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Introduction

As one of the most practical and convenient synthetic routes in polymer chemistry and material synthesis in recent years, the thiol-ene reaction has attracted significant attention.^{1,2} The reaction was first reported in early 1900s,3 and because of its facile, efficient and robust characteristics, it has become a great success in the preparation of linear, networked polymers and related materials. The process of thiol-ene reaction involves the addition of -SH functionality to the C=C bond (hydrothiolation), and it has numerous advantages, such as producing high yields, excellent regiospecificity and stereospecificity, insensitivity to oxygen or water and reactivity to a wide variety of readily available starting compounds. Therefore, this coupling reaction has been included into the category of "click" chemistry.^{1,2,4} The thiol-ene polymerization proceeds through an alternating combination of propagation and chain transfer reactions, in which a thiyl radical propagates through a carbon-

Phosphorus-containing polymers from tetrakis-(hydroxymethyl)phosphonium sulfate III. A new hydrolysis-resistant tris(allyloxymethyl)phosphine oxide and its thiol-ene reaction under ultraviolet irradiation[†]

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Two kinds of new phosphorus-containing crosslinked polymer materials were prepared *via* thiol-ene photopolymerization and their properties were studied. In order to prepare these crosslinked polymer materials, multifunctional monomer tris(allyloxymethyl)phosphine oxide (TAOPO) was synthesized from an eco-friendly raw material, tetrakis(hydroxymethyl) phosphonium sulfate (THPS). Crosslinked poly(phosphine oxide) networks were then produced by a thiol-ene reaction in which TAOPO reacts with the two kinds of polythiol under ultraviolet (UV) irradiation. The new crosslinked polymers possess long-term hydrolysis-resistance property because the monomer TAOPO contains a phosphorus–carbon bond. The crosslinked polymers have a high gel content, high dielectric constant, low dielectric loss, and excellent transparency with a high refractive index and high Abbe number. DMA and TGA results indicated that all cured poly(phosphine oxide) were uniform networks and exhibited a high thermal stability.

carbon double bond, generating a carbon-centered radical that abstracts a hydrogen atom from a thiol group to regenerate a thiyl radical. Except for the traditional thermally activated radical initiators or photoinitiators, transition-metal-based catalysts⁵ and ultra-sound⁶ have always been involved in the thiol-ene reaction. More recently, Bowman and co-workers7 reported that the thiol-ene click reactions were initiated by redox initiation systems. In addition, the thiol-ene reaction possess the ability of delaying the gelation of multifunctional monomer systems, which reduces both the shrinkage and the shrinkage stress induced by polymerization.14,8 Taking all these merits into account, it is understandable that the thiol-ene click reaction has been widely utilized as a versatile tool in numerous macromolecular synthetic strategies.1,2 Moreover, the wellknown sulfur-containing polymer and other heteroatoms, such as silicon,9-11 germanium12 and metal atoms13 have been successfully introduced into polymers by the thiol-ene reaction.

Surprisingly, up to now, there were only a few reports concerning the phosphorus-involved thiol-ene reaction.¹⁴⁻¹⁶ In addition, phosphorus is one of the most abundant elements on the earth and small amounts of phosphorus in a polymer can be greatly advantageous.¹⁷⁻²² In general, two kinds of phosphoruscontaining polymer have been widely studied, namely poly-(phosphoester) and poly(phosphine oxide). Polyphosphoesters have been attracting significant attentions in the field of phosphorus-containing polymers for its excellent properties, such as biodegradability, biocompatibility and the ease of

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Scheme 1 Synthesis of tris(allyloxymethyl)phosphine oxide (TAOPO).



Scheme 2 Thiol-ene reaction of TAOPO with polythiols under UV irradiation.

preparation. However, the main disadvantage of polyphosphoester is the lack of long-term hydrolytic stability, which limits their use in many practical applications.¹⁷ Whereas, poly(phosphine oxide)s show excellent resistant to hydrolysis because this kind of polymer is formed though P–C bond linkages.^{23–26} In recent years, phosphorus–carbon bonds containing monomers and polymers have been the subject of extensive research.^{27–31}

In this article, a convenient method to prepare crosslinked poly(phosphine oxide) by the aid of thiol-ene reaction is proposed for the first time. The corresponding phosphorus– carbon bonds containing trifunctional monomer, tris(allyloxymethyl)phosphine oxide (TAOPO) was prepared from tetrakis(hydroxymethyl)phosphonium sulfate (THPS), which is an environment-friendly chemical (Scheme 1). This monomer then underwent a thiol-ene reaction with polythiols (Scheme 2) under UV irradiation to form poly(phosphine oxide)s networks. The crosslinked material showed excellent optical, thermal and dielectric properties.

