Comonomer Isomers Result in Varied Optical Properties for Long Wavelength Infrared-Transmitting ORMOCHALC Polymers

Darryl A. Boyd[1*], Vinh Q. Nguyen[1], Frederic H. Kung[2], Nia A. Pollard,[3] Jason D. Myers[1], Daniel J. Gibson,[1]
Collin C. McClain[4], Colin C. Baker[1], Andre Z. Clayborne,[3] Woohong Kim[1], and Jasbinder S. Sanghera[1]

[1]Optical Sciences Division, Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375, USA
[2]University Research Foundation, 6411 Ivy Ln Ste 110, Greenbelt, MD, 20770, USA
[3]George Mason University, Chemistry & Biochemistry Department, 4400 University Dr, Fairfax, VA 22030
[4]Johns Hopkins University, Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723

* darryl.boyd@nrl.navy.mil

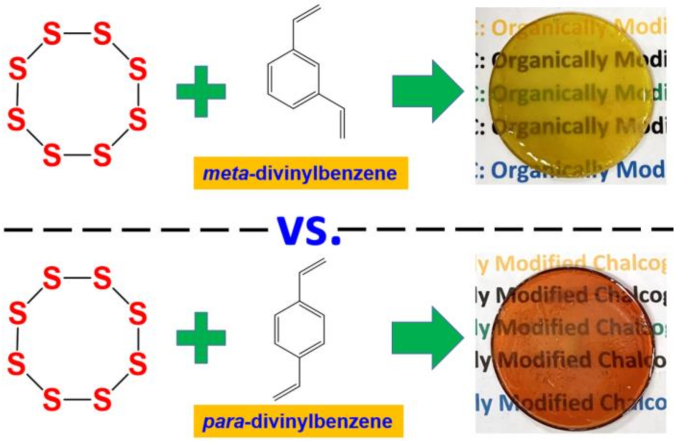
Comonomer Isomers Result in Varied Optical Properties for Long Wavelength Infrared-Transmitting ORMOCHALC Polymers

Darryl A. Boyd[1*], Vinh Q. Nguyen[1], Frederic H. Kung[2], Nia A. Pollard,[3] Jason D. Myers[1], Daniel J. Gibson,[1] Collin C. McClain[4], Colin C. Baker[1], Andre Z. Clayborne,[3] Woohong Kim[1], and Jasbinder S. Sanghera[1]

[1]Optical Sciences Division, Naval Research Laboratory, 4555 Overlook Ave SW, Washington, DC 20375, USA
[2]University Research Foundation, 6411 Ivy Ln Ste 110, Greenbelt, MD, 20770, USA
[3]George Mason University, Chemistry & Biochemistry Department, 4400 University Dr, Fairfax, VA 22030
[4]Johns Hopkins University, Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723
*darryl.boyd@nrl.navy.mil

Keywords: inverse vulcanization, sulfur, divinylbenzene, isomer, infrared transmission, polymer, high refractive index

Abstract



Inverse vulcanization is a method by which sulfur is combined with comonomer molecules to develop stable materials termed organically modified chalcogenide (ORMOCHALC) polymers. Although various comonomers have been used in the fabrication of ORMOCHALC polymers in prior studies, this study was performed to determine the effect of using molecular isomers, as comonomers in separate reactions, on the optical properties of ORMOCHALC polymers. For the study, *meta*-divinylbenzene (*m*-DVB) and *para*-divinylbenzene (*p*-DVB) were separately combined with sulfur in equivalent atomic percentage amounts to form poly(S-*r*-*m*-DVB) and poly(S-*r*-*p*-DVB), respectively. The use of these isomers resulted in polymers with notable differences in their optical properties, including the polymer color, optical transmission and refractive index. The impact of comonomer selection on the optical character of ORMOCHALC polymers is investigated and the results detailed.

Introduction

In recent years, the development of sulfur-based polymers using the inverse vulcanization processing method has opened several possibilities for polymer use in various applications.[1-2] This includes use as battery cathode materials,[3-5] dye-sensitized solar cells,[6-7] or as infrared-transmitting optical lenses and materials.[8-12] Variations of the inverse vulcanization process have also been employed in order to fabricate sulfur-based polymers at milder temperatures than in the initial reports.[13-15] A significant portion of the research has focused on using different comonomers to combine with the sulfur-rich backbone. These comonomers are commonly polyvinyl and they are often synthetic, but they can also be naturally occurring and/or renewable.[16-21] Using different comonomers often leads to polymers with vastly different properties, and therefore portends different uses for those polymers.

