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# Photopolymer Resins from Sulfenyl Chloride Commodity Chemicals for Plastic Optics, Photopatterning and 3D-Printing

*Chisom Olikagu, Shafagh Khoshsorour, Satya D. Dulam, Hyun-Seok Yu, Natasha A. Graham, Kyung-Jo Kim, Byeongjoon Jeong, James L. Hedrick, Amber Bunnag-Stoner, Kimberley Cheng, Benjamin L. Batchelor, Woongbi Cho, Seung Bin Park, Jeong Jae Wie, Young-Jae Kim, Min-Gap Bog, Nithiyaa Bala Krishnan, Yi Yan Yang, Jon T. Njardarson, Robert A. Norwood,* and Jeffrey Pyun**

**The development of a low-cost photopolymer resin to fabricate optical glass of high refractive index for plastic optics is reported. This new free radically polymerizable photopolymer resin, termed, disulfide methacrylate resin (DSMR) is synthesized by the direct addition of allyl methacrylate to a commodity sulfur petrochemical, sulfur monochloride ($S_2Cl_2$). The rapid rates of free radical photopolymerization confer significant advantages in preparing high-quality, bulk optical glass. The low-cost, optical glass produced from this photopolymer possesses a desirable combination of high refractive index ($n \approx 1.57$–$1.59$), low birefringence ($\Delta n < 10^{-4}$), high glass transition values ($T_g \approx 100$ °C), along with optical transparency rivaling, or exceeding that of poly(methyl methacrylate) (PMMA) as indicated by very low optical absorption coefficients ($\alpha < 0.05$ cm$^{-1}$ at 1310 nm) measured for thick glass DSMR photopolymer samples (diameter ($D$) = 25 mm; thickness = 1–30 mm). The versatile manufacturability of DSMR photopolymers for both molding and diamond turn machining methods is demonstrated to prepare precision optics and nano-micropatterned arrays. Finally, large-scale 3D printing vat photopolymerization of DSMR using high-area rapid printing digital light processing additive manufacturing is demonstrated.**

## 1. Introduction

Photopolymerization-based production of polymeric raw materials into high-value components and products is a central capability for modern manufacturing. The development of high refractive index ($n$, or RI) photopolymer resins for plastic optics and photonic device applications remains an important frontier of new polymer chemistry developments. Current efforts in this area include the synthesis of new optical monomers possessing a high sulfur and/or aromatic content for thin film holographic photonic applications.[1] The development of high RI photopolymer resins and optical materials was pioneered by Bowman and MacLeod et al., primarily using thiol-ene, or thiol-yne photopolymerizations with aliphatic thiols and unsaturated organic monomers to fabricate high RI optical components for holography and

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C. Olikagu, S. Khoshsorour, S. D. Dulam, H.-S. Yu, N. A. Graham,
J. T. Njardarson, J. Pyun
Department of Chemistry and Biochemistry
University of Arizona
1306 East University Blvd., Tucson, AZ 85721, USA
E-mail: jpyun@arizona.edu

K.-J. Kim, B. Jeong, R. A. Norwood, J. Pyun
J. C. Wyant College of Optical Sciences
University of Arizona
1630 East University Blvd., Tucson, AZ 85721, USA
E-mail: rnorwood@optics.arizona.edu

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202418149

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**DOI: 10.1002/adma.202418149**

J. L. Hedrick, A. Bunnag-Stoner, K. Cheng, B. L. Batchelor
Azul 3D
8111 St Louis Ave #2, Chicago, IL 60076, USA

W. Cho, S. B. Park, J. J. Wie
Department of Organic and Nano Engineering
Hanyang University
222 Wangsimmni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

W. Cho, S. B. Park, J. J. Wie
Human-Tech Convergence Program
Hanyang University
222 Wangsimmni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

J. J. Wie
Department of Chemical Engineering
State University of New York College of Environmental Sciences and Forestry
Syracuse, NY 13210, USA

Y.-J. Kim, M.-G. Bog
Y&DK Co.
Ltd
169–148 Gwahak-ro, Yuseong-gu, Daejeon 34133, Republic of Korea

related thin film photonic components.[2] While thiol compounds are commercially produced, a limited scope of dithiol and multi-thiol compounds are available as monomers for polymer synthesis. Furthermore, polysulfides made from aliphatic thiol monomers typically possess low glass transition temperature ($T_g$) values, which precludes application for numerous plastic optic products.[3] While these advances in high RI photopolymer resins have been impactful for holography, the development of high RI photopolymers for bulk optical components remains challenging. Classically, the synthesis of high RI polymer thermoplastics and thermosets was achieved by the introduction of high molar refraction atoms (S, Se, and Br) or functional groups (phenyl; haloarenes, aromatics) into optical monomers and polymers.[4] This important area of materials science was pioneered by Ueda et al.,[4a] and explored more recently by Stiegman et al.,[5] primarily through the synthesis of high sulfur/heteroatom content monomers and polymers. However, this concept is economically challenging for commodity bulk optics, and often has technical issues including coloration of the photopolymer resin (often incurred with chalcogenides) or birefringence/haziness in thick bulk optical glass forms (aromatic groups cause haziness in thick solid-state glass) along with chemical requirements for liquid forms that are photopolymerizable. Hence, the development of inexpensive photopolymer resins that afford colorless, robust optical glass in the visible and infrared (IR) spectrum that also possess a higher RI ($n \approx 1.6$) would make a significant impact on manufacturing plastic optics. Furthermore, the use of high RI photopolymer resins offers significant sustainability advantages, as higher RI plastic optics require less optical material in the final optical element.

Advances in additive manufacturing (AM) via stereolithography (SLA) and digital light processing 3D printing have been important innovations in photopolymer-based manufacturing. Accelerated 3D DLP printing methods for manufacturing include the use of oxygen inhibition layers for continuous liquid interface production by DeSimone et al.,[6] and the use of immiscible fluorinated oil layers between the vat resin and the digital light source by Mirkin and Hedrick et al. which was termed, high area rapid printing (HARP) 3D DLP.[7] Photopolymerization fabrication techniques offer significant advantages over classical melt polymer processing methods for polymer manufacturing with respect to rapid curing times, precise spatial control of polymerization, and accelerated prototyping of novel components when coupled with AM.[8] Despite the tremendous advances in this area, one of the primary limitations to photopolymerization-based manufacturing is the limited availability of novel photopolymer resins. New photopolymer resin development is particularly restrictive since new formulations must be miscible, optically transparent, low viscosity fluids, and amenable to rapid photopolymerization crosslinking chemistry. To our knowledge, photopolymer resins for the production of high RI commercial plastic optics have not been widely deployed due to challenges in achieving high optical quality fabrication and resin chemistry limitations (i.e., cost, final resin and polymer bulk properties). These challenges are particularly evident for the large-scale production of commodity plastic optics via photopolymerization methods for the production of high-quality optical glass that is color-free, defect-free, optically transparent, and structurally robust, while maintaining low materials/production costs.[9] A key challenge for developing photopolymer resins for commodity optics (e.g., windows for construction–transportation–aerospace, plastic optics for consumer eyewear and smartphones) is the reliance on existing (meth)acrylate, or epoxy photopolymer resins,[8] the vast majority of which are low refractive index ($n \leq 1.6$) and hence, lagging behind the optical performance of higher refractive index optical thermoplastics/thermosets.[9e]