Materials and methods

Materials

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS, 75%) was purchased from Hubei Xingfa Chemical Company, China; 2,3bis[(2-mercaptoethyl)thio]-1-propanethiol(tri-thiol, >98%) was obtained as a gift from Zhenjiang Junshi Optics Co., Ltd, China; pentaerythritol tetrakis(2-mercaptoacetate) (tetrathiol, \geq 95%) was purchased from Qingdao Jiahua Chemical Co., Ltd, China; allyl chloride (>98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, >98%), benzyltriethylammonium chloride (>98%), H₂O₂ (30%), chloroform (\geq 99.0%), Na₂SO₄ (\geq 99.0%), NaOH (\geq 99.0%) and anhydrous ethanol (\geq 99.7%) were purchased from Sinopharm Group Co., Ltd and used directly without further purification.

Synthesis of tris(hydroxymethyl)phosphine oxide (THPO)

THPO was prepared according to a previously reported procedure³² with some modifications. NaOH aqueous (30%) was dropped into THPS solution (500 g, 75%, 0.92 mol) with

vigorous stirring, and the reaction system was maintained below 5 °C. When the pH value of the mixture reached 12, the reaction was continued for another 2 h, and then successively at room temperature for half an hour. The reaction temperature was then raised to 50-60 °C. The reaction process was monitored by ³¹P NMR and was stopped when a single peak was obtained at 48.19 ppm. The mixture was neutralized to pH 7 by the addition of H₂SO₄ solution (1 M), after cooling it to room temperature. Ethanol (1 L) was then added to the mixture and the precipitated Na₂SO₄ was removed by filtration. The procedure was repeated for several times, until no SO₄²⁻ was detected by a Ba²⁺ test. All the volatiles were separated out by rotary evaporation at 90 °C under vacuum, producing 220 g (yield 82%) of a colorless viscous liquid. ¹H NMR (400 Hz, DMSO-d₆, δ): 3.83 (6H, CH₂), 5.45(3H, OH). ³¹P NMR (400 Hz, DMSO-d₆, δ): 48.19. IR: $\nu = 3314.28(\text{O-H})$, 1423.44 (O-H), 2897.86, 2825.13(CH₂), 1135.73 (P=O), 1042.76 (C-O-C).

Synthesis of tris(allyloxymethyl)phosphine oxide (TAOPO)

To a mixture of THPO (7 g, 0.05 mol) and benzyltriethylammonium chloride (0.7 g, 10% weight percent of THPO), an aqueous solution of NaOH (20 mL, 30%) was added at such a pace that the temperature of the reaction mixture was maintained below 35 °C with mechanical stirring. After the addition, the mixture was cooled to 0 °C by immersing it in an ice-water bath. Allyl chloride (15.23 g, 0.195 mol) was slowly added dropwise to this solution with stirring for 2 h maintaining the temperature below 5 °C. The temperature was then increased and maintained at 50 °C for 10 h. After cooling it to room temperature, required amount of water was added to dissolve the byproduct, NaCl. The organic layer was separated and washed several times with water, until no Cl⁻ ion was detected, and then dried overnight with anhydrous Na₂SO₄. After filtration, the remaining allyl chloride was distilled out at 40 °C under normal pressure. Finally, the remaining product was placed in high vacuum to remove all the volatiles. 10.4 g (yield 80%) of colorless or light yellow liquid was obtained. ¹H NMR (400 Hz, DMSO-d₆, δ): 4.07(6H, P-CH₂-O), 3.87(6H, O- CH_2 -C), 5.86 (3H, -CH=), 5.22-5.31 (6H, =CH₂). ¹³C NMR (400 Hz, DMSO-d₆, δ): 63.64-64.42 (CH₂-P), 73.99 (CH₂-O), 117.63 $(=CH_2)$, 134.58 $(=CH_2)$. ³¹P NMR (400 Hz, DMSO-d₆, δ): 37.43. IR: $\nu = 3080.74$ (=C-H), 2982.43, 2855.63(CH₂), 1645.05(C=C), 1185.22 (P=O), 1091.66 (C-O-C). HRMS(ESI): m/z: calcd for $C_{12}H_{21}O_4P [M + Na]^+$ 283.2563; found 283.1067.