A number of reports involving inverse vulcanization have been published in which sulfur is combined with divinylbenzene (DVB) as the comonomer, to produce poly(S-*r*-DVB).[15, 22-25] Many of these reports focus on developing sulfur-based polymers for use as cathode materials in rechargeable lithium-sulfur batteries, with DVB participating in some portion of the polymer synthesis.[22-23, 26] Yet some reports focus on other aspects of poly(S-*r*-DVB).[24-25, 27] Despite the common use of DVB as a comonomer in inverse vulcanization reactions, rarely is the isomeric composition of the DVB discussed in relationship to the resulting materials properties. This is the case even though the DVB utilized in such studies is usually an 80% mixture of DVB isomers, with other side molecules accounting for the remaining 20%. Nevertheless, many of the reports utilize DVB "as is," without further purification or isomer isolation.

To date, there have been no inverse vulcanization reports of the different properties that arise from using DVB comonomer solutions containing > 90% of a single DVB isomer (e.g. *meta*-DVB) versus using another solution containing > 90% of a different DVB isomer (e.g. *para*-DVB). To further understand the effect of comonomer differences on the resulting optical properties of ORMOCHALC polymers, herein we compare ORMOCHALCs synthesized with similar comonomers, including DVB comonomer isomers.

Materials and Methods

Sulfur was purchased from All-Chemie Ltd. and purified to 99.999% purity as previously described.[9] The 80% DVB (mixed-DVB) and 90% *para*-DVB (*p*-DVB) were purchased from Sigma Aldrich. The 98% *meta*-DVB (*m*-DVB) was purchased from Combi-Blocks. The 97% 1,3-diisopropenyl benzene (DIB) was purchased from TCI America. All non-sulfur comonomers were used as received.

Polymer Fabrication: ORMOCHALC polymers were synthesized as previously described.[10] In general, 0.0095 mol (30 wt%) of the comonomer (i.e. DIB, *m*-DVB, *p*-DVB or mixed-DVB) was added to molten sulfur at ~135 °C, and stirred for ~8 min in a non-stick container. The non-stick container was then placed in a preheated furnace, and the product cured at ~175 °C for 1 hr. Finally, the non-stick container was removed from the furnace to allow the ORMOCHALC polymer to cool and be extracted in freestanding form. Polymer specimen thicknesses ranged between 1.0 and 1.7 mm, and specific thicknesses for each polymer specimen are explicitly stated in **Table 1**. Note: It is important that all reactions be carried out in ventilated conditions (e.g. in a fume hood).

Optical Imaging: A digital camera was used to image the polymer specimens in the visible wavelength range. Short-wavelength infrared (SWIR) images were taken using a FJW Industries FIND-R-SCOPE SWIR imager that had an upper wavelength limit of 1.3 µm. Mid-wavelength infrared (MWIR) images of polymer specimens were taken using a SOFRADIR-EC Model IRE-640BB camera with a lens operating in the 3 – 5 µm wavelength region. Long-wavelength infrared (LWIR) images of polymers were taken using a FLIR T600 Camera in the wavelength range of 7.5 – 14 µm.

Spectroscopic Analysis: UV-visible-NIR transmission data was obtained using an Agilent Technologies Cary 7000 Universal Measurement Spectrophotometer. Longer wavelength data was obtained using a Thermo Scientific *Nicolet iS50R* FT-IR Spectrometer. The data for the individual comonomers was taken by separately placing a drop of comonomer between two potassium bromide (KBr) disks and loading the sandwiched sample into the FT-IR. Similarly, FT-IR data for sulfur was taken by heating sulfur between KBr disks until it was a molten thin film, and then loading the sandwiched sample into the FT-IR. Spectroscopic measurements were conducted in dry $N_{2(g)}$ atmosphere and background corrected for the environment. Raman data was obtained using a Thermo Scientific *Nicolet iS50* Raman fitting on the *Nicolet iS50R* FT-IR Spectrometer.

Refractive Index Determination: Refractive index values were determined using a Metricon 2010/M Prism Coupler refractometer, with laser sources at 636.3, 983.6 and 1548.4 nm. The Metricon 2010/M Prism Coupler refractometer utilized a standard Rutile prism whose index was calibrated at each respective wavelength using a reference "Hi-Index" (Schott N-LaF3) glass. The recorded index values were averaged over five instrument scans. The refractive indices for all of the ORMOCHALC polymers at the various interrogated wavelengths are given in **Table 2**.

Differential Scanning Calorimetry Analysis (DSC): DSC was performed on a TA Instruments Q200. The reference/control material used for this analysis was an empty Tzero alodined DSC cup, and nitrogen gas was flowed at 50 ml/min over the sealed cups. The temperature was ramped from -40 to 125 °C at a rate of 5 °C/minute. The glass transition temperatures (T_g) are given in **Table S1**.

