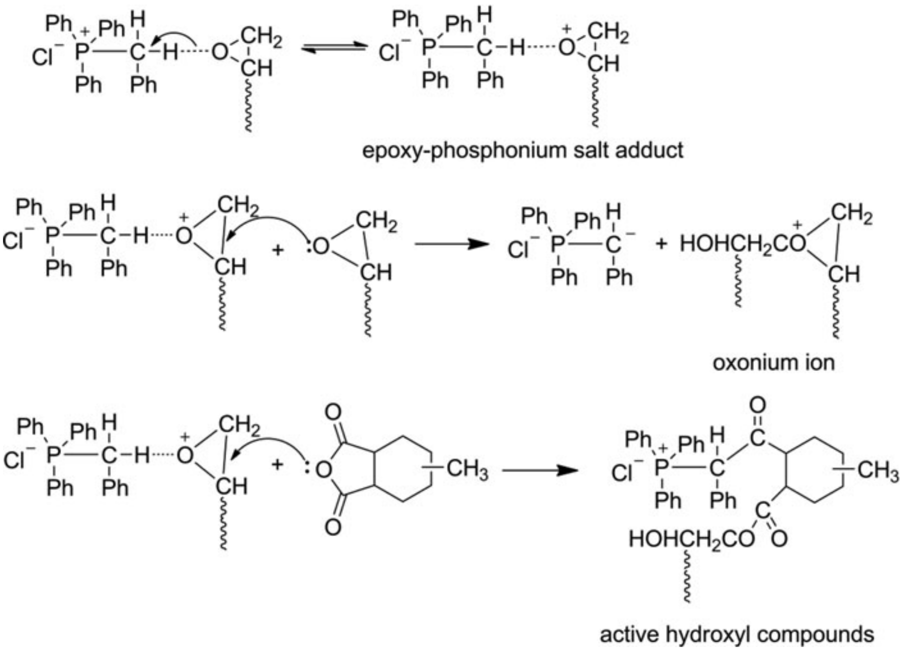


Figure 6. Proposed mechanism of the curing of 4SEP with MeHHPA with phosphonium salt (BPP).

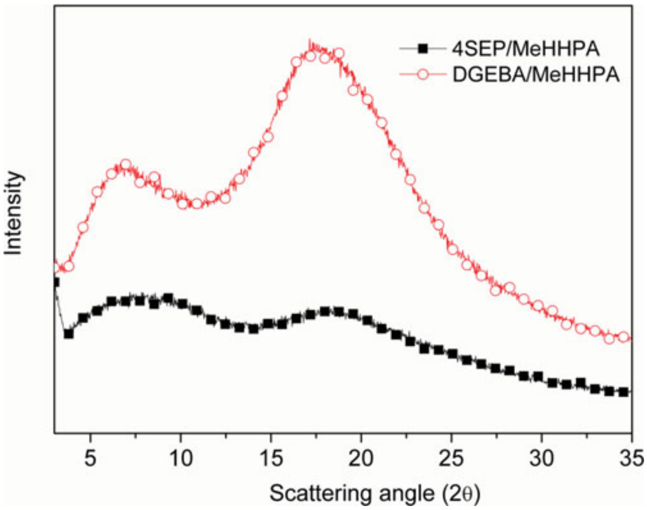


Figure 8. X-ray diffraction patterns of cured 4SEP/MeHHPA and DGEBA/MeHHPA.

Table 2. XRD diffraction patterns and thermal properties of the cured epoxy resins.

	Halo					
Samples	2θ	d(A°)	T_g (°C)	T_5[a] (°C)	T_{10}[a] (°C)	W_{700}[b] (%)
4SEP/MeHHPA	18.49	4.79	150.9	323.1	331.3	37.82
DGEBA/MeHHPA	17.40	5.09	136.5	371.0	392.8	6.93

[a]Temperatures at 5%, 10% weight loss. [b] Residue at 700 °C.

polymer chains, while the flexible thioether groups increased the flexibility of the polymer chains, as a competition result, the molecular chains of 4SEP/MeHHPA packed more tightly than those of the DGEBA/MeHHPA.