The development of improved photopolymer resins (monomers, prepolymers, and initiators) has been an emerging area of continuous progress, in many cases for use in SLA or DLP 3D printing. Significant effort has been made in the synthesis of photoactive molecular systems to initiate photopolymerization operating in the visible, or NIR spectrum beyond classical UV initiators, which include the use of photoswitches by Hawker and Hecht et al.,[10] photoinduced electron/energy transfer reversible addition–fragmentation chain transfer polymerization methods by Boyer et al.,[2c] multi-component photoredox systems by Paige et al.,[11] and triplet upconverting systems.[12] Furthermore, the development of orthogonal photoinitiation chemistry at different wavelengths has been demonstrated by Boydston et al., for epoxy and acrylate photopolymer resins for DLP 3D and 4D printing.[13] Molecular engineering of photopolymer resins for mechanical property enhancement was demonstrated by Long et al., by synthesizing polyimide-containing photopolymer resins for SLA 3D printing.[14] Dove et al. recently developed a sustainably sourced photopolymer resin from disulfide based-lipoate monomers for circular stereolithographic 3D printing,[15] in addition to circular polythiourethane photopolymer resins development by Long, Sadron, and coworkers.[16]

A new approach to low-cost, high-refractive index polymers was developed by Pyun et al., via the use of elemental sulfur ($S_8$) and $S_8$-derived petrochemical feedstocks for optical materials in the visible and infrared spectrum.[17] The very low cost of elemental sulfur ($S_8$) and sulfur-derived reagents arise from the megaton generation of these petrochemicals from petroleum refining. Furthermore, the use of $S_8$-derived feedstocks for polymer materials has emerged as a new direction in sustainable polymer science as a means to consume elemental sulfur generated from crude oil and gas refining.[18] The inverse vulcanization polymerization of $S_8$ with unsaturated organic comonomers afforded very high sulfur content organopolysulfides, which has enabled the first class of optical polymers for IR imaging and photonics in the mid and long wave IR (MWIR, LWIR).[17b,18,19] Conversion of $S_8$ via chlorination affords sulfur monochloride ($S_2Cl_2$), an inexpensive commodity chemical, for which the Pyun group invented a polymerization, termed sulfenyl chloride inverse vulcanization, to prepare a new class of high RI ($n \approx 1.6$–$1.65$) and transparent

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N. B. Krishnan, Y. Y. Yang
Bioprocessing technology institute
Agency for Science
Technology and Research (A*StAR)
20 Biopolis Way, centros#06- 01, Singapore 138668, Singapore

R. A. Norwood
Department of Materials Science & Engineering
College of Engineering
University of Arizona
1235 James E. Rogers Way, Tucson, AZ 85719, USA

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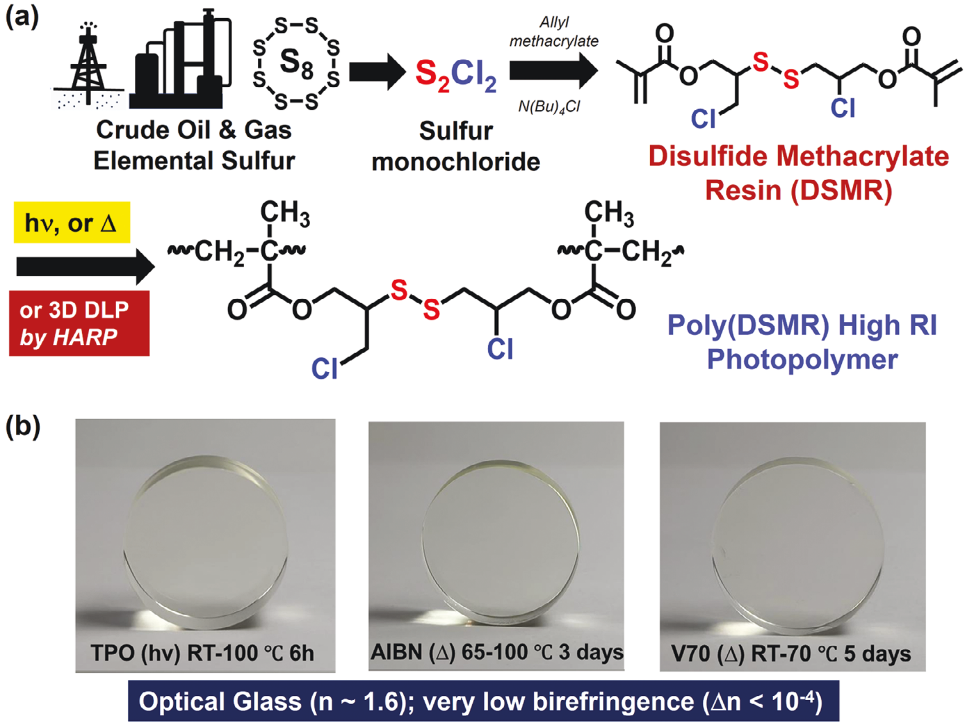

**Figure 1.** a) Generalized scheme for production of elemental sulfur from crude oil refining, chlorination of $S_8$ to form sulfur monochloride ($S_2Cl_2$) and the synthesis of disulfide methacrylate resin (DSMR) from one-step addition of allyl methacrylate to $S_2Cl_2$ followed by either thermal, photopolymerization, or 3D DLP HARP AM for the fabrication of a high RI photopolymer glass. b) DSMR-cured optical glass windows (diameter ($D$) = 25 mm, thickness = 6 mm) prepared by photopolymerization with a thermal post-treatment done in 6 hours, versus thermally cured windows requiring multiple days for defect-free fabrication.

optical polymers for use at visible, near IR and telecommunication optical wavelengths.[20] However, both $S_8$ and $S_2Cl_2$ are currently not amenable for photopolymerization processes and typically afford polysulfide materials that are strongly colored in the visible spectrum.[17c,19c] Furthermore, $S_2Cl_2$ is chemically reactive to water and nucleophiles, requiring the exclusion of these reagents before polymerization. Hence, the development of new synthetic chemistry to prepare photopolymerizable monomers from these sulfur petrochemical feedstocks remains a significant technological opportunity to prepare low cost, high RI photopolymer optical glass. This type of commodity polymer would further provide a new avenue for more sustainable elemental sulfur utilization.