Thermogravimetric Analysis (TGA): TGA was performed on a TA Instruments 2960 SDT. The samples were heated from 25 to 500 °C at 10 °C/minute under a nitrogen gas purge. The degradation temperature values given in **Table S1** represent the temperature at which 95 mass % and 90 mass % of the sample remained, respectively.

Density Measurements: Density was calculated for five samples using the Archimedes method. A Micromeritics AccuPyc II 1345 gas pycnometer was used to measure the volume of each sample. An aluminum cylinder approximately 1.75" diameter by 2" tall (~79 cm^3) was used to reduce the internal volume of the standard 100 cm^3 measurement chamber for each sample measurement. The instrument empty volume was calibrated immediately before measurements were made. The density of a silica glass plate was used as the control. Measured densities are given in **Table S2**.

Results and Discussion

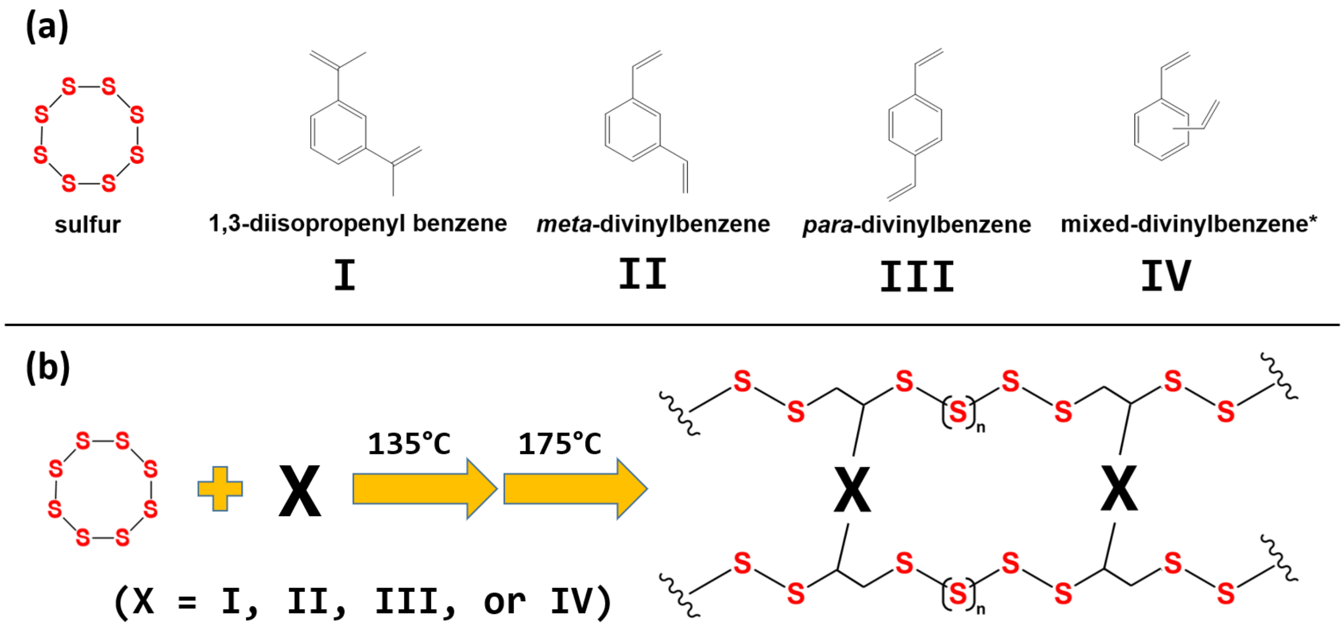


Figure 1. (a) Molecular structures for S_8 and the four comonomers that were reacted with S_8 in separate reactions to produce ORMOCHALC polymers for this study. (b) Synthetic scheme for ORMOCHALC polymers. *The given structure for **IV** is used to indicate that the solution is primarily a mixture of *m*-DVB and *p*-DVB isomers.

Table 1. Thicknesses of ORMOCHALC polymer specimens used for UV-vis and FTIR analyses.

Comonomer	ORMOCHALC	Thickness (mm)
I	poly(S-*r*-DIB)	1.65
II	poly(S-*r*-*m*-DVB)	1.00
III	poly(S-*r*-*p*-DVB)	1.10
IV	poly(S-*r*-mixed-DVB)	1.69

The synthesis of the ORMOCHALC polymers was carried out via inverse vulcanization (**Figure 1**). The only reagents involved in the syntheses were sulfur and one of **I**, **II**, **III** or **IV**. The **IV** used in this study was 80% DVB containing four compounds with manufacturer given values of 55% *m*-DVB, 25% *p*-DVB, 18.6% ethylvinylbenzene, and 0.03% diethylbenzene. Therefore, to evaluate the significance of using one isomer in favor of another, both **II** and **III** were separately combined with sulfur to produce unique ORMOCHALC polymers using inverse vulcanization. Data for the ORMOCHALC polymer fabricated using **I** is included herein because its structure is similar to that of **II** (Figure 1), and because it is considered the benchmark comonomer for polymers synthesized via inverse vulcanization.[3] Data for the ORMOCHALC polymer fabricated using **IV** is included because of its use in prior works, and because it contains both the *meta*- and *para*- isomers of DVB. The resulting ORMOCHALC polymer specimens did vary in thickness (**Table 1**), but all of the data reported herein comes from polymers that were at least 1.0 mm in thickness.

