A Novel High-Refractive Index Episulfide-Thiol Polymer for Nanoimprinting Optical Elements

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A novel optical polymer with a high refractive index (n = 1.707 at 590 nm) was developed consisting of episulfide and thiol bifunctional monomers. The episulfide derivative of 9,9-bis(4-glycidyloxyphenyl) fluorene, synthesized by the reaction of an epoxide and inorganic thiocyanate, reacts by a ring-opening polymerization with 4,4-thiodibenzenethiol to produce the optical polymer with high transparency over the visible region of the spectrum and thermally stable up to 290°C. The developed episulfide-thiol optical polymer can be thermally nanoimprinted at 160°C with nanoscale size resolution. Different nanostructures including sub-micron and nanoscale size gratings, two-dimensional photonic crystals, and plano-convex semispherical microlenses were successfully nanoimprinted with excellent pattern fidelity and low defectivity. These results exhibit the episulfide-thiol optical polymer as a potential candidate for applications in optical and optoelectronic devices.

Introduction

The patterning of high refractive index polymers with micro- and nanoscale resolution can drive the development and commercialization of novel high performance optical devices at low costs over large scales. High refractive index polymers are an important class of materials for optical components due to their lightweight, high impact resistance, low cost and easy processing. They can find applications in various optical and optoelectronic devices including light-emitting diodes (LEDs), organic-LED (OLED) systems,[1-5] microlens components for high performance complementary image sensors and high resolution imaging.[6-9] The development of polymeric resins with high refractive index that can act as a functional material for nanoimprint lithography (NIL) is desirable for expanding several applications now confined to research laboratories.[10-14] NIL is a high resolution technology with the potential to realize a cost-effective fabrication of large scale patterns with high precision.[15,16] Very few reports on the direct nanopatterning of high refractive index polymers are available[17]: most common optical polymers exhibit low refractive index (~1.50) and the efforts to reach higher values with high optical transparency and easy processability have encountered significant challenges. The synthesis of organic polymers with refractive index higher than 1.70 has been pursued in recent decades introducing sulfur-containing substituents,[18-26] aromatic conjugated structures into the chemical structure.[27-35] One representative example includes a two component resin with a refractive index of 1.74 and high transparency commercially available from Mitsui Chemicals for ophthalmic lenses.[36] Polymers with refractive index close to 1.80 or higher have also been developed such as poly(phenylene thioether) derived from triazines,[22] hyperbranched molecules,[32] cyanuryl polyimines[34] and thianthrene-based poly(phenylene sulfide)s[21] and polythioamides synthesized in the presence of elemental sulfur.[18] In addition, composites comprising organic polymers blended with high refractive index inorganic nanoparticles have also been reported.[37-45] However, the introduction of these moieties is normally accompanied with a reduction of the optical transparency and deep coloration in the visible region, insoluble and leads to poor processing properties thus restricts their practical application in optical and optoelectronic devices.

Nanoimprinting of high refractive index patterns such as planar optical devices and photonic crystals has been performed using hybrid organic-inorganic materials.[46,47] A concern related to organic-inorganic hybrids involves the large volumetric shrinkage the patterns suffer during a required thermal annealing step.[11,14,48-50] This has been solved developing alternate routes such as reverse imprinting in which the material shrinkage occurs during an intermediate stage.[46,51] A simpler approach would be