Thiol-ene reaction of TAOPO with polythiols under UV irradiation

Under an argon atmosphere, DMPA (1% weight of ene monomer) was added as a photoinitiator to a certain amount of trithiol(or tetra-thiol), and completely dissolved by stirring. A certain amount of oxygen-free TAOPO was added to the mixture and stirred under argon atmosphere until a homogeneous system was formed. The obtained mixture was transferred to a quartz mold under argon and then exposed to UV light to accomplish the polymerization. In order to avoid excessive



heating, it was exposed to UV light in a discrete manner with 3 min intervals between two successive exposures.

Characterization

¹H, ¹³C and ³¹P NMR spectra of the monomers were recorded using a 400 MHz Bruker NMR spectrometer in DMSO-d₆ containing small amounts of TMS as internal standard. Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex 70 FTIR spectrometer. Liquid samples were prepared by casting on KBr windows and recorded at room temperature in the region of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. Cured polymer samples attached to an ATR plate with a horizontal ATR accessory were used for the measurements. The spectra were obtained by collecting 1024 scans with a spectral range of 4000- 650 cm^{-1} with a resolution of 2 cm⁻¹. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer Thermal Analyser under a N₂ atmosphere at a rate of 20 °C min⁻¹ from 40 to 850 °C. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMA) apparatus (Perkin Elmer, Diamond DMA). Specimens (50 \times 10 \times 1.0 mm) were tested in three-points bending mode. The thermal transitions were studied in the scope of 20-200 °C at a heating rate of 4 °C min⁻¹ and at a fixed frequency of 1 Hz. Optical transmission measurements were performed on polished polymers using an UV-vis spectrophotometer (Shimadzu UV-2550). Samples were ground and polished to a path length of 2.5 mm. The refractive indices were obtained at 546 nm using an Abbe refractometer (NAR-4T) at 20 °C. The bulk density of the polymers was obtained by placing dry, preweighed samples in a glass pycnometer, and filling the rest of the volume with distilled water at 20 °C. The densities were calculated from the weight difference and the known density of water at 20 °C. Five observations were taken for each sample, and the average was used for density calculation. Dielectric constant and dielectric loss were measured at room temperature in an air atmosphere by two parallel plate modes at 125-18 000 Hz using an Agilent 4294A Precision Impedance Analyzer. Prior to each measurement, the sample was thoroughly dried under vacuum to reduce the influence of the absorbed moisture on the dielectric constant. The gel content of photopolymerized polymer was measured by standard solvent-extraction method, and chloroform was used as the extraction solvent.

Results and discussion

Synthesis of THPO and TAOPO

The new phosphorus-containing triallyl ether monomer, TAOPO was synthesized as shown in Scheme 1. First, the THPS underwent decomposition reaction under strong basic conditions to form tris(hydroxymethyl)phosphine (THP). The THP was very sensitive to oxygen, therefore it was immediately oxidized by air to stable THPO, under the reaction conditions.³³ The reaction was monitored with ³¹P NMR (Fig. S1 in ESI†). According to the results of monitoring, the reaction for preparing THPO was completed within 5 hours at 50–60 °C.

TAOPO was prepared by the standard with the aid of phase transfer catalyst (PTC). Williamson method involves



Fig. 2 FT-IR spectrum of reaction mixture for different UV (0.61 mW cm^{-2}) exposure time. (a): 0 min; (b): 1 min; (c): 2 min; (d): 3 min; (e): 4 min; and (f): 5 min.