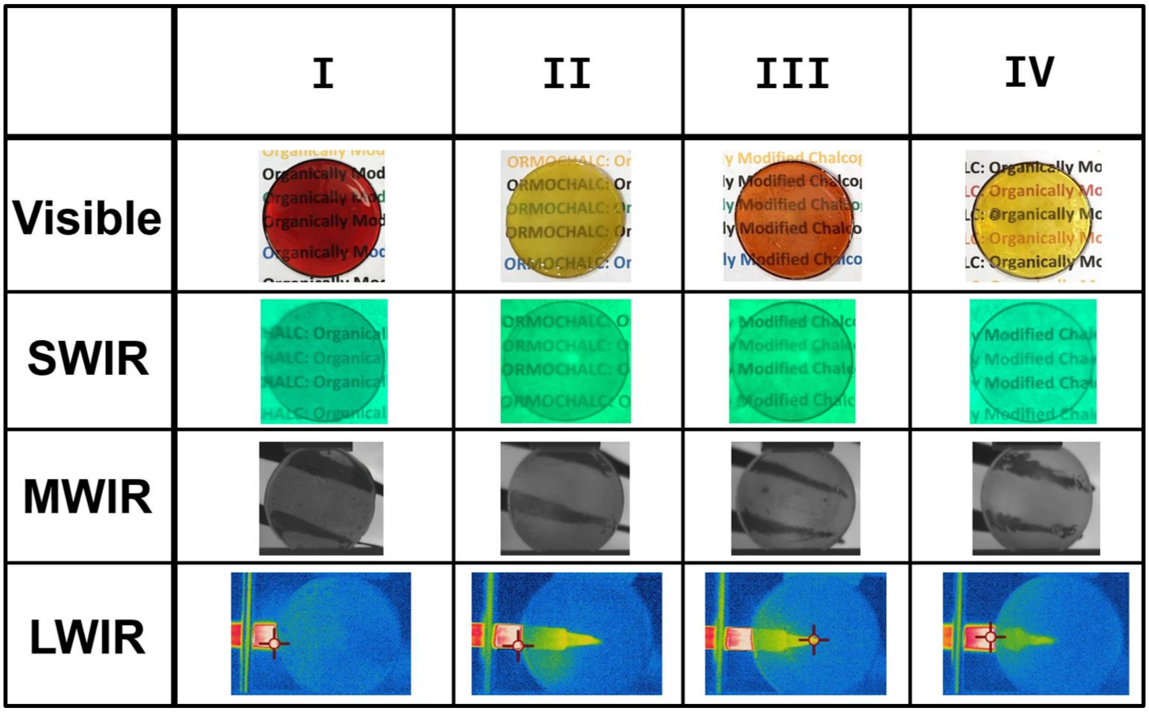


Figure 2. Images taken in the visible wavelength range, SWIR wavelength range, MWIR wavelength range and LWIR wavelength range for ORMOCHALC polymers made using comonomers **I** – **IV**. Text is visible through the polymers in visible and SWIR rows, human fingers are visible through the polymers in the MWIR row, and a hot soldering iron is visible through three of the polymers in the LWIR row.

The combination of sulfur with **I** resulted in poly(S-*r*-DIB), and yielded a polymer that was transparent red in appearance (**Figure 2**). Both **I** and **II** feature benzene rings substituted at the 1- and 3- positions, with **I** substituted with isopropenyl groups, and **II** substituted with vinyl groups. Even though comonomer **II** is structurally similar to comonomer **I**, which yielded a transparent red ORMOCHALC polymer when combined with sulfur, the ORMOCHALC formed using **II** (poly(S-*r*-*m*-DVB)) was transparent yellow in appearance. In addition, despite the fact that **II** is a structural isomer of **III**, using **III** in the inverse vulcanization process yielded a transparent orange ORMOCHALC polymer, designated poly(S-*r*-*p*-DVB). When comonomer **II** was used instead of **III**, this difference was not only in the color, but also in the clarity, with poly(S-*r*-*m*-DVB) being qualitatively hazy, and poly(S-*r*-*p*-DVB) showing no visible haziness. The combination of sulfur with **IV** yielded a transparent yellow polymer, and is designated poly(S-*r*-mixed-DVB) herein. Poly(S-*r*-mixed-DVB) had qualities similar to both poly(S-*r*-*m*-DVB) and poly(S-*r*-*p*-DVB). For example, poly(S-*r*-mixed-DVB) had the yellow color of poly(S-*r*-*m*-DVB), but a transparency and qualitative clarity more similar to that of poly(S-*r*-*p*-DVB). The colors and transparencies for all ORMOCHALC polymer specimens were reproducible and consistent throughout multiple samples made for each type.