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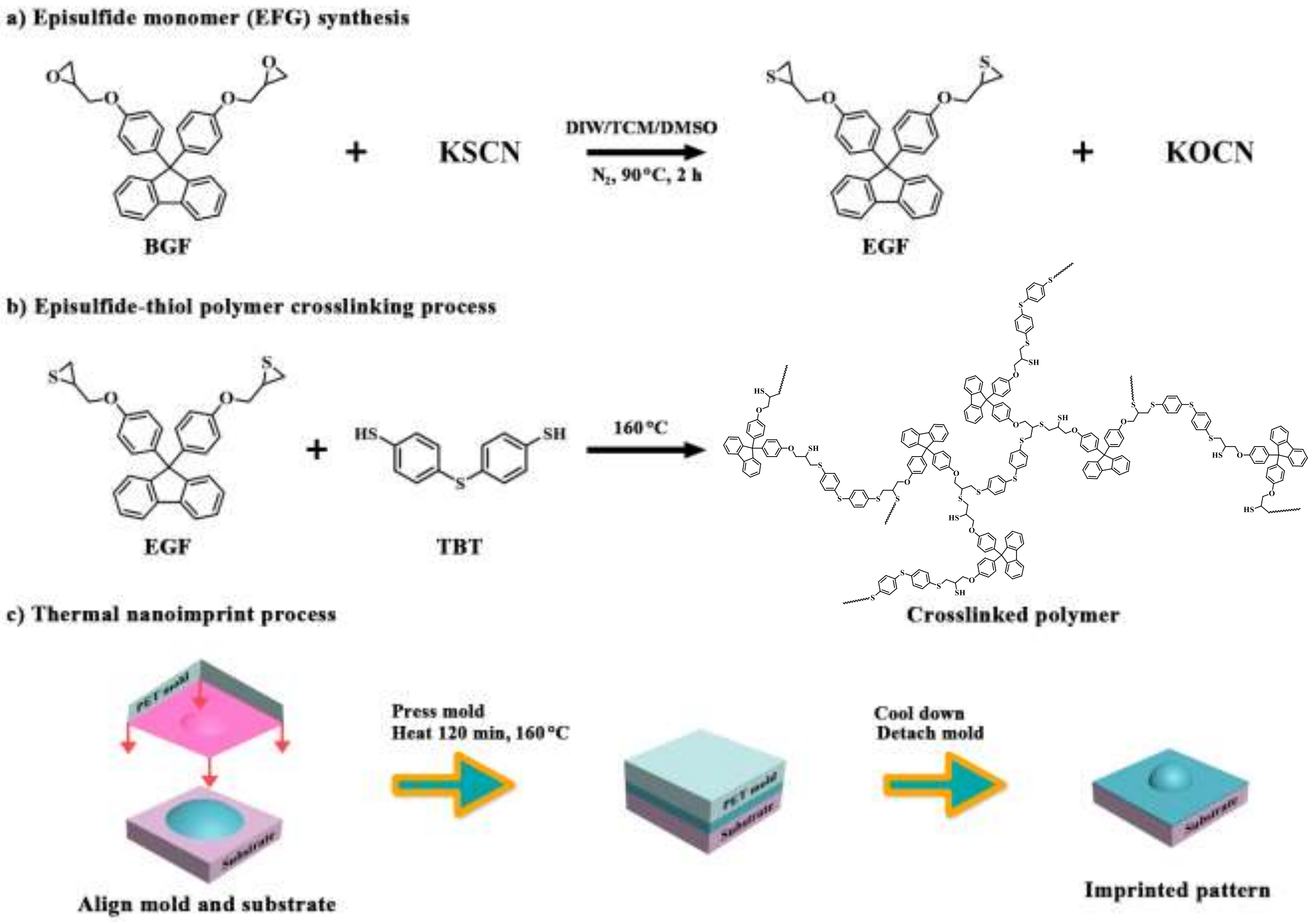

Scheme 1. Schematic illustration of EGF synthesis and patterns fabrication. (PET: polyethylene terephthalate).

to directly imprint organic polymers since they do not require complex processing steps and shrinkage is minimal. However, there are no reports of nanoimprinted organic polymers with a refractive index larger than 1.70.

Here, we developed a novel episulfide-thiol thermoset optical polymer with a high index of refraction that can be imprinted with micro- and nanoscale resolution. The high refractive index episulfide-thiol optical polymer prepared by ring-opening polymerization (ROP) with an equimolar mixture of synthesized episulfide derivative of 9,9-bis(4-glycidyloxyphenyl) fluorene (EGF) and 4,4-thiodibenzenethiol (TBT). The theoretical fundament of this development lays on the well-known Lorentz-Lorenz equation,[52,53] which predicts sulfur and aromatic groups as effective components to enhance the refractive index of polymers based on their high polarizability.[54,55] This represents the first reported effort of episulfide-thiol chemistry for nanoimprinting of high refractive index polymers. The developed high refractive index polymer can be thermally imprinted at a temperature of 160°C and different micro- and nanoscale structures, including nanoscale gratings, photonic crystals and plano-convex semispherical microlenses (PCSML), were successfully patterned. The imprinted microlens with a 0.9 μm focal spot size, reveals the episulfide-thiol optical material as a suitable polymer for high microlens efficiency. These fabricated patterns with low defectivity indicate the episulfide-thiol optical polymer exhibits excellent imprintability. Furthermore, the developed polymer shows high optical transparency and is thermally stable at high temperatures: a weight loss of 5% at 294°C was measured. The combination of these excellent properties makes the episulfide-thiol optical polymer an attractive candidate for applications in various optical and optoelectronic devices.