Herein, we report on the first photopolymer resin derived from commodity sulfur petrochemicals to afford a high RI optical glass via photopolymerization-based methods. We are able to capitalize both on the low cost and high reactivity of $S_2Cl_2$ to couple efficiently to the allylic groups of an inexpensive methacrylate monomer (i.e., allyl methacrylate, **Figure 1**). We observe the chemical specificity of sulfenyl chloride addition to allyl moieties, allowing for the synthesis of an inexpensive methacrylate-based resin carrying the $\beta$-halodisulfide moiety, as previously observed for sulfenyl chloride inverse vulcanization polymerizations with diallyl monomers.[20,21] This new photopolymer resin, termed, disulfide methacrylate resin (DSMR) is chemically stable and can be handled/stored like conventional methacrylate monomers. Furthermore, DSMR is a colorless, low-viscosity liquid resin that is highly miscible with other monomers/photoinitiators and can be thermally, or photopolymerized via free radical processes. The cured DSMR photopolymer also retains high RI ($n \approx 1.57$), high transparency, very low birefringence/haziness, and robust thermomechanical properties. Photopolymerization-based curing with DSMR enabled accelerated fabrication of high quality, bulk optical glass (controllable thickness from 1–30 mm) with total fabrication times achieved within hours versus classical thermal casting/curing methods requiring several days to fully cure without defects, or cracks in the final glass. Finally, we demonstrate the versatility of DSMR photopolymer processing for the fabrication of bulk precision optics using molding, or diamond turn machining methods. The photopolymerization of DSMR to prepare high aspect ratio nanostructured arrays and large-scale 3D printing vat photopolymerization using the novel HARP DLP process was also conducted, highlighting the amenability of DSMR for a wide range of manufacturing processes. The ensemble of the low cost, synthetic scalability, and photopolymerizability of DSMR, coupled with robust bulk thermomechanical and optical properties of DSMR photopolymers represents a significant technological advance at the nexus of the petrochemical, polymer, and optical industrial sectors.

## 2. Results and Discussion

The synthesis of the DSMR photopolymer resin was conducted using a one-step synthetic process with sulfur monochloride ($S_2Cl_2$) and allyl methacrylate (Figure 1a). This approach

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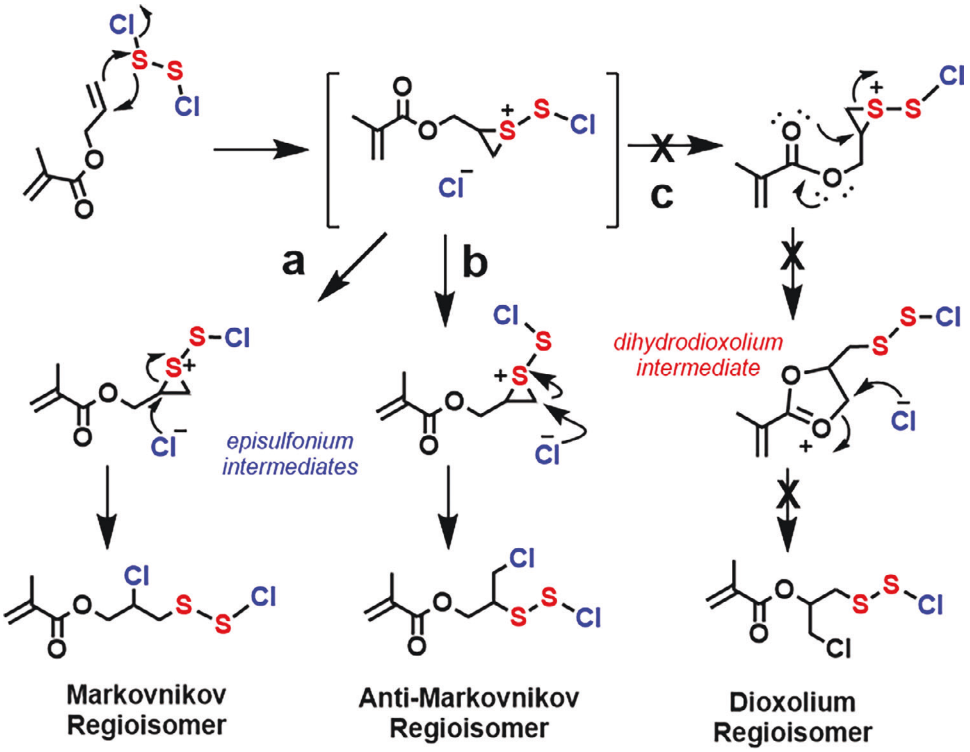

**Scheme 1.** Reaction mechanism for selective electrophilic addition of sulfenyl chlorides from $S_2Cl_2$ to allyl groups of allyl methacrylate followed by different possible pathways via episulfonium intermediates affording both a) Markovnikov, b)/anti-Markovnikov and c) dioxolium derived regioisomers. The addition of tetrabutylammonium salts suppresses the dihydrodioxolium pathway shown in Scheme 1c.

harnessed the high reactivity of sulfenyl chloride groups (R-S-Cl) to unhindered olefins via electrophilic addition reactions,[22] which resulted in selective addition to allyl groups in the presence of methacrylate moieties, to prepare free-radically crosslinkable resins. We previously reported that allylic monomers were well-suited for SC-IV polymerizations with $S_2Cl_2$, while (meth)acrylate monomers did not polymerize.[20] Hence, we utilized the differential reactivity of $S_2Cl_2$ sulfenyl chloride groups to promote effective coupling of the allylic moieties in allyl methacrylate in a single step.