Because **II** bears structural similarities to both **I** and **III**, the drastic difference in optical appearance observed amongst those three resulting ORMOCHALCs was not expected. It can be concluded that the difference between the polymers resulting from **I** and **II** was the presence of the methyl groups in comonomer **I**. Similarly, it can be concluded that the difference between the polymers resulting from **II** and **III** was the location of the isomeric vinyl substituents. Since comonomer **IV** contains a combination of *m*-DVB and *p*-DVB, which are found in **II** and **III**, respectively, it is not surprising that the resulting ORMOCHALC polymer exhibited notable qualities similar to both of the ORMOCHALC polymers that **II** and **III** produced when combined with sulfur.

As previously noted, numerous groups have reported using inverse vulcanization to synthesize polymers by combining sulfur with comonomer mixtures similar to **IV** used in this report. For example, Salman et al. reported the fabrication of "poly(S-*r*-DVB)," in which the DVB comonomer was a mixture of *ortho*-DVB, *m*-DVB and *p*-DVB.[24] The inverse vulcanization synthetic procedure carried out by Salman et al. entailed melting elemental sulfur at 160 °C, stirring in DVB as the temperature was increased to 200 °C, and proceeding until a homogeneous solution formed. Once the homogeneous solution formed, the mixture was heated at 200 °C for 10 additional minutes, then allowed to gradually cool to room temperature. The polymers that resulted were reddish brown in color. This differs greatly from the transparent yellow ORMOCHALC obtained in the current report when molten sulfur was combined with **IV**. The difference in color may be attributed to the different combination of DVB isomers in the solution used by Salman et al. in comparison to the combination in the current report. Differences in curing times may also be a factor in the observed color differences. Moreover, the samples fabricated in the current study were made without ever heating the reaction to, or curing the product at temperatures greater than 175°C. Jenkins and co-workers recently noted that procedural differences can play a major role in the properties exhibited by polymers made via inverse vulcanization.[28] Therefore, an alternative explanation for the difference in the polymer colors between the current report and reports from other groups may be due to procedural differences in the polymer synthesis; specifically the timescales and temperatures at which the reactions were carried out.

It is unclear what the contributions of diethylbenzene and ethylvinylbenzene were to the properties of poly(S-*r*-mixed-DVB) in the current report. With a concentration of 0.03% within the mixed-DVB solution, the contribution of diethylbenzene on the materials properties of poly(S-*r*-mixed-DVB) was likely minor. However, with ethylvinylbenzene accounting for nearly 20% of the mixed-DVB solution (**IV**), it is possible that its presence within the inverse vulcanization reaction had a non-trivial effect on the materials properties of poly(S-*r*-mixed-DVB).