Thermal properties of the cured epoxy resin

The thermal properties of the polymers were evaluated by DSC and TGA measurements under a nitrogen atmosphere. The results are summarized in Table 2. The glass transition temperature (T_g) of the polymers, which is one of the most important key parameters for optical device fabrication, was determined by DSC (Figure 9). It can be seen that the T_g of 4SEP/MeHHPA was 150.9 °C, about 14°C higher than that of DGEBA/MeHHPA. This is attributable to the rigid thianthrene unit which prohibits the free motions of the molecular chains.

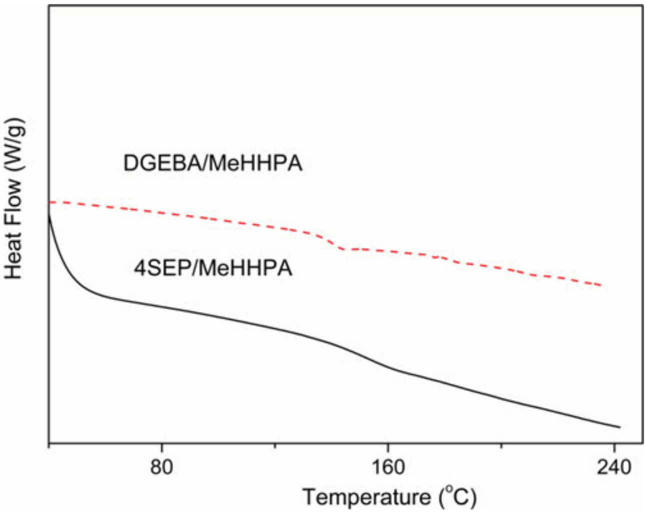


Figure 9. DSC curves of cured 4SEP/MeHHPA and DGEBA/ MeHHPA.

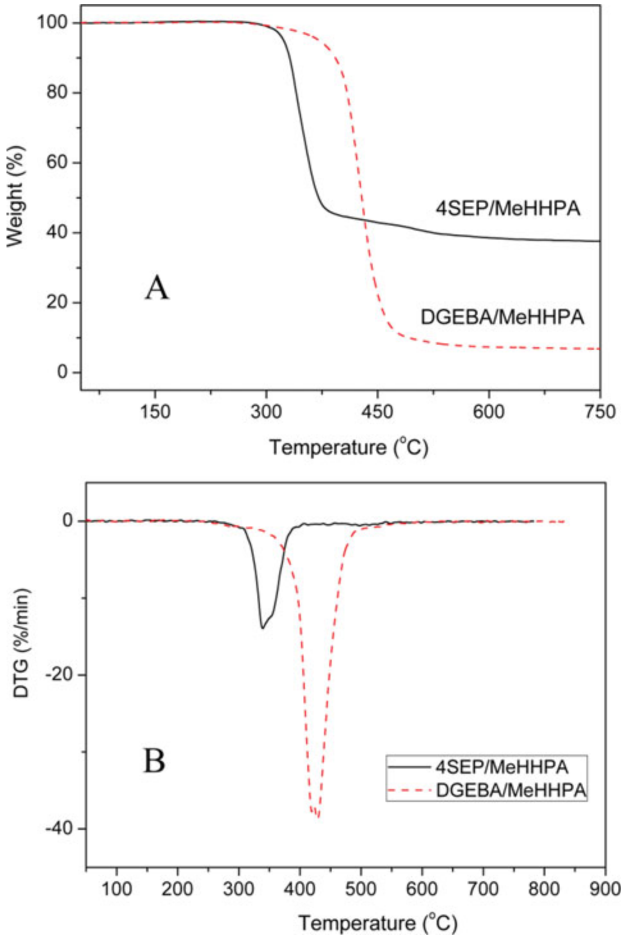


Figure 10. TG (A) and DTG (B) curves of the cured 4SEP/MeHHPA and DGEBA/MeHHPA.

The TG and DTG curves are shown in Figure 10. The cured epoxy resins exhibit good thermal stability up to 323°C. However, the degradation temperatures of 4SEP/MeHHPA are lower than those of the DGEBA/MeHHPA. The low thermal stability of 4SEP/MeHHPA was attributed to the introduction of thioether into the backbone of 4SEP/MeHHPA, as the bonding energy of C-S (272 kJ/mol) is much lower than that of C-O (326 kJ/mol). The residual weight at 700°C of 4SEP/MeHHPA was much higher than that of DGEBA/MeHHPA, indicating its potential as fire retardant.[28,29]

Optical properties of the cured epoxy resin

The refractive indexes of the epoxy prepolymers and the cured epoxy resins were summarized in Table 3. The refractive index

Table 3. Refractive indexes of prepolymer, uncured and cured resins of 4SEP and DGEBA.