The mechanism of sulfenyl chloride addition is proposed to proceed via ionic episulfonium intermediates, followed by the addition of the chloride anion to form $\beta$-halothioether organosulfur halides. In the case of sulfenyl chloride addition to allylic monomer groups, the reaction affords a mixture of Markovnikov, Anti-Markovnikov regioisomers formed by chloride anion addition to episulfonium intermediates (**Scheme** 1a,b).[20,21] We also observed the formation of a third regioisomeric unit formed in the $S_2Cl_2$ electrophilic addition to allylic ester monomers/substrates proceeding through dihydrodioxoloim intermediates as an unexpected side reaction (Scheme 1c) in the absence of tetraalkylammonium salts. NMR spectroscopic analysis indicated the formation of anti-Markovnikov (68-mol%), Markovnikov (16-mol%), and dihydrodioxolium (16-mol%) addition products under these conditions.[21] Conversely, upon the addition of catalytic amounts of tetrabutylammonium chloride (1-mol%), nearly exclusive formation of the anti-Markovnikov addition product was observed (90-mol%, as determined from NMR spectroscopy, see Figure S3, Supporting Information), while suppressing the competing dihydrodioxolium intermediate pathway (see Figure S1, Scheme S1, Supporting Information). The use of tetraalkylammonium salts to control the regiochemistry of sulfenyl chloride addition is, to our knowledge, a novel synthetic finding. Detailed molecular characterization of DSMR was conducted by NMR spectroscopy, LC-MS (see Figures S3–S7a–d, Supporting Information), which indicated the formation of mono, disulfide, and trisulfide dimethacrylate compounds (1:2:1.2 molar ratios), which arose from alternative pathways from the episulfonium intermediates (see Figure S1, Supporting Information). This synthesis of DSMR (comprised of 90-mol% anti-Markovnikov/10-mol% Markovnikov units) was readily conducted in good yield (85%) on appreciable scale (143 grams per batch) after purification by column chromatography, which removed any residual yellow coloring in the final photopolymer resin. DSMR readily polymerized using either thermal or photochemical free radical initiators, where the inclusion of sulfide moieties in the final resin raised the refractive index of the resulting thermoset or photopolymer without the need for introducing aromatic or heavy atoms which could compromise haziness, or coloration, of the final optical glass. Furthermore, the DSMR was chemically stable and easily stored under refrigeration in direct contrast to moisture-sensitive handling required with $S_2Cl_2$ for polymerizations. To our knowledge, this is the first, direct, one-step synthesis reported for a photopolymer resin from any sulfur petrochemical, namely from $S_2Cl_2$, enabling

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both large-scale synthetic accessibility and low materials costs.

Due to the incorporation of methacrylate groups as the polymerizable moieties, the DSMR photopolymer resin was readily photochemically and thermally cured via classical free radical polymerizations into thermomechanically robust, highly transparent optical glasses. We note that appropriate personal protective equipment was required in the direct handling of bulk DSMR before formulation to avoid direct skin exposure. Photopolymerizations with DSMR resulted in complete monomer conversion and rapid vitrification into a solid, colorless glass within 120 s using conventional photoinitiators (e.g., Darocure-TPO, 0.3-mol% at 385 nm). Post-thermal treatment of photopolymerized DSMR was required to afford thermomechanically robust optical glass, at elevated temperatures ($T$ = 140 °C, or 100 °C). The higher post-cure temperature ($T$ = 140 °C for 5–12 h) was found to afford maximal glass transition values and tensile strength, as detailed below, but was accompanied by a slight yellow tinting. The lower post-bake temperature ($T$ = 100 °C for 6 h) of photopolymerized DSMR networks was applied to avoid coloration during the post-bake step, while still affording an optical glass suitable for plastic optics, as detailed below. IR spectroscopy of DSMR photopolymer before and after post-bake treatments indicated the presence of residual macro-vinyl groups in the final glassy network (Figure S8, Supporting Information). Hence, this two-stage photopolymerization and thermal post-bake process weas employed to prepare high-quality optical glass windows when cast and cured in glass vials ($D$ = 25 mm; thickness = 1.5–30 mm, Figures 1c and 3a), or polydimethysiloxane (PDMS) molds. The rapid photocuring step of DSMR (within 1–2 min) into a glassy pre-polymer state proved advantageous for stabilizing the glass against defects, bubbles, or cracks in the final thermally cured window, which also allowed for much shorter post-bake times (6 h). Similarly, thermally cured DSMR with AIBN (at $T = 60$ °C), or using low-temperature thermal initiators (V70, $T$ = 30 °C) were also viable routes to prepare poly(DSMR) windows, but required much longer reaction times to vitrify from bulk polymerizations (3–5 days) (Figure 1c; Figure S9, Supporting Information). The DSMR photopolymer was found to be thermomechanically robust, possessing thermal stability comparable to PMMA and poly(vinyl chloride) as determined from thermogravimetric analysis (TGA, $T_{\text{decomposition}} \approx 250$ °C, see Figure S11a, Supporting Information). Furthermore, the fully cured DSMR photopolymer was found to be hydrolytically stable to neutral water, basic (10-wt.%-NaOH), or acidic (10-wt.% HCl) media, consistent with our prior finding with polyhalodisulfides made from SC-IV of $S_2Cl_{2.}$ (see Figure S10, Table S1, Supporting Information)[20] DSC analysis of photo-cured DSMR (without additional thermal treatment) afforded a featureless DSC thermogram, indicating that the rapid photo-cure step was sufficient to form a glassy, crosslinked network (see Figure S11b, Supporting Information). However, dynamic mechanical analysis (DMA) of this photo-cured DSMR glass without further thermal treatment indicated the material possessed low glass transition values (broad $T_g = -20$ to 35 °C, Figure S12a, Supporting Information). After treating the photo-cured DSMR photopolymer with a post-bake step ($T$ = 140 °C, 12 h) a much higher, broad glass transition ($T_g \approx$ 80–100 °C, **Figure** 2a; Figures S12a, S13, Supporting Information) was obtained as most readily observed in the temperature-resolved tan $\delta$ ($E''/E'$) plot (Figure 2a). The DMA analysis of this DSMR photopolymer confirmed that a high plateau storage modulus ($E'$) from $T$ = 50–200 °C was retained without observation of a viscous flow regime, indicative of chemically crosslinked network formation (Figure 2a). The DSMR photopolymer cast into PDMS molds and post-baked ($T$ = 140 °C) were also found to possess robust tensile properties and enhanced ductility (tensile strength = 25–30 MPa, 13–15% elongation at break, Figure 2b) versus classical optical glasses. DSMR photopolymerized and post-baked at lower temperatures ($T$ = 100 °C) afforded materials possessing two glass transition values as determined by DMA analysis (2 broad $T_g$ values, $T_g$ = 13 and 88 °C, Figure S12a, Supporting Information), however, similar mechanical properties were obtained for the higher post-bake condition (Figure S12b, Supporting Information). Finally, DSMR photopolymers were found to be non-toxic as confirmed by L929 fibroblast cell and ARPE-19 human eye cell culture studies, which pointed to the safe and viable handing of DSMR photopolymers for plastic optics (See Figure S14, Supporting Information).