Results and discussion

Synthesis of episulfide monomer (EGF)

Our interest in episulfide-thiol chemistry lays on the possibility of producing polymers containing high molar refraction components including sulfur and aromatic groups. In contrast to other classes of monomers such as thiols, the commercial availability to different types of episulfide monomers is more restricted. Thus, the initial effort of this work was directed towards the synthesis of an episulfide monomer which could provide a high refractive index. We hypothesized 9,9-bis(4-glycidyloxyphenyl) fluorene (BGF) could potentially present a high refractive index due to its fluorene components. As shown in Scheme 1a, EGF was synthesized from BGF and alkali thiocyanate in the presence of deionized water (DIW), chloroform (TCM) and dimethyl sulfoxide (DMSO) at 90°C for 2 h, which is a common method for preparing episulfides.[56-58] The product was obtained as a white powder with a yield of 86%. The structure of EGF was confirmed by FT-IR and NMR spectroscopies. The FT-IR spectrum (Figure S1) shows typical characteristic absorptions of episulfide three-membered ring appears at 612 cm^{-1}. The characteristic absorptions due to phenyl ether linkages reveal at 1246 and 1048 cm^{-1}. In addition, the characteristic absorptions of phenyl group are observed at 1605, 1580, 1500 and 732 cm^{-1}. The ^{1}H and ^{13}C NMR spectra are shown in Figure S2, together with full assignments of the observed resonances. The protons to aliphatic alkyl and aromatic group are observed at 2.19–4.08 ppm and 6.65–7.68 ppm respectively. In the ^{13}C NMR spectrum (Figure S2b), fourteen characteristic peaks related to the structure symmetry are clearly observed, which agree well with the expected structure. In addition, the elemental compositions of the C, H, N and S elements are consistent with the calculated values of EGF. These results clearly showed that EGF was successfully synthesized.

Formulation and crosslinking of episulfide-thiol monomers

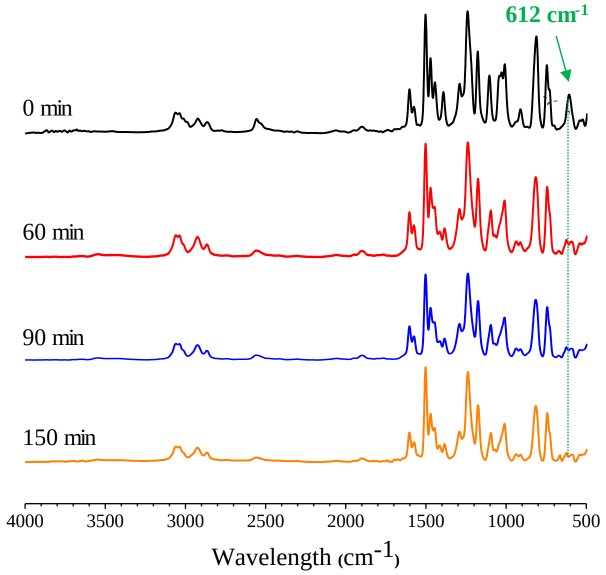

Figure 1. FT-IR absorption spectra of episulfide-thiol monomers cured at 160°C for different times.

Scheme 1b shows the formation of the episulfide-thiol polymer. The episulfide-thiol optical polymer was produced by mixing equimolar amounts of EGF and TBT monomers in either dichloromethane (DCM) or dimethylformamide (DMF) solvents. Initially, a curing agent 4,4-diaminodiphenyl methane was added to accelerate the crosslinking process but this produced a cured polymer with a yellow tinting. Thus, the final polymer formulation did not contain any other thermal initiator and the final product was a colorless transparent polymer. The episulfide and thiol monomers crosslink through a thermal initiated ROP process induced by the strong nucleophilicity of TBT (Scheme 1b). The temperature insensitivity of the ROP of episulfide and thiol compounds prevents the effective detection of any changes in the heat flow of reaction by DSC. Therefore, we employed FT-IR to monitor the ROP process by comparing the peak loss attributed to the stretching vibration associated with the three-membered ring episulfide group at 612 cm^{-1}. The FT-IR absorption spectra at a temperature of 160°C for different curing times are shown in Figure 1. There, we can observe how the intensity of the episulfide three-membered ring absorption peak decreases gradually as the curing time increases. This indicates that the ROP of EGF and TBT monomers proceeds even without the presence of any catalyst until it reaches a conversion of 75.7% at 150 min.

The shrinkage of the episulfide-thiol resin induced by the crosslinking, determined with ellipsometry for a curing time of 150 min, was only 2%. This low shrinkage guarantees a high pattern fidelity during the nanoimprint process.

Optical properties of episulfide-thiol polymer

An optically transparent polymer with a high refractive index is desired for the fabrication of several optical devices including microlens array, photonic crystals among others. High refractive index polymers have been previously reported but they show low transparency in the visible region. For instance, a polymer with a refractive index larger than 1.85 was obtained through the reaction of elemental sulfur and vinyl monomers. However, the high sulfur content induced low transparency in the visible wavelength.[59-61] A picture of a microscope glass slide having a 30 μm thick coating of the episulfide-thiol polymer (right) along with an uncoated glass slide serving as a control sample (left) can be observed in the insert picture of Figure 2(a); it is evident the high optical transparency of the developed polymer. The transmittance of the episulfide-thiol optical polymer was measured by UV-Vis spectrophotometer. As shown in Figure 2(a), a 30 μm thick film of the episulfide-thiol optical polymer exhibits a high transmittance of 89% in the visible region. This good transparency originates in the aliphatic and thioether units, which prevents intermolecular packing between the polymer chains.