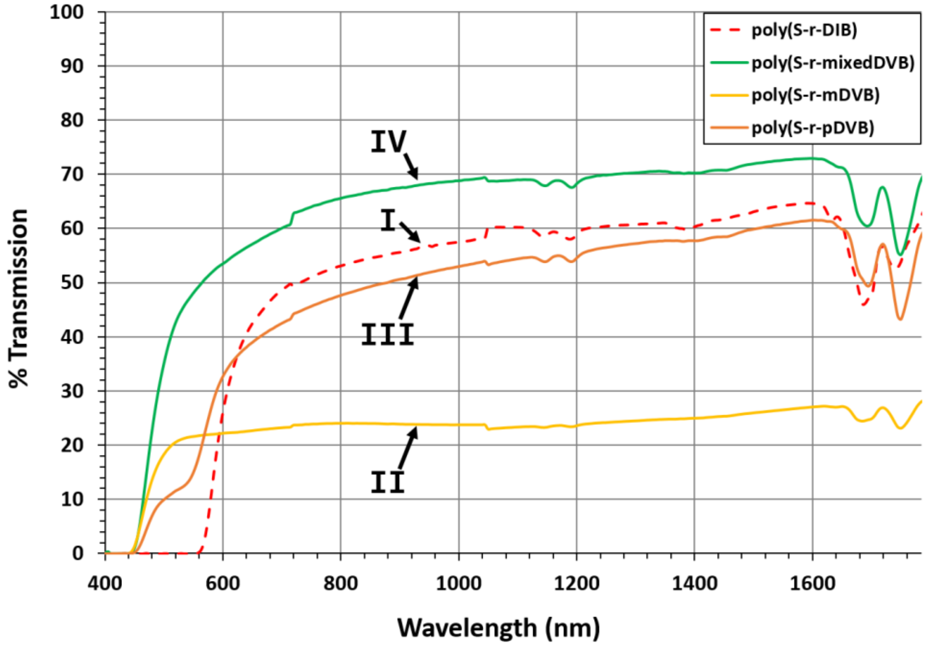


Figure 3. UV-vis-near IR comparison plot of ORMOCHALC polymer specimens. Symbols **I**, **II**, **III** and **IV** indicate the comonomer used in making the ORMOCHALC polymer. The samples measured had different thicknesses (Table 1) and data was not corrected to account for Fresnel reflections and scattering from a non-polished surface.

The spectral analysis given in **Figure 3** agrees with what is qualitatively visible in **Figure 2**. All of the ORMOCHALC polymers have characteristic absorbances between 1650-1800 nm, with smaller absorbances at 1150-1200 nm (**Figure 3**). The two ORMOCHALC polymers that appear yellow (poly(S-*r*-*m*-DVB) and poly(S-*r*-mixed-DVB)) had notable transmission beginning at ~475 nm. Transmission for the orange poly(S-*r*-*p*-DVB) also began at ~475 nm, but exhibited a shoulder at ~575nm. The red poly(S-*r*-DIB) transmittance increases sharply at ~600nm (**Figure 3**). The maximum transmittance observed came from poly(S-*r*-mixed-DVB), with values around 70% from the near infrared through the SWIR region. The measured transmission for poly(S-*r*-*m*-DVB) was remarkably less than that of the other ORMOCHALCs (**Figure 3**) for nearly all wavelengths in the visible through near infrared. This coincides with the visible hazy nature of the polymer specimen (**Figure 2**) suggesting that the overall low-transmission of this sample is primarily due to optical scattering. This is further supported by the monotonic increase in transmission with respect to wavelength in the infrared (**Figure 4**). Overall, the absorbances that arose in all of the polymers were consistent with those seen in prior reports.[8] Of particular note here is the reasonably high transmission (> 55%) in most of the region that spans the visible to the SWIR for all of the ORMOCHALCs except for poly(S-*r*-*m*-DVB) despite all of these specimens being >1 mm thick (**Table 1**) and despite signal losses due to surface reflections not being accounted for. Polishing the sample surface to eliminate extrinsic optical scattering suggests optics made from these materials can be utilized in a broad array of applications.

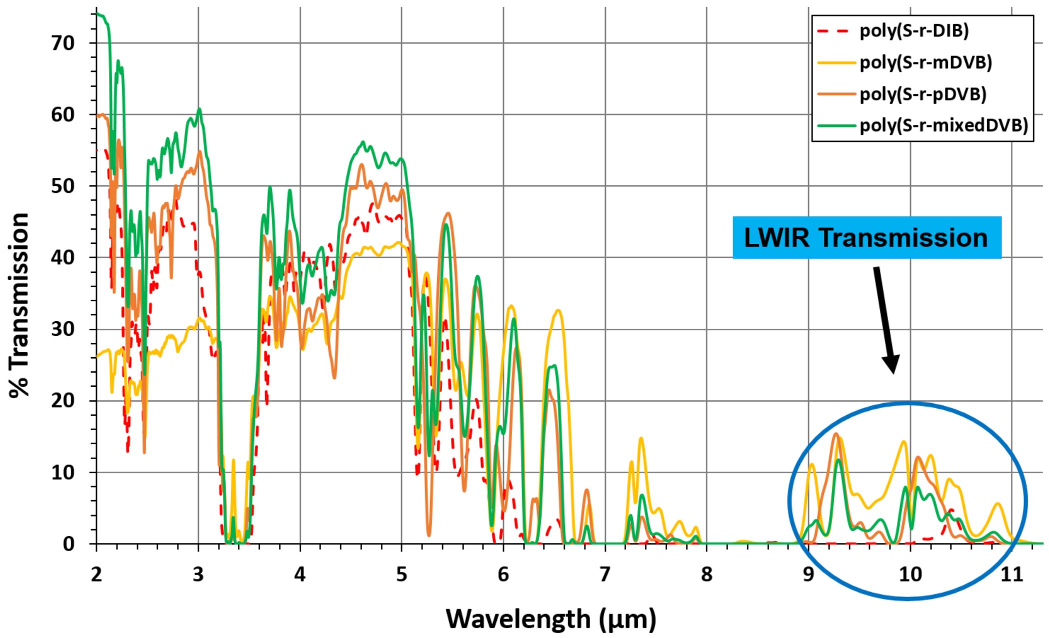


Figure 4. FTIR comparison plot of ORMOCHALC polymers from the near-IR to LWIR wavelengths. The samples measured had different thicknesses and data was not corrected to account for Fresnel reflections.