DSMR photopolymers exhibited excellent optical transmittance and higher refractive index across the visible and NIR spectrum, which was particularly evident in direct comparisons with PMMA windows of exact size and thickness ($D = 25$ mm; thickness = 1.5 mm) (Figure 2c,d). In contrast to optical polymer thermosets of $S_2Cl_2$ in our previous report which were yellow tinted,[20] DSMR afforded optical glasses with minimum color in the visible spectrum as observed in the UV–vis–NIR optical transmission spectra, which was most notably observed by the optical absorption edge (≈400 nm), very comparable to PMMA windows (Figure 2c). The RI of DSMR photopolymers ($n_{532\ nm} = 1.57$) was determined by ellipsometry from 300–1600 nm and calibrated by prism coupling measurements conducted at 532, 632, 816, 1305, and 1554 nm; the RI was considerably higher than PMMA in these optical spectra windows ($n_{532\ nm} = 1.49$, Figure 2d). While the DSMR photopolymer Abbe number ($V_D$ = 36) was lower than that of our measured values of PMMA ($V_D$ = 51), indicating slightly higher refractive index dispersion for DSMR, direct comparison of DSMR photopolymer and PMMA windows of identical dimensions exhibited nearly identical optical transparency across the visible and NIR/SWIR spectrum after Fresnel correction; the Abbe number of DSMR is high enough that chromatic aberration should not be a concern in most applications. Furthermore, the birefringence of DSMR photopolymer glass was found to be extremely low and below the detection threshold of Metricon prism coupling measurements ($\Delta n < 0.0001$) (see Table S2, Supporting Information), which was comparable to the near zero-birefringence observed for free radically synthesized PMMA. It was anticipated that DSMR optical glasses exhibited comparable optical transparency and birefringence to stereochemically-atactic PMMA since both polymers possess an atactic polymethacrylate polymer backbone. However, the enhanced RI of the DSMR photopolymer is distinctive and directly correlated to the inclusion of sulfide groups throughout the crosslinked network.

The facile processing advantages of DSMR photopolymer resins were highlighted by the molding of very thick free-standing optical windows with diameters of 25 mm and varying thickness from 1–30 mm (**Figure** 3a). Optical

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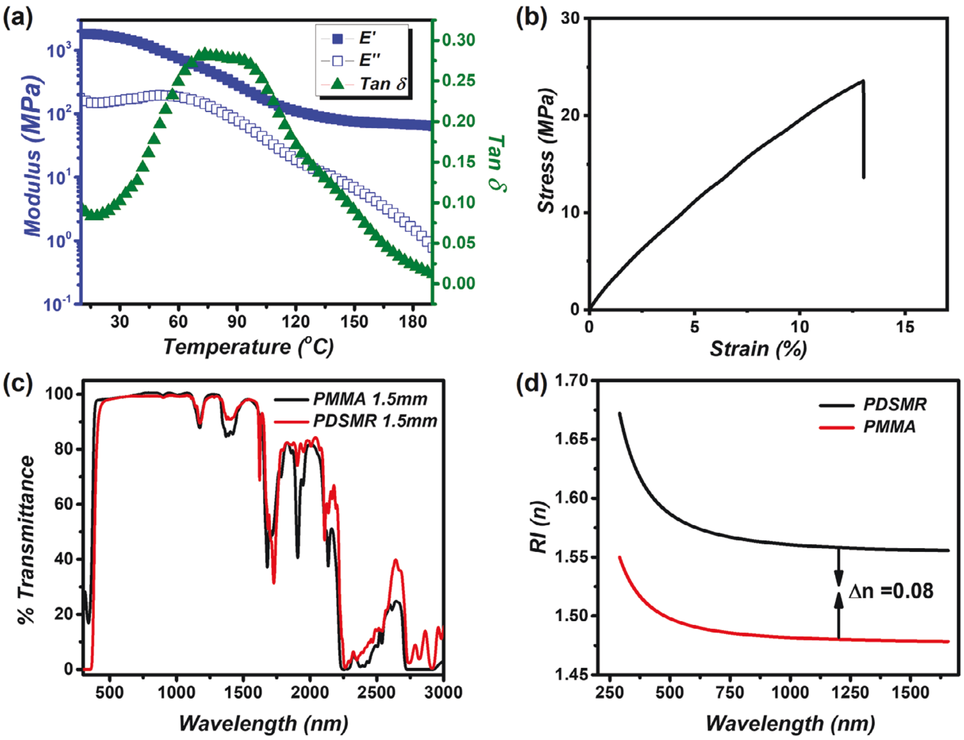

**Figure 2.** a) Plot of tensile storage (E′ solid blue) and loss (E″, hollow blue) modulus versus temperature of DSMR photopolymer with the plot of tan delta of DSMR photopolymer. b) Tensile stress versus strain plot of DSMR photopolymer photo- and thermally cured A4 dogbone samples. c) Fresnel corrected optical transmittance in the VIS–NIR–SWIR spectrum of DSMR photopolymer (red line) versus PMMA (black line) windows (1.5 mm thickness) and d) RI versus wavelength (nm) plots of DSMR photopolymer versus PMMA from ellipsometry and prism coupling measurements.

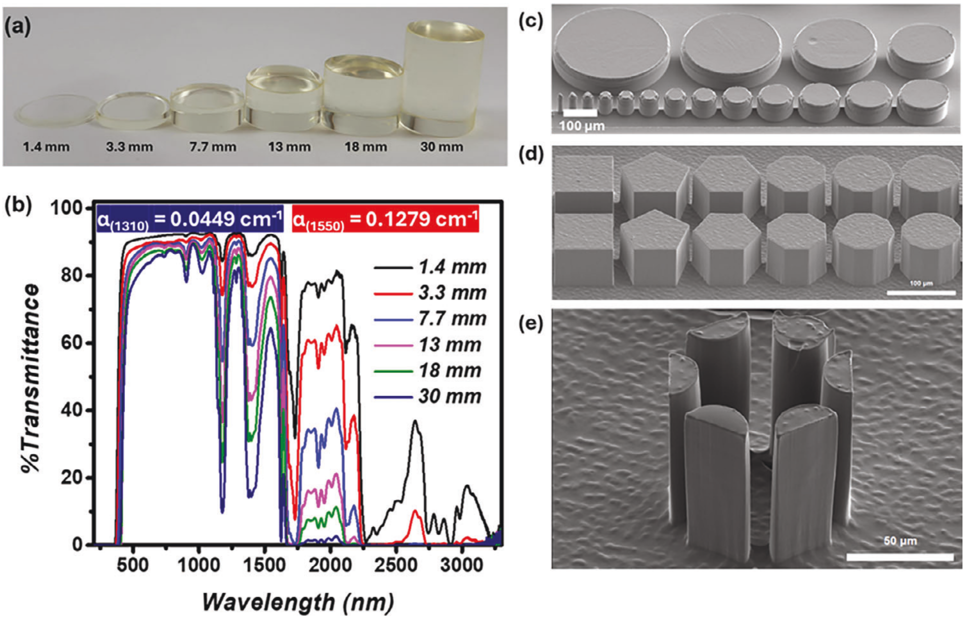

**Figure 3.** a) DSMR photopolymer windows of different thicknesses ($D$ = 25 mm, thickness = 1.4–30 mm) fabricated by photopolymerization and thermal-post bake ($T$ = 100 °C, 6 h); b) UV–vis–NIR transmittance spectra of DSMR photopolymer windows of different thicknesses with up to 90% transmittance at 1.4 mm thick; c) SEM micrograph of photopatterned DSMR cylindrical pillar arrays of varying diameter and aspect ratio; d) polygonal prisms with different base from square to dodecagon; and e) high magnification SEM micrograph of closely arranged high aspect ratio semicylindrical micropillars.