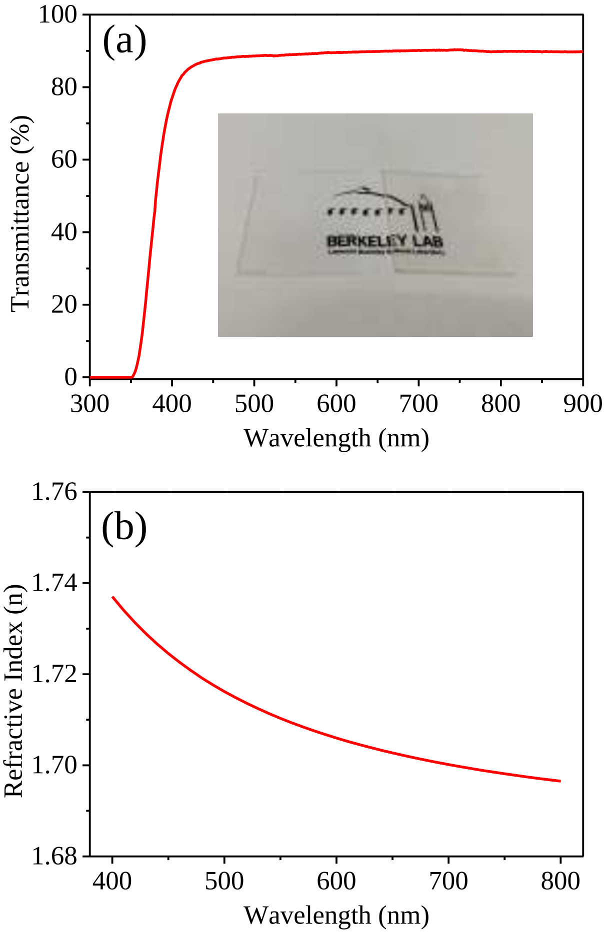

Figure 2. Optical properties of the episulfide-thiol polymer: (a) UV-Vis transmittance spectrum (film thickness: 30 μm) and (b) refractive index curve measured by ellipsometry. Insert:

photograph of a bare piece of glass (left) and episulfide-thiol polymer film with thickness of 30 μm on a glass (right).

The refractive index dispersion in the visible wavelength of the episulfide-thiol polymer was determined using ellipsometer and is presented in Figure 2(b). A value of 1.7067 (n = ~1.707) was measured at 590 nm which is larger than most traditional polymers. This polymer exhibits, high refractive index, resulting from the fact of that the polymer chain contains fluorene structure and high percent of highly polarizable sulfur atoms.

Thermal property of episulfide-thiol polymer

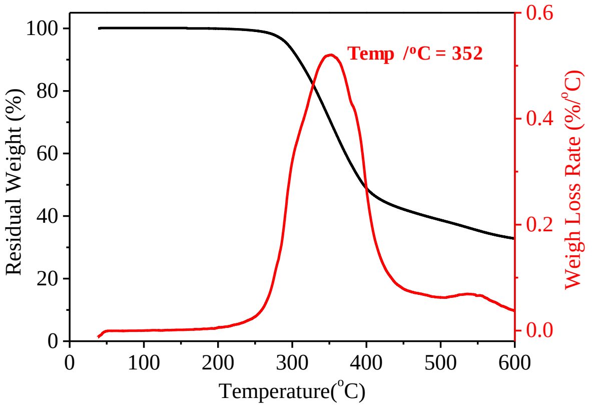

Figure 3. Thermogravimetric analysis (black line) and derivative thermogravimetric (red line) curves of episulfide-thiol polymer.

A large number of applications require a thermally resistant material for stability during the fabrication process and for long term durability of the final device. The thermal stability of the episulfide-thiol polymer was measured with thermal gravimetrical analysis. The thermal analysis of episulfide-thiol polymer at a heating rate of 10°C/min under a nitrogen atmosphere is displayed in Figure 3. It is observed the episulfide-thiol optical polymer is thermally stable up to a 5% weight loss temperature of 294°C, which satisfies several applications. A major weight loss reached a maximum rate at 352°C. The residual weight ratio is 32.8% at 600°C. It is believed the weight loss is related to the degradation of thioether and mercaptan groups in the episulfide-thiol optical polymer. In general, these results indicate the developed polymer presents high thermal stability which can be explained by its chemical structure consisting of thioether and aromatic moieties.

Thermal nanoimprinting of episulfide-thiol polymer.