In agreement with what is qualitatively depicted in **Figure 2**, the FTIR comparison given in **Figure 4** revealed that each of the ORMOCHALC polymers possessed functionally useful transmission in both the SWIR and MWIR wavelength regions (**Figure 4**). The transmission values for poly(S-*r*-DIB) and poly(S-*r*-*p*-DVB) were both less than poly(S-*r*-mixed-DVB) from 2-3 µm, but substantially larger than the transmission values for poly(S-*r*-*m*-DVB) in the same range. It is worth noting that together, **Figure 3** and **Figure 4** show poly(S-*r*-mixed-DVB) had the greatest transmission of all of the polymers reported for most of the range from ~475 nm until ~5 µm, despite having the greatest thickness (**Table 1**).

While the visible and IR transmission curves reported for each of the four polymer types in this study were all less than 60%, these measurements do not account for optical signal losses due to Fresnel reflections (which are on the order of 7-9% per face) and sub-optimal surface quality (i.e. the samples were not polished to optical quality). Nevertheless, all four polymers transmit from the visible through the MWIR, and the DVB based polymers demonstrated transmission in the LWIR range significant enough to permit thermal imaging as shown in **Figure 2**.

As seen in **Figure 2**, and confirmed in **Figure 4**, there were differences in transmission in the LWIR when **I** was used as a comonomer with sulfur, versus when **II**, **III** or **IV** were used. Using **I** as a comonomer with sulfur in the inverse vulcanization process resulted in a polymer that did not transmit in the LWIR, which is a result that is consistent with our prior report[10] and a subsequent report by Kleine, et al.[29] Surprisingly, when separately combined with sulfur via inverse vulcanization, comonomers **II**, **III**, and **IV** all produced ORMOCHALC polymers that were LWIR-transmitting, as seen in **Figure 2** and **Figure 4**. This is a rare report of bulk polymers transmitting in the LWIR at thicknesses of 1 mm or greater.[10, 29] In the 1st report of bulk polymer LWIR transmission, it was hypothesized that the polymer transmitted in the LWIR due to the presence of a metal in the organometallic comonomer tetravinyltin.[10] The results in the present report, along with the results from the report by Kleine, et al.,[29] demonstrate that a metal is not necessary for LWIR transmission in bulk polymers. With DIB being so similar in structure to DVB, it is not exactly clear why poly(S-*r*-DIB) is opaque in the LWIR, while the DVB-containing ORMOCHALC polymers are transmissive. However, it seems apparent that the two terminal methyl groups from the isopropenyl groups in DIB play some role in the lack of LWIR transmission for poly(S-*r*-DIB). It must be noted that poly(S-*r*-DIB) is opaque in the LWIR despite the fact that both of its comonomers (sulfur and DIB) show significant transmission in the LWIR, and despite the fact that DIB has fewer absorptions from 7.5-14 µm than the DVB comonomers which produce LWIR transmitting polymers when combined with sulfur (**Figure S2**). In addition to the transmission noted from 7.5-14 µm, extended FTIR analysis indicated all of the ORMOCHALC polymers fabricated for this study possess transmission upwards of 20% in the range from 15-20 µm (**Figure S1**).

There is tremendous value in developing polymers that transmit in the LWIR.[30] This includes the ability to visualize objects in complete darkness via high-resolution thermal imaging.[29, 31-32] Advantages also include the fact that polymers, like the ORMOCHALC polymers detailed herein, can be fabricated with cheap and abundant resources, and they tend not to be as qualitatively brittle as common IR-transmitting materials such as germanium and chalcogenide glasses.

Table 2. Refractive index values for ORMOCHALC polymers at various wavelengths.