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transmittance spectral measurements revealed high transmittance in the VIS–NIR–SWIR spectrum, with even the thickest DSMR photopolymer windows (30 mm) retaining over 60–80%T in the VIS–NIR spectrum (Figure 3b). To our knowledge, this type of photopolymerization-based fabrication of a high RI, polymeric optical glass has not been previously conducted and is enabled by the scalability of this sulfur-based resin, coupled with the benefits of photopolymerization-based fabrication. The ability to readily fabricate very thick (large pathlength) high-quality optical glass windows enabled the determination of optical absorption coefficients ($\alpha$) for these highly transparent, non-absorbing materials (Figure 3a). The absorption coefficients for DSMR photopolymer glass were determined from the optical transmission spectra of the windows shown in Figure 3b and found to be remarkably low at 1310 nm ($\alpha_{1310\ \mathrm{nm}} = 0.045\ \mathrm{cm}^{-1}$) and 1550 nm ($\alpha_{1550\ \mathrm{nm}} = 0.128\ \mathrm{cm}^{-1}$) and notably lower than for PMMA,($\alpha_{1310\ \mathrm{nm}} = 0.075\ \mathrm{cm}^{-1}$; $\alpha_{1550\ \mathrm{nm}} = 0.180\ \mathrm{cm}^{-1}$),[9b] which was consistent with the optical transmission comparison discussed Figure 2c.

While recent reports of new optical polymers have emphasized the observation of high Abbe numbers from thin film ellipsometry to report on optical transparency, the variation of thin film surface homogeneity is sufficient to affect the accuracy of the calculated Abbe number values. This issue is illustrated in our thin film ellipsometry measurements, where PMMA was found to possess a higher Abbe number ($V_\mathrm{D} = 51$) versus DSMR photopolymers ($V_\mathrm{D} = 36$). However, the optical transmittance of DSMR photopolymer thick bulk windows shown in Figure 3a is clearly comparable, or superior to PMMA which illustrates the potential problems in using thin film measurements and Abbe number as the sole method to report on the optical transparency of new polymeric materials; Abbe number actually only relates to the dispersion of the refractive index. A high Abbe number does indicate, generally, that absorption is low, but it says nothing about the ability of the material to be made into large-thickness, homogeneous optical elements. Furthermore, this comprehensive study of optical transmittance versus thickness of DSMR photopolymer windows confirms the need for robust and facile processing methods for new optical polymer development. While the fabrication and measurement of thick optical glass samples for absorption coefficients are challenging and rarely conducted, this analysis is central to the validation of new optical polymers for plastic optics.

Having established the ability to fabricate large thick optical glass windows from DSMR photopolymers, the fabrication of demanding microstructured photopatterns was also conducted. This type of capability is technologically useful for the direct fabrication of micro-optical components, such as microlens arrays and flat diffractive optics, which include metalens-type constructs.[2e,3b,17c,19d,23] Using our previously developed micropillar master of varying cavity size,[24] liquid DSMR was infiltrated into these PDMS negative molds initially with cavities of varying dimensions, geometry and aspect ratios and subjected to the two-stage curing process previously described, in this case with a photoirradiation using a 385 nm source for 10 min and a post-bake step ($T = 140$ °C). Photopatterned cylindrical features of DSMR photopolymers exhibited high fidelity from low aspect ratio ($AR = 0.1$) structures starting from 500 µm in size down to high aspect ratio ($AR = 2.5$) cylinders 20 µm wide and 50 µm in height (Figure 3c). Furthermore, photopatterns of increasing geometrical edge complexity from square to hexagon and decagon on the order of 100 µm in diameter, all retained sharp edge features (Figure 3d). Finally, high aspect ratio, closely arranged semi-cylindrical micropillars (≈20 µm in diameter, 50 µm in height) were successfully replicated without incidence of pattern tilting or collapse during the harvesting process of DSMR photopolymer from the negative mold, pointing to the mechanical integrity of the DSMR optical glass structure (Figure 3e).

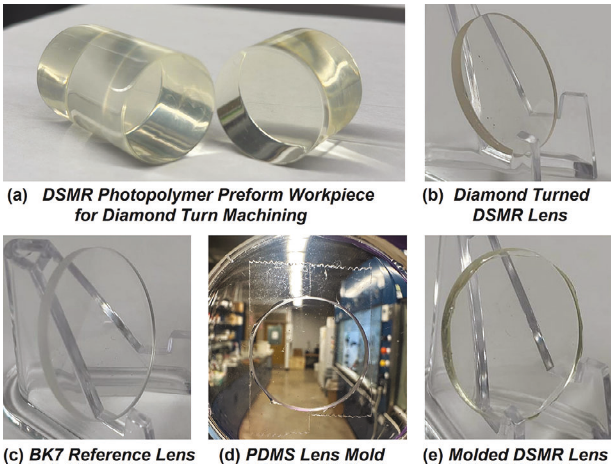

**Figure 4.** a) DSMR photopolymer windows used as preform workpieces for diamond turn machining fabrication; b) DSMR photopolymer plano-convex lenses fabricated from diamond turning: c) BK7 plano-convex lens used as reference and master for plastic lens fabrication; d) PDMS mold of BK7 lens; and e) molded DSMR photopolymer lens.

To demonstrate the processing versatility of DSMR photopolymers for precision plastic optics, well-defined plano-convex lenses were fabricated using optical machining and molding methods (**Figure 4**), where a commercially available crown glass (BK7) plano-convex lens (LA1229 from Thorlabs, $D = 25.4$ mm, $H = 2.9$ mm, radius of curvature = 90.1 mm; shown in Figure 4c; Figure S16, Supporting Information) was used as the reference/master for DSMR lens fabrication. The fabrication of DSMR photopolymer plano-convex lenses was initially done using single-point diamond turn machining[9c] using DSMR photopolymer windows as preform workpieces ($D = 25$ mm, thickness = 30 mm, fabricated with a $T = 100$ °C post-bake, shown in Figure 4a). Diamond turn cutting is an established, computer-numerically controlled subtractive polymer machining process that is the preferred technique in the optics industry for custom prototyping of precision optics.