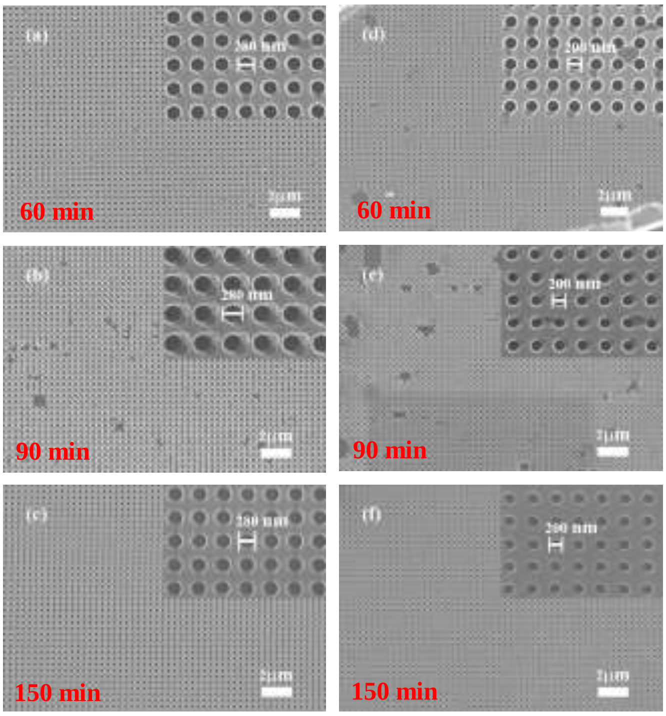

Figure 4. SEM images of nanoimprinted 2D photonic crystals with a pattern size of (a-c) 280 nm and (d-f) 200 nm cured at different times. Magnification images are inserted in the upright corner.

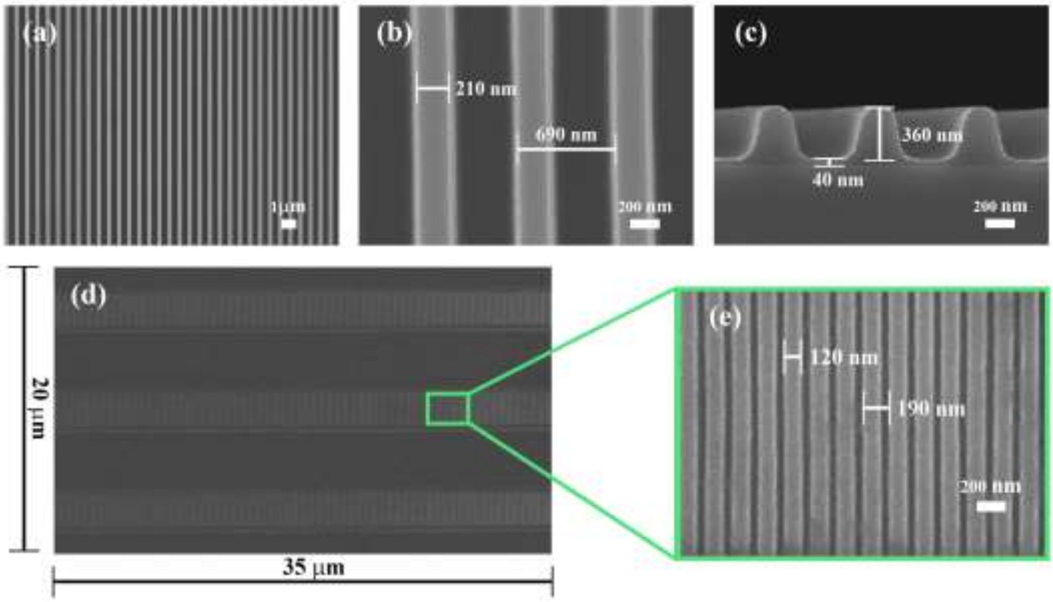

Figure 5. SEM images of different thermally nanoimprinted patterns with the episulfide-thiol optical polymer. (a) Sub-micron size gratings (690 nm pitch, 210 nm linewidth and 360 nm depth) at different magnifications and angles. (d) High resolution nanoscale size imprinted gratings with 190 nm pitch and 120 nm linewidth.