Samples	Prepolymers	Uncured resins	Cured resins
4SEP	>1.7000	—	—
DGEBA	1.5730	—	—
4SEP/MeHHPA	—	1.6338	1.6808
DGEBA/MeHHPA	—	1.5452	1.5639

of 4SEP was over 1.70, beyond the range of Abbe refractometer, which is higher than the ever-reported highest refractive index of extant epoxy resins.[12] The refractive indices of uncured and cured 4SEP/MeHHPA were 1.6338 and 1.6808, which were 0.0886 and 0.1169 higher than the corresponding values of DGEBA/MeHHPA resin. The introduction of nonplanar thianthrene moieties was expected to increase molecular free volume of the obtained resins[27] and thus cause a possible decrease in the refractive indexes according to the Lorentz-Lorenz equation. In contrast, the refractive indexes of 4SEP increased. As shown by the XRD results, the thioether of 4SEP increased the dense molecular packing of 4SEP/MeHHPA. Moreover, the sulfur atoms having a high atomic refraction also increased the refractive index of 4SEP/MeHHPA, as 4SEP has a much higher sulfur content (32.67 wt%) than DGEBA (0 wt%). Both the dense molecular packing and high sulfur content contributed to the high refractive index of 4SEP/MeHHPA.

Conclusions

A novel epoxy resin, containing thianthrene and thioether units, was synthesized and characterized by ^{1}H NMR, FT IR and FD-MS analyses. The curing kinetics of 4SEP/MeHHPA was studied using nonisothermal differential scanning calorimetry. The reactivity of 4SEP was improved compared to that of DGEBA, due to weakened electron-withdrawing effect of thioether on the epoxy group.

Cured 4SEP exhibited higher T_g compared with the cured DGEBA, while the thermal stability of the cured 4SEP was lower than that of the cured DGEBA. Due to the high sulfur content, the novel epoxy resin 4SEP showed a very high refractive index ($n_d > 1.70$), which is one of the highest refractive index epoxy resins developed so far.

Experimental

Materials

4-Fluorothiophenol, potassium tert-butoxide, benzylmercaptan, Bis(cyclopenta -dienyl) titanium(IV)dichloride (Cp_2TiCl_2) and dibutylmagnesium were purchased from Sigma-Aldrich, and used as received. DGEBA epoxy resin with an epoxide equivalent weight of 185 g/equiv was purchased from Wuxi resin factory of Blue Star New Chemical Materials Co., Ltd and used as received. MeHHPA and the curing accelerator benzyltriphenylphosphonium chloride (BPP) were purchased from new Japan Chemical Co., Ltd. and Aldrich, respectively. Epichlorohydrin (ECH), sodium hydroxide, methyl isobutyl ketone (MIBK) and ethanol were supplied by Beijing Chemical Reagents Company (China) and used as received. Other commercially available reagents and solvents were used as received.

Synthesis of 2,7-difluorothianthrene (2,7-DFT)

The compound was synthesized according to the reported procedure.[30] FT IR (KBr), (ν_{max}, cm^{-1}):3082 (C-H$_{arom}$), 1596 and 1458 (C=C), 1251 and 1213 (C-F), 1101 (C-S-C). ^{1}H-NMR (400 MHz, DMSO-d$_6$, ppm): 7.61 (m, 2H, Ar-H), 7.54(m, 2H, Ar-H), 7.24(m, 2H, Ar-H).