Only a small set of synthetic polymers are suitable for diamond turning machining for plastic optics, as dependent on the thermomechanical and fracture properties of the material of interest.[25] Hence, the robust thermomechanical properties of DSMR photopolymers were demonstrated to enable plastic optic fabrication via established machining processes. Both white light interferometry (WLI) and atomic force microscopy (AFM) measurements of diamond-turned optical flats and plano-convex lenses of DSMR photopolymers (Figure 4b) confirmed the fabrication of high precision surfaces with very low surface roughness ($R_\mathrm{a}$ from WLI; $R_\mathrm{q}$ values from AFM) below the $\lambda/20$

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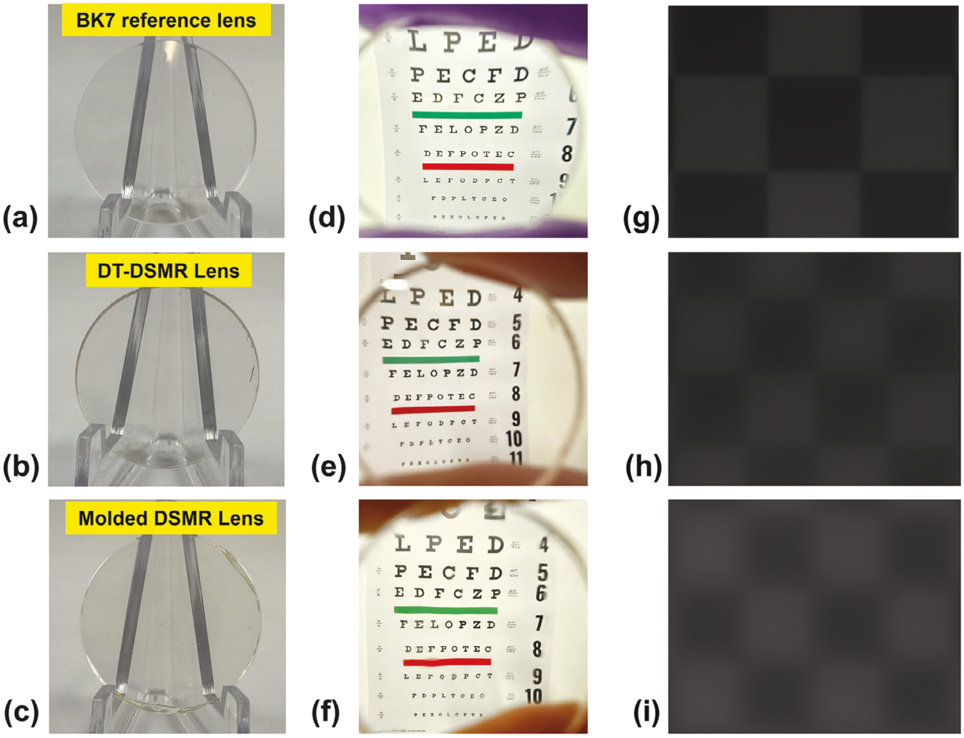

**Figure 5.** a) Commercial BK7 crown glass plano-convex lens; b) diamond turned (DT) DSMR photopolymer plano-convex lens of identical dimensions as BK7 lens from Figure 5a from single-point diamond turned machining; c) plano-convex poly(DSMR) lens fabricated by photopolymerization by casting into PDMS mold from a BK7 lens master; d) Snellen eye-chart images taken an IPhone 14 Pro Max camera using a BK7 crown glass lens ($n = 1.51$), DSMR photopolymer lenses ($n = 1.57$) from diamond turning (e) or PDMS molding; f) FOV images of checkerboard target taken with a CMOS camera using the BK7 lens (g) from Figure 5a, the DSMR photopolymer lens fabricated from diamond turning (h) from Figure 5b and the DSMR photopolymer lens fabricated from molding (i) from Figure 5c.

scale required for precision optics (See Table S3, Figure S15a–d, Supporting Information). Independently, molds from BK7 lens masters were cast using Sylgard 184 silicone elastomer (Figure 4d) to enable photopolymerized-based fabrication of DSMR photopolymer lenses (Figure 4e) by the photopolymerization and thermal post-treatment process discussed previously. Both WLI and AFM of molded DSMR photopolymer lenses confirmed replication of high-quality optical surfaces with $R_a$ and $R_q$ values well below the $\lambda/20$ length scale, with the exception of intermittent large particulate features associated with dust particles, or other macroscopic debris embedded into the PDMS mold during fabrication. Nevertheless, these examples validated the application of diamond turn machining and molding methods to fabricate high-quality DSMR photopolymer plastic optics with excellent replication of lens height and dimension of the BK7 reference lens.

Comparative imaging experiments were done for DSMR photopolymer lenses made from diamond turning and photopolymerization-based molding versus BK7 (**Figure** 5a–c) to assess the quality of the bulk optical glass, fabrication methods, and the effect of the higher refractive index. Qualitative imaging of ambient light backgrounds with the BK7 versus DSMR photopolymer lenses was conducted using a standard Snellen eye-chart, where bright, well-resolved imaging with an IPhone 14 Pro Max camera was achieved for all of these lenses, pointing to the successful fabrication of precision plastic optics. Imaging of RI effects on the field of view (FOV) was conducted with a checkboard imaging target using a complementary metal oxide semiconductor (CMOS) camera, where a wider field of view (FOV = 1.3×) was observed due to the higher RI of the DSMR photopolymer lens ($n \approx 1.57$) versus BK7 ($n \approx 1.51$) as noted by a higher density of boxes in images from both DSMR photopolymer fabricated lenses at identical focal lengths (Figure 5g–i). A gradual loss of checkerboard target resolution was observed for DSMR photopolymer lenses fabricated by diamond turning and soft PDMS molding versus the industrially polished BK7 reference lens. This was attributed to differences in fabrication methods versus intrinsic properties of the photopolymer material. While direct photopolymerization fabrication of bulk precision optics with precision polymer machining would be more desirable in the long term (and currently in progress), these fabrication and imaging demonstrations point to the viability of DSMR photopolymers as an optical glass for visible spectrum commodity plastic optics.

Finally, to demonstrate the amenability of DSMR photopolymer resins for larger-scale manufacturing methods, AM vat photopolymerization was conducted utilizing the HARP 3D printing technology (**Figure** 6a,b).[6] While HARP has proven successful for AM vat photopolymerization with a wide range of commercially available acrylic and methacrylic monomers, utilization of new monomers, particularly with new high RI photopolymer resins, had not been conducted. As an initial proof