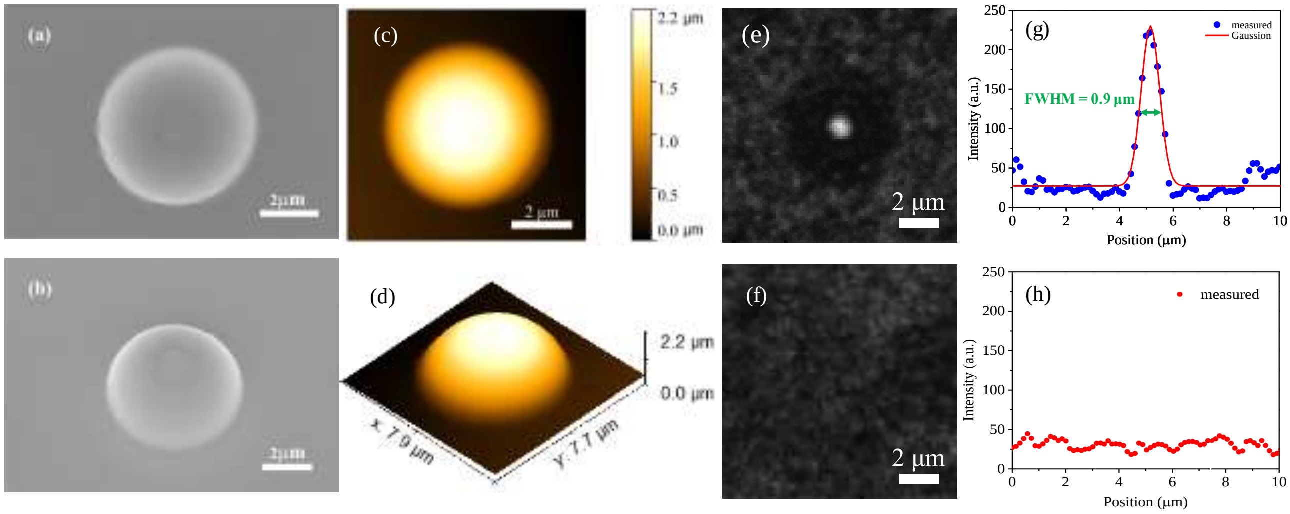

Figure 6. (a) Top-view and (b) 30° tilted-view SEM images of the episulfide-thiol PCSML. (c) 2D view and (d) 3D AFM images of the episulfide-thiol PCSML. Microscope images of (e) the episulfide-thiol PCSML focal spot and (f) a flat region used as a reference. Light profile distribution of the (g) PCSML focal spot and (h) the flat reference region.

The direct patterning of high refractive index polymers is a simple approach that can produce photonic devices in one single step while avoiding complex and expensive fabrication processes such as electron beam lithography and etching. An evaluation was performed to determine if the developed polymer could be nanopatterned following a thermal nanoimprinting process with good fidelity and precision. The episulfide-thiol optical polymer contains EGF and TBT monomers which are solid at room temperature. It is preferred for a faithful replication that the resin exists in a liquid or viscous phase before the crosslinking step. Since the melting points of EGF and TBT monomers are 143°C and 114°C respectively, a higher temperature, 160°C, was chosen as the set point for imprinting. The complete patterning process consisted of a pre-cure step at 160°C for 30min followed by the imprinting step at the same temperature under applied pressure. The imprinting process was then conducted at three different times to optimize the best condition: 30 min, 60 min and 120 min for a total crosslinking time of 60 min, 90 min and 150 min respectively. These chosen crosslinking times were based on previous FT-IR results which showed the degree of reaction of EGF and TBT are near to completion after 150 min at 160°C. A mold with photonic crystal structures patterned on the surface was used for this purpose. The SEM images showing the imprint results at different times are presented in Figure 4. It can be seen that crosslinking times of 60 and 90 min create patterns with several defects which can be a consequence of an incomplete cure of the monomers. The photonic crystal structures improve significantly when the crosslinking is performed for 150 min as revealed in Figure 4(c and f) where patterns without defect can be observed. This can be related to a higher degree of crosslinking achieved with increasing the curing time and indicates the imprinting results are consistent with the FT-IR measurements presented in Figure 1.

Additional patterns with different geometries and dimensions were nanopatterned to demonstrate the capabilities of the developed polymer as a high refractive index nanoimprint material. These include sub-micron size gratings (690 nm pitch, 210 nm linewidth, and 360 nm depth) and high resolution nanoscale patterns (190 nm pitch and 120 nm linewidth) which were nanoimprinted with good fidelity and low defectivity as shown in Figure 5. All these imprint results reveal that the episulfide-thiol optical polymer has a good embossability by NIL.

As a proof of concept, we fabricated microlens structures plano-convex semispherical microlenses (PCSML) with high refractive index and demonstrate the developed polymer is suitable for optical devices. Top-view and 30° tilted-view SEM images of the episulfide-thiol PCSML can be seen in Figure 6(a and b). As can be noticed the PCSML was imprinted with high surface quality. The profile and surface roughness of a microlens plays a very vital role on its optical properties. The topography of the episulfide-thiol PCSML was characterized by AFM to get further insight into its profile. As shown in Figure 6(c and d), the dimensions of the patterned PCSML are 5.5 μm in diameter and 2.2 μm in height.