Table 1 The gel content of the cured products with different formulations

$n_{\mathrm{C}=\mathrm{C}}: n_{-\mathrm{SH}}$	1:0.5	1:0.7	1:0.9	1:1	1:1.1
Gel/% (tri-thiol)	79.6	93.6	96.1	96.1	98.9
Gel/% (tetra-thiol)	85.6	95.7	96.5	98.0	98.2

transformation of hydroxyl group into sodium alkoxide with sodium hydroxide, and successive treatment with allyl chloride.³⁴ The optimal concentration of NaOH was 30% (w/w) in this preparation. For the details of the optimal concentration of NaOH please refer to the literature.³⁵

The chemical structure of TAOPO was confirmed by NMR spectroscopy. Fig. 1a indicates that only one septet peak appeared, centered at 37.43 ppm, which implies that the phosphorus atom was surrounded by three carbon atoms. This result was in good agreement with the desired structure. The ¹H NMR spectrum (Fig. 1b) indicated that a signal attributed to P-CH₂-O was located at 4.07 ppm, the signal for O-CH₂-C was at 3.87 ppm, the signal for -CH= was at 5.86 ppm and the signal for ==CH₂ was at 5.22–5.31 ppm. The integration ratio between



Fig. 3 Digital images of UV-cured resin samples, (a) TAOPO/tri-thiol, (b) TAOPO/tetra-thiol, (the inside characters implies the molar ratio of vinyl group to thiol group).

Table 2 Optical properties of crosslinked polymer networks

these signals agreed with the monomer structure bearing three allyl moieties. The ¹³C NMR (Fig. 1c) spectrum indicated that a signal at 63.64–64.42 ppm attributed to the carbon connecting to phosphorus atom, the signal at 73.99 ppm attributed to the carbon between oxygen and vinyl group, and the signal at 117.63 ppm and 134.58 ppm attributed to the two vinyl carbons, respectively. ESI-MS results and FTIR spectrum also gave positive proof for the chemical structure of TAOPO (Please see Experimental section).

Preparation of crosslinked polymer network

The thiol-ene coupling reaction between TAOPO and trithiol (vinyl–SH = 1 : 1) was monitored by FTIR spectrum. As shown in Fig. 2, under UV irradiation, the reaction progressed smoothly and the typical absorption band gradually decreased with extending irradiation time. The absorption peaks at 1644 cm⁻¹ for C=C double bond and at 2535 cm⁻¹ for S-H bond completely disappeared within 5 minutes, which implies that all monomers were consumed to form a highly crosslinked polymer network.³⁶

According to optimal polymerization conditions, a series of cured polymer samples were prepared. All samples were transparent with light yellow color. The gel content of the samples was measured by a solvent-extraction method to estimate the crosslinking degree of cured resins,³⁷ and the results were collected in Table 1. At high vinyl/thiol molar ratio (1 : 0.5), the gel content of cured samples was less than 90%. When the molar ratio of double bond to thiol group approached to 1 : 1, the gel content of cured samples increased to about 99%, which implies that nearly all the monomers joined the crosslinked network.

Optical properties of crosslinked polymer network

Transparent optical-quality plastics provide large advantages over metal oxide glasses in terms of weight reduction and fracture resistance.³⁷ The refractive index is very significant for optical resins. A great effort has been made in designing and preparing high refractive index polymers. The universal method to improve the refractive index of polymers is to introduce polarizable atoms and groups into the backbones of polymers

TAOPO	$n_{\rm C=C}: n_{\rm -SH}$	1:0.5	1:0.7	1:0.9	1:1	1:1.1
Tri-thiol	$n_{\rm D}^{\ a}$	1.6270	1.6365	1.6385	1.6456	1.6545
	$V_{\rm D}^{\ \ b}$	62.0	37.7	36.1	34.0	35.1
	Cutoff ^c UV/nm	304	308	304	306	298
	Transmittance ^d /%	70.1	70	70.5	79.4	84.9
	Density/g cm $^{-3}$	1.199	1.241	1.253	1.264	1.267
Tetra-thiol	n _D	1.5835	1.5905	1.5945	1.5952	1.5965
	V_{D}	43.9	36.0	42.2	38.3	42.4
	Cutoff UV/nm	308	308	310	310	309
	Transmittance/%	72.3	76.8	80.3	84.5	85.4
	Density/g cm^{-3}	1.244	1.292	1.317	1.327	1.331

^{*a*} The refractive indices were obtained at 546 nm at 20 °C. ^{*b*} Abbe number. ^{*c*} UV cut-off wavelength. ^{*d*} Optical transmission measurements were performed on polished polymers at 550 nm.