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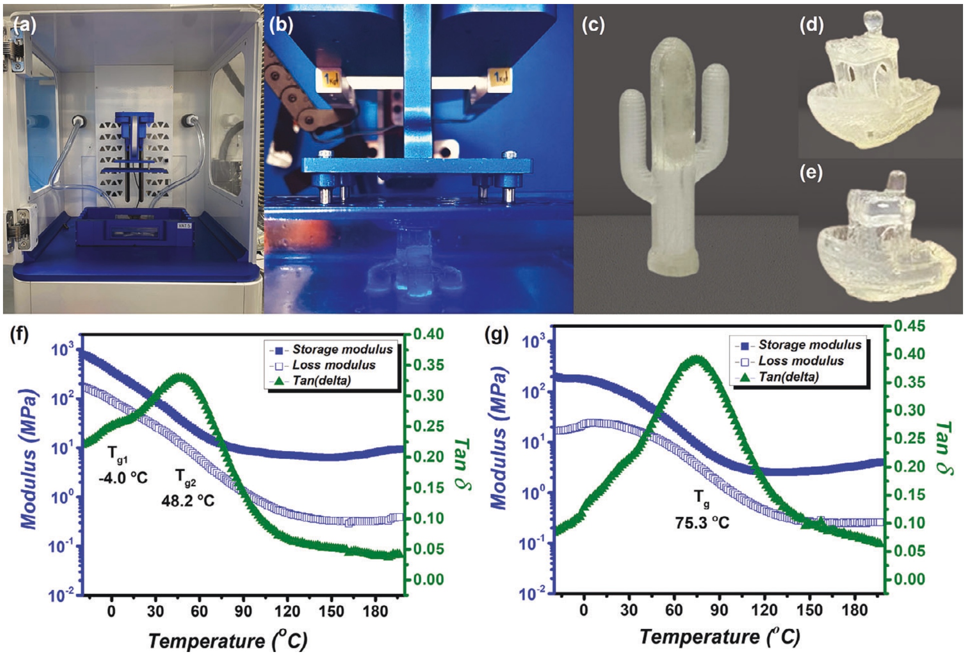

**Figure 6.** a) HARP DLP printer and b) HARP DLP printer in operando with DSMR photopolymer formulated resin with cactus print; c) 6 cm tall cactus printed from 60-vol% DSMR and HARP; d) benchies printed from the HARP printer with 60-vol% DSMR resin formulation; e) DMA plot printed DSMR formulation without thermal post cure; and f) DMA plot of printed DSMR formulation followed by a thermal post cure at 140 °C.

of concept, DSMR was formulated on 0.1 L batches (60-wt.% DSMR) with existing commercially available acrylate functional prepolymers, acrylate and diacrylate diluents with standard photoinitiators (ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate, tradename, TPO-L, 0.3 mol%). This photopolymer resin formulation was found to be homogeneous, colorless, and of appropriate viscosity for use in HARP DLP without further processing steps. Printing of the DSMR photopolymer resin was found to be successful via HARP at rates of 10 $\mu m^{-1}$ s speed, 70% intensity, and 385 nm wavelength, as demonstrated by the fabrication of complex printed objects, such as a multi-armed cactus (height = 6 cm, Figure 6c) and a 3 cm-sized benchy (Figure 6d), both of which required sufficient thermomechanical integrity throughout the printed part to be self-load bearing. Free-standing rectangular printed windows ($W = 12.5$ mm, $L = 35$ mm, thickness = 3 mm; were also successfully fabricated enabling DMA analysis of HARP printed windows before and after post-bake treatment confirming comparable high $T_g$ values as observed for poly(DSMR) neat material (Figure 6e,f). The success of this initial 3D printing demonstration with the HARP processes using the high RI, low-cost DSMR photopolymer formulation points to future large-scale manufacturing of large optical windows and high refractive index plastic optics for consumer eyewear. However, further photopolymer resin development and 3D-printing optimization are required to achieve the high optical quality, robust thermomechanical properties, and low cost of state-of-the-art commodity plastic optics.

## 3. Conclusion

The development and application of a new high RI, low-cost photopolymer resin to afford high-quality optical glass via photopolymerization methods is reported. This new methacrylate and sulfur-based resin, termed, disulfide methacrylate resin (DSMR) is amenable to classical free radical-based photopolymerization methods and affords colorless, thermomechanically robust optical glass of high RI ($n \approx 1.57$), high transparency and very low birefringence. This is the first example, to our knowledge, of using an inexpensive, sulfur petrochemical, sulfur monochloride, to prepare a high refractive index photopolymer resin suitable for rapid free radical photopolymerization. Both the low cost and selective reactivity of sulfenyl chloride groups in $S_2Cl_2$ toward allylic moieties enabled the large-scale synthesis of this colorless, low-viscosity liquid resin. DSMR photopolymers can be cast into thick free-standing optical forms, which has not been achieved with this suite of chemical features, low cost, and bulk properties. Importantly, DSMR photopolymer glass was also found to be non-toxic in L929 mouse fibroblast cell and ARPE-19 human eye cell culture studies. The rapid photopolymerizability offers significant advantages in preparing high-quality, bulk optical glass of controllable thickness (1–30 mm) and is sufficiently robust to enable high aspect ratio photopatterning, and precision machining fabrication into plastic optical lenses. Finally, we demonstrate the scalability of DSMR for 3D printing vat photopolymerization using the HARP DLP process, pointing to the viability of DSMR sulfur-based photopolymer resins for commodity plastic optics. Clearly, significant further development in the DSMR photopolymer is required to further raise the refractive index and enhance the thermomechanical properties of the final optical glass to compete with state-of-the-art commodity optical thermoplastics and thermosets where the upper limit of refractive index now exceeds $n = 1.7$ in the visible spectrum. Furthermore, significant optimization of photopolymerization and 3D-printing conditions are also required to afford direct fabrication of precision

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optical components of high surface quality without the need for additional fabrication steps (e.g., polishing, cutting, grinding). Nevertheless, these collective findings project to impact high volume markets for consumer eyewear and multi-lens assemblies in smartphone electronics where the use of high refractive index plastic optics offers significant advantages that reduce the form factor of optical components and devices.

## 4. Experimental Section

Detailed experimental procedures and instrumentation can be found in Supporting Information.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors gratefully acknowledge the National Science Foundation (CHE-2201155), the U.S. Air Force Asian Office of Aerospace Research and Development (AOARD; FA2386-24-1-4045), and the Agency for Science, Technology, and Research, Singapore for support of this work. All NMR data were collected in the Nuclear Magnetic Resonance Facility, RRID: SCR_012716, in the Department of Chemistry and Biochemistry at the University of Arizona. The purchase and upgrade of the Bruker AVANCE DRX 500 spectrometer was partially supported by the National Science Foundation under Grant Numbers 9214383 and 9729350, the Office of Naval Research, and the University of Arizona. All Cypher AFM images and data were collected in the W.M. Keck Center for Nano-Scale Imaging, RRID: SCR_022884, in the Department of Chemistry and Biochemistry at the University of Arizona. The Cypher instrument purchase was supported by the National Science Foundation under Grant Number 1337371.

## Conflict of Interest

R. A. Norwood is an owner and officer of Norcon Technologies Holding, Inc with which a financial conflict of interest exists

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

3D-printing, high refractive index, optics, photopolymers

Received: November 21, 2024
Revised: February 9, 2025
Published online: March 2, 2025

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