The optical properties of the episulfide-thiol PCSML were investigated and characterized with an optical setup. The focal spot of the episulfide-thiol PCSML can be observed as a white bright dot at the center of the optical picture presented in Figure 6(e). A picture of a flat region of the episulfide-thiol resin, next to the microlens, is shown in Figure 6(f) as a reference; as expected, the white bright dot was not detected. The light intensity distribution (blue dotted line) microlens focal spot across its center is displayed in Figure 6(g) along with the Gaussian fitting curve (red line). The focus spot size of the episulfide-thiol PCSML determined by calculating the full width at half maximum (FWHM) of the Gaussian fitting of the curve is 0.9 μm, which indicates that the episulfide-thiol PCSML is an efficient microlens structure. The light intensity distribution of the flat region next to the microlens, shown in Figure 6(h), shows a constant intensity over the entire path length.

Conclusions

In conclusion, a high refractive index resin (n=1.707 at 590 nm), based on episulfide-thiol chemistry, was successfully developed for optical applications. An episulfide monomer containing highly polarizable sulfur atoms and fluorene structure was synthesized and characterized by FT-IR, NMR spectroscopy, and element analysis. The synthesized episulfide monomer can react with commercially available thiol monomer through a ring opening polymerization at 160°C for 150 min to form an optically transparent polymer with high thermal stability. The combination of episulfide and thiol monomers can be thermally nanoimprinted with high resolution, fidelity and low defectivity to fabricate different type of micro- and nanostructures including gratings, photonic crystal and microlenses. It suggested potential optical applications of the novel episulfide-thiol optical polymer.

Experimental

Materials

9,9-bis(4-glycidyloxyphenyl) fluorene (BGF), 4,4-thiodibenzenethiol (TBT) and trichloro(1H,1H,2H,2H-perfluorooctyl) silane were purchased from Sigma-Aldrich Technology Corporation (Missouri, USA). Potassium thiocyanate, chloroform (TCM), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and other reagents were of analytical grade and were used without further purification. The Undoped double side polished silicon with the thickness of 375 μm ± 25 μm for FT-IR was purchased from Virginia Semiconductor Inc. (Virginia, USA).

Synthesis of EGF

BGF (2.00 g, 4.33 mmol), potassium thiocyanate (3.36 g, 34.62 mmol), 10 mL DIW, 20 mL TCM and 30 mL DMSO were mixed together in a three-necked round bottom flask equipped with a magnetic stirrer, a thermometer and a condenser and heated at 90°C for 2 h under nitrogen. The solution was cooled to ambient temperature, the mixture was extracted with TCM (100 mL) and washed twice with saturated aqueous sodium chloride (2x100 mL). The organic layer was dehydrated with anhydrous sodium sulfate and concentrated under vacuum. The crude product was further purified by column chromatography using 1:1:4 dichloromethane/ethyl acetate/petroleum as eluent to give a white powder (EGF) in an 86% yield.

FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (USA). The ^{1}H NMR and ^{13}C NMR spectra were measured on a 400 MHz NMR instrument (Bruker Corporation, AVANCE III HD, Germany) at 298 K with $CDCl_3$ as the solvent. The composition of C, H and S in EGF was determined with an Element Analyzer (Elementar Analysen systeme, Vario EL cube, Germany) equipped with Mettler Toledo XP6 (Mettler Toledo GmbH, Germany) in CHNS operation mode.

FT-IR, ν(cm^{-1}): 3060, 3030, 2925, 2921, 2860, 1605, 1505, 1447, 1246, 1180, 1030, 825, 750, 732, 612 (Figure S1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.67 (d, J = 7.5 Hz, 1H), 7.27 (ddd, J = 12.5, 6.3, 2.6 Hz, 2H), 7.18 (td, J = 7.6, 1.2 Hz, 1H), 7.03 (m, 4H), 6.67 (m, 2H), 4.06 (ddd, J = 7.3, 4.0, 3.1 Hz, 1H), 3.75 (dd, J = 10.2, 7.1 Hz, 1H), 3.14 (dd, J = 6.9, 5.5 Hz, 1H), 2.50 (d, J = 6.1 Hz, 1H), 2.20 (dd, J = 5.3, 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 156.11, 150.59, 138.91, 137.63, 128.21, 126.68, 126.36, 124.93, 119.13, 113.22, 71.51, 63.12, 30.33, 22.94 (Figure S2). Anal. calcd for C, 75.27%; H, 5.30%; S, 12.96%. Found: C, 75.48%; H, 5.41%; S, 13.05%.

Crosslinking study of episulfide-thiol optical polymer

FT-IR spectrometer was used to study the crosslinking process of the episulfide-thiol optical polymer which proceeds through a ROP of the episulfide and thiol monomers. The episulfide resin consists an equimolar mixture of EGF and TBT dissolve in chloromethane or dimethylformamide. Typically, few drops of solution of the episulfide resin were placed on top of an undoped double side polished silicon wafer, cured at 160°C for different times (0, 60, 90, 150 min) and measured by FT-IR spectrometer. A Perkin Elmer Spectrum One FT-IR spectrometer (USA) was used for this purpose. Each spectrum from the FT-IR spectrometer was the average of 32 scans over the wavenumber range 500–4000 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were baseline corrected and normalized using the characteristic absorption peak of substituted phenyl at 750 cm^{-1}.

Thermal property of episulfide-thiol optical polymer

The thermal property of the episulfide-thiol optical polymer was determined with thermogravimetric analysis measurements recorded on a Q500 (TA Instrument, Thermo Fisher Scientific, USA) under nitrogen atmosphere with a nominal flow rate of 60 mL/min. A 20.0 mg polymer sample was added to ceramic reinforced platinum pans and heated to 600°C at a heating rate of 10°C/min.

Shrinkage of episulfide-thiol optical polymer

A uniform thin film of the episulfide-thiol resin was prepared by spin coating on a silicon wafer. The thickness of the film was measured with ellipsometry before and after curing at 160ºC for 150 min to determine the rate of shrinkage.

Optical properties of episulfide-thiol polymer

The UV-Vis transmittance of episulfide-thiol optical polymer cured at 160°C for 150 min and coated on a glass slide, with a thickness of 30 μm, was measured with a Hitachi U-3010 UV-Vis spectrophotometer (Hitachi High-Technologies Corporation, Japan) at ambient temperature. The refractive index of the episulfide-thiol optical polymer was carried out using a Horiba Jobin Yvon UVISEL Spectroscopic Ellipsometer in the wavelength range of 400-800 nm.

Fabrication of nanoimprint mold

The original master molds were fabricated on a silicon wafer with electron beam lithography followed by dry etching to reveal the structures. The master molds were coated with an anti-sticking layer of trichloro(1H,1H,2H,2H-perfluorooctyl) silane and replicated on OrmoStamp (Micro Resist Technology) with polyethylene terephthalate (PET) as a supporting layer to create working stamps. The OrmoStamp/PET working molds were also treated with trichloro(1H,1H,2H,2H-perfluorooctyl) silane to create an anti-sticking layer and use them for the final imprinting of the episulfide-thiol resin. The parameters and SEM images of the molds are shown in SI Table 1.

Thermal nanoimprinting of episulfide-thiol polymer

The thermal nanoimprinting was operated by a homemade thermal imprinting system in the Nanofabrication Division of

Molecular Foundry at LBNL. The novel episulfide-thiol optical polymer was thermally nanoimprinted at 160°C with different pattern geometries and sizes. 2D photonic crystal molds with diameters of 280 nm and 200 nm were used to optimize the cure time of episulfide-thiol optical polymer. After baking on a hotplate at 160°C for 30min, the imprinting was performed at 160°C for different times: 30, 60 and 120 min. Sub-micron size gratings, nanoscale gratings and PCSML were used also used for imprinting purposes. Typically, 49.5 mg (1.0 mmol) EGF and 25.0 mg (1.0 mmol) TBT were added into a glass bottle with 4 mL of DCM or DMF. The solution was exposed to ultrasonication at room temperature for 10 min and filtered with a 0.2 μm pore size membrane filter to obtain a colourless and transparent episulfide-thiol solution. The optimized imprint process for the episulfide-thiol optical polymer is as follows: (1) drop cast a solution of high refractive index optical resin, dissolved in either DCM or DMF on a silicon substrate; (2) pre-cure the film at 160°C for 30 min; (3) place the mold on top, transfer to a hydraulic thermal imprint tool and heat for additional 120 min (for a total crosslinking time of 150 min) at 160°C under an applied pressure of 200 psi; (d) cool down and detach the mold to obtain desired pattern (Scheme 1c). The fabricated patterns were characterized by Zeiss Ultra 60 Field Emission-Scanning Electron Microscope.

The surface morphology of episulfide-thiol PCSML was evaluated by Atomic Force Microscopy (AFM) with a nasoscope resolution under ambient conditions. The height of episulfide-thiol PCSML on a silicon substrate was determined by calculating the height between the surface and the highest position of microlens. Tapping mode images were analyzed using the Gwyddion software (gwyddion.net).

Optical properties of episulfide-thiol PCSML

The focal spot size of the fabricated episulfide-thiol PCSML was measured with a setup consisting of a helium–neon laser light source operating at the wavelength of 632.8 nm, a 40x objective lens and a camera. The focus spot size of PCSML was determined by calculating the full width at half maximum.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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A Novel High-Refractive Index Episulfide-Thiol Polymer for Nanoimprinting Optical Elements

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A novel episulfide-thiol optical polymer with a high refractive index (n = 1.707) can be thermally nanoimprinted at 160°C with nanoscale size resolution including sub-micron and nanoscale size gratings, photonic crystals and microlenses with excellent pattern fidelity and low defectivity, which exhibit the material as a potential candidate for applications in optical and optoelectronic devices.