Fig. 4 n_D varying with P and S content% (a) TAOPO/tri-thiol, (b) TAOPO/tetra-thiol.

or as attached pendant groups.² Recent interests have been focused on the incorporation of sulfur atoms into polymer structure because this approach can provide a high refractive index and Abbe number for optical plastics.^{38,39} The thiol-ene reaction is obviously an ideal route to reach this target. In order to vividly show the transparency of UV-cured polymers, the



Fig. 5 Transmittance of the cured products, (a) TAOPO/tri-thiol, and (b) TAOPO/tetra-thiol.

polymer samples of 2 mm thickness were kept on a paper with printed characters and their transparency were estimated by observing the definition of characters. The digital images of UVcured resin samples (Fig. 3) indicated that all samples possessed excellent transparency.

The optical properties of samples are shown in Table 2. The refractive index $(n_{\rm D})$ of cured resins increased with the amount of polythiol. The refractive index values of TAOPO, tri-thiol and tetra-thiol, were 1.4874, 1.5530 and 1.6324, respectively. After photopolymerization, the refractive index of TAOPO/tri-thiol based resin changed from 1.6270 to 1.6545 at different monomer ratios, while, the refractive index of TAOPO/tetrathiol based cured resins changed from 1.5835 to 1.5965. All samples showed high refractive index and possessed potential to be used as optical resins. The relationship between refractive index and content of P and S atom is shown in Fig. 4. The refractive index improved with the increase of S content. In general, S atom is a highly polar element and introducing it into polymer chains would result in a high refractive index resin. The idea has been widely accepted for the prescription of eyewear design.

The Abbe number is another important character for high quality optical resins. It is a measure of the material's dispersion (variation of refractive index with wavelength) in relation to the refractive index, where high value of Abbe number indicates low dispersion. From Table 2, it is clear that all samples have high Abbe number due to the aliphatic characteristics of all the monomers and the large atomic refraction of sulfur and phosphorus atoms.⁴⁰

The UV cut-off wavelength of all cured resin samples were about 300 nm, which indicated that currently prepared polymers had excellent blocking effect on short wavelength UV light, although this formulation did not contain any aryl unit. All resins showed high transmittance at 550 nm in the range of 70% to 85% (Fig. 5). The methods for further improving the transmittance include decreasing the amount of photoinitiator, or adopting new initiating system, as suggested by Stiegman and coworkers.¹² In fact, our recent results showed that the transmittance of cured resins could be improved over 90% at 550 nm if the self-initiation method was adopted to prepare the optical polymer. The density data of all the resins are also listed in Table 2, showing that the density increased with the amount of polythiol.



Fig. 6 E' and tan δ curves of the cured products (a) TAOPO/tri-thiol and (b) TAOPO/tetra-thiol.

Table 3 $T_{\rm g}$, E' (in $T_{\rm g}$ +50 °C) and Young's modulus (*E*) of the cured products

$n_{\rm C=-C}: n_{\rm -SH}$	1:0.7	1:0.9	1:1	1:1.1
Tri-thiol $T_{g}/^{\circ}C$	-18.7	-11.2	-8.9	-8
Tetra-thiol $T_{o}/^{\circ}C$	-5.6	11.7	15	15.7
Tri-thiol E'/MPa	14.26	18.18	19.07	19.16
Tetra-thiol E'/MPa	14.02	19.29	19.7	20.9
Tri-thiol E/MPa	7.52	10.34	10.54	10.82
Tetra-thiol <i>E</i> /MPa	3.4	6.09	7.88	8.27

Mechanical properties and thermal stabilities of crosslinked polymer networks

The mechanical properties of cured resins were estimated by DMA analysis (Fig. 6) and the results are collected in Table 3. The storage modulus (E') and the glass transition temperature (T_g), determined from the peak in the loss tangent, increased with the molar ratio of vinyl group to thiol group. Moreover, the storage modulus and T_g of TAOPO/tetra-thiol series are higher than those of TAOPO/tri-thiol series at the same monomer ratio due to the different crosslinking density.