ORMOCHALC	636.4 nm	983.6 nm	1548.4 nm
poly(S-*r*-DIB)	1.831	1.799	1.790
poly(S-*r*-*m*-DVB)	1.855	1.825	1.815
poly(S-*r*-*p*-DVB)	1.781	1.757	1.744
poly(S-*r*-mixed-DVB)	1.924	1.888	1.875

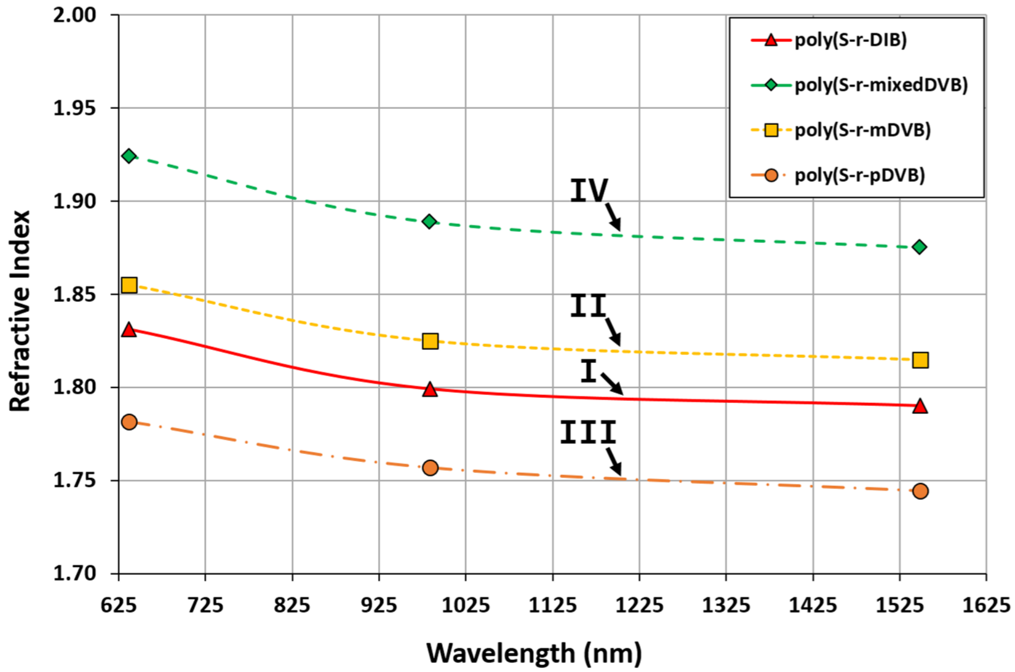


Figure 5. Refractive indices of ORMOCHALC polymers at three wavelengths. Symbols **I**, **II**, **III** and **IV** indicate the comonomer used in making the ORMOCHALC polymer. Lines are fits to the three discrete data points indicated in the plot.

As is common with polymers synthesized via inverse vulcanization, all of the ORMOCHALCs containing DVB comonomers exhibited ultra-high refractive indices for polymers, with values at 636.3 nm ranging from 1.78 for poly(S-*r*-*p*-DVB) to 1.92 for poly(S-*r*-mixed-DVB) (**Table 2**). The poly(S-*r*-*p*-DVB) ORMOCHALC had the lowest refractive indices at all wavelengths, returning values that were not only less than that of poly(S-*r*-DIB), but also significantly less than that of poly(S-*r*-*m*-DVB) (**Figure 5**). This result again highlights the significance of using one isomer versus another isomer as the inverse vulcanization reaction comonomer. Perhaps the most remarkable result was the fact that despite containing large percentages of both *m*-DVB and *p*-DVB, poly(S-*r*-mixed-DVB) exhibited refractive index values substantially greater than the ORMOCHALCs fabricated using either **II** or **III** as reaction comonomers at each wavelength interrogated (**Figure 5**). This poly(S-*r*-mixed-DVB) refractive index result may be due to the presence of the ethylvinylbenzene and/or the diethylbenzene that make up ~20% of the mixed-DVB stock solution.

Conclusions

In summary, we report the synthesis of ORMOCHALC polymers using sulfur with one of four comonomers that have similar structures, including the isomers *m*-DVB and *p*-DVB. The ORMOCHALC polymers exhibited vastly different optical properties when compared with one another despite the comonomer similarities. These differences included their colors, transmission ranges, and refractive indices. Although there were notable differences in their optical properties, a notable commonality was the LWIR transmission for all of the bulk ORMOCHALC polymers that contained DVB comonomers. LWIR has rarely been reported for bulk polymers.[10, 31] This result demonstrates that it is possible for bulk polymers (> 1 mm thickness) to transmit in the LWIR, even in the absence of nanoparticles, organometallic components, or large/bulky comonomers, and it opens up further possibilities for the development of optical polymers with IR sensing capabilities.

It is noteworthy that the greatest SWIR and MWIR transmission was observed in the poly(S-*r*-mixed-DVB) sample, which was markedly thicker (~1.7 mm) than lower-transmitting poly(S-*r*-*m*-DVB) and poly(S-*r*-*p*-DVB) (~1 mm), indicating that it had significantly less attenuation. It is not readily apparent whether this is due to lower intrinsic absorption, improved surface quality, or more favorable internal morphology with reduced scattering. Follow-on work will include the fabrication of samples appropriate for accurate measurement of optical properties (