Synthesis of 2,7-dibenzylthiothianthrene (DBTT)[16]

Potassium tert-butoxide (9.70 g, 86.0 mmol), 2,7-DFT (7.96 g, 31.6 mmol) and N,N-dimethylformamide (DMF) (30 mL) were added into a 100 mL round flask under a nitrogen atmosphere. Benzylmercaptan (10.2 mL, 84 mmol) was slowly added into the mixture cooled with an ice bath. The solution was stirred at 60 °C for 30 h and was poured into water (150 mL). The precipitate was filtered and dried at 80 °C in vacuum. The crude product was recrystallized from 2-methoxyethanol to give 5.56 g of 2,7-dibenzylthiothianthrene as a yellow crystal (70% yield). FT IR (KBr), (ν_{max}, cm^{-1}): 3064, 3035 (C-H$_{arom}$), 2954, 2925 (C-H$_{aliph}$), 1603, 1563, 1450 (C=C), 1103 (C-S-C). ^{1}H-NMR (400 MHz, CDCl$_3$): $\delta = 7.37$ (d, 2H, Ar-H), 7.30 (s, 1H, Ar-H), 7.27 (m, 5H, Ar-H), 7.23–7.24 (m, 6H, Ar-H), 7.13 (d, 1H, Ar-H), 7.06 (d, 1H, Ar-H), 4.07 (s, 4H, CH$_2$). Anal. Calcd. for $C_{26}H_{20}S_4$ (460): C, 67.78; H, 4.38. Found: C, 67.56; H, 4.58%.

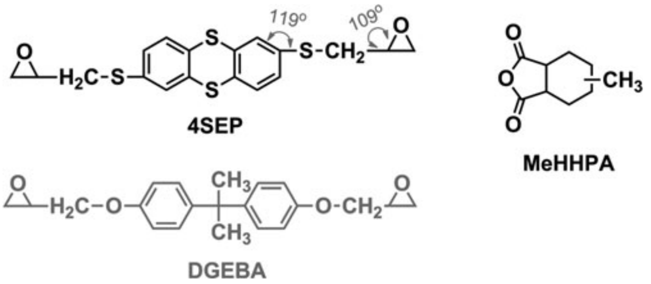
Synthesis of thianthrene-2,7-dithiol (TDT)[16]

DBTT (2.76 g, 6.0 mmol), Cp_2TiCl_2 (0.156 g, 0.62 mmol) and diglyme (20 mL) were added into a freshly dried 100 mL three necked round flask under a nitrogen atmosphere at 0 °C. Dibutylmagnesium (40 mL, 2.5 M) was slowly added to the mixture and the solution was stirred for 5 h. The aqueous solution of Na_2CO_3 (40 mL) was slowly added to the reaction mixture at 0 °C. 50 mL dichloromethane was added to the reaction mixture and mixed thoroughly, after laid still for 1 h, the mixture separated into two layers. The upper aqueous layer was separated, then 30 mL × 3 water was added to the mixture. With a similar procedure, the aqueous layer was separated. The separated aqueous layers were combined, hydrochloric acid was added and the solution was stirred for 1 h. The precipitate was filtered and dried in vacuum to give an ivory-colored powder TDT (0.814 g, 48% yield).

FT IR (KBr), (ν_{max}, cm^{-1}): 3062, 3042 (C-H$_{arom}$), 2533 (-SH), 1568, 1447 (C=C), 1103 (C-S-C). ^{1}H-NMR (400 MHz, CDCl$_3$): $\delta = 7.39$ (d, 2H, Ar-H), 7.32 (s, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.15 (d, 1H, Ar-H), 7.12 (d, 1H, Ar-1H), 3.45 (s, 2H, Ar-H). ^{13}C-NMR (400 MHz, CDCl$_3$): $\delta = 136.80$ (C$_1$), 132.27 (C$_2$), 131.02 (C$_3$), 129.12 (C$_4$), 129.04 (C$_5$), 128.63 (C$_6$). Anal. Calcd. for $C_{12}H_8S_4$ (279): C, 51.39; H, 2.88. Found: C, 51.18; H, 3.02%.

Synthesis of 2,7-bis(β-epoxypropylthio)thianthrene (4SEP)

TDT (4.21 g, 0.015 mol), ethanol (8 mL) and epichlorohydrin (11.8 mL) were added into a 50 mL three-necked round-bottomed flask, which was equipped with a thermometer, stirrer, reflux condenser and nitrogen inlet. When the reaction solution was heated to 50 °C, 1 mL of 20% solution of sodium hydroxide was added and stirred for 30 min. Then 12 mL MIBK was added at a time and 13 mL 20% solution of sodium hydroxide was added drop-wise for 30 min. After stirring at 50 °C for another 2 h, 15 mL MIBK was added. The organic phase was separated and washed with distilled water until neutral. Finally, the solvent and excess epichlorohydrin were distilled out under reduced pressure to yield the thiother glycidyl resin 4SEP as a light yellow transparent viscous liquid (4.0 g, 68% yield). FT IR (KBr) (ν_{max}, cm^{-1}): 3487 (OH), 3058 (C-H$_{arom}$), 2999, 2918 (C-H$_{aliph}$), 1568, 1532, 1443 (C=C), 1102 (C-S-C), 920 (epoxy



Scheme 2. Chemical structures of epoxy resins and curing agent.

group). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (s, 2H, Ar-H), 7.26 (d, 2H, Ar-H), 7.19 (d, 2H, Ar-H), 3.00–3.06 (m, 4H, CH_2), 2.89–2.93 (m, 2H, CH epoxy), 2.70 (t, 2H, CH_2 epoxy), 2.47(dd, J = 6.0 Hz, 2H, CH_2 epoxy). ^{13}C-NMR (400 MHz, $CDCl_3$): 136.5 (C_9), 135.8 (C_8), 133.4 (C_7), 129.6 (C_6), 129.2 (C_5), 129.0 (C_4), 50.9 (C_3), 47.3 (C_2), 36.6 (C_1). FD-MS (m/z): 392.25 (M^+).

Preparation of cured epoxy resins

MeHHPA were used as curing agent to thermally cure the 4SEP and DGEBA epoxy resins. The chemical structures of the epoxy resins and curing agent are shown in Scheme 2. The reaction compositions were mixed homogeneously in a 1:1 molar ratio according to the EEW values. The mass ratio of the accelerator BPP to resin was 0.5:100. The mixtures were degassed in a vacuum and poured into a preheated stainless steel mold, and was cured according to the following curing regime: 120 °C-2 h, 150 °C-1 h.

Characterization

The ^{1}H-NMR was recorded on a BRUKER AVANCE 400 MHz NMR spectrometer, using deuterated chloroform as solvent and tetramethylsilane as internal reference.

The FT IR AQ2 measurement was performed on a BRUKER TENSOR-27 FT IR spectrometer at room temperature in the range of 4000–400 cm^{-1}. Field Desorption mass spectrometry (FD-MS) was carried out on Thermo Fisher Scientific DFS High resolution dual focusing magnetic mass spectrometer with average molecular weight ranging from 80 to 1200 $g.mol^{-1}$, using chloroform as solvent.

DSC was used to investigate the curing behavior of epoxy blends by scanning with a SII EXSTAR6000-DSC6220 from 50 to 300 °C at a heating rate of 5, 10, 15, 20 °C/min in nitrogen. The instrument was calibrated with a high-purity indium standard, and α-Al_2O_3 was used as the reference material. The average activation energy (E_a) for each epoxy system was determined using the Ozawa's methods, as shown Eqs. (1).

$$\frac{d(\ln\beta)}{d(1/Tp)} = \frac{1.052Ea}{R} \tag{1}$$

where β is heating rate, A is preexponential factor, R is universal gas constant, E_a is activation energy of the reaction, and T_p is peak temperature at which the reaction rate is maximum. The plots of lnβ vs 1/T_p give straight lines. E_a values were calculated from the respective slopes of the straight line of the plots. The reaction order was determined using Crane equation shown in Eq. (2)

$$\frac{d(\ln\beta)}{d(1/Tp)} = \frac{Ea}{nR} \tag{2}$$

where n is the reaction order, other parameters are the same as Eq. (1).

TGA was carried out on a SII EXSTAR6000-TGA6300 in nitrogen at 10 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature on a PANalytical EMPYREAN X-ray diffractometer at 40 KV and 40 mA with CuKα radiation ($\lambda = 0.1541$ nm). Refractive indexes of the epoxy monomers and epoxy systems before curing were determined using WZS-1 Abbe refractometer (Shanghai optical instrument factory). Refractive indexes of the 2 mm cured epoxy films formed on 7.62 cm silicon wafers were measured at the wavelength of 632.8 nm with a Metricon Model 2010/M prism coupler.

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