Another interesting fact was that all loss tangent peaks of the two series had very sharp appearance and the widths were very narrow. From these results, we could deduce that the triallyl ether and polythiol formed a uniform cross-linked network after photopolymerization.⁴¹ The results were significantly consistent with the aforementioned conclusion and proposed polymerization mechanism. Young's moduli of all samples are also given in Table 3. The values of Young's modulus of all resins were not high enough to meet practical need. One of the next efforts is to improve the mechanical properties of the cured resin.

The thermal stabilities of all polymers were studied by TGA and the results are shown in Fig. 7 and Table 4. All the samples, except for the formulation in which the ratio of double bond vs. thiol is 1 : 0.5, showed high thermal stability below 350 °C, however, the crosslinked polymers decomposed rapidly around 400 °C. The char yields of all samples at 850 °C and the limited oxygen index (LOI) based on the char yield are listed in Table 4. Though the calculated LOI value cannot essentially reflect the fire-retardant property of polymer, it is indeed a useful reference for choosing suitable polymers for specific purposes.⁴²



Fig. 7 TGA curves of the cured products (a) TAOPO/tri-thiol and (b) TAOPO/tetra-thiol

Table 4 TGA data of the cured products							
	$n_{C=C}: n_{-SH}$	1:0.5	1:0.7	1:0.9	1:1	1:1.1	
TAOPO/tri-thiol	$T_{5\%}{}^a$ (°C)	204.8	285.8	291.6	293.7	303.3	
	$T_{10\%}^{a}$ (°C)	262.5	309.8	307.2	313.4	322.6	
	$Y_{\rm c}^{\ b}$ (850 °C)	14.29	14.16	14.24	14.26	6.03	
	LOI ^c	23.22	23.16	23.2	23.2	19.91	
TAOPO/tetra-thiol	$T_{5\%}$ (°C)	214.7	310.3	315.8	331.7	343.7	
	$T_{10\%}$ (°C)	292.7	354.7	355.3	356.6	365.7	
	$Y_{\rm c}$ (850 °C)	10.79	14.92	12.36	14.72	14.58	
	LOI	21.82	23.47	22.4	23.39	23.33	

^{*a*} Temperature at which 5 or 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹ under N₂. ^{*b*} Weight percentage of material left after TGA analysis at a maximum temperature of 850 °C under N₂. ^{*c*} Limited oxygen index based on char yield Y_c (850 °C) from semi-empirical formula: LOI = 17.5 + 0.4 Y_c .



Fig. 8 The dielectric constant and dielectric loss of cured products. (a) TAOPO/tri-thiol and (b) TAOPO/tetra-thiol.

Dielectric properties of crosslinked polymer network

The dielectric properties of the thiol-ene systems have attracted a significant attention in recent years because such systems provide a convenient method to prepare crosslinking polymer networks with desired dielectric properties and facilitates the preparation procedure of some microelectronic devices.41,43-45 Therefore, we studied the dependence of the dielectric constant and dielectric loss of TAOPO-polythiol systems on the frequency of the applied field at room temperature. As indicated in Fig. 8, both dielectric constant and dielectric loss of all the samples showed similar variation trends with an increase of frequency because the dielectric constant and dielectric loss of materials depend on the electronic, atomic, and dipolar polarization rate. As the frequency of the applied field increases, the orientation of the polarization of dipolar is suppressed, resulting in a decrease in the dielectric constant and dielectric loss of materials. Comparing with reported results,43 the TAOPO based thiol-ene crosslinking networks showed high dielectric constant and low dielectric loss.

Conclusions

Tris(allyloxymethyl)phosphine oxide, a novel multifunctional monomer, was successfully prepared from an environment-

friendly tetrakis(hydroxymethyl)phosphonium sulfate. The phosphorus–carbon bonds containing monomer showed a high reactivity with polythiol under UV irradiation through a thiolene radical mechanism. As the molar ratio of the double bond to the thiol was near to 1, the gel contents of all crosslinked samples were above 96%. Because of its uniform nature, all samples were highly transparent. The highest refractive index was 1.6545, and the corresponding Abbe number was 35.1. The resulting network polymers showed high thermal stability below 350 °C, and the char yield was above 10% at 850 °C, and the highest LOI based on the char yield from semi-empirical formula was 23. In addition, the TAOPO based thiol-ene crosslinking network polymers showed high dielectric constant and low dielectric loss compared with the reported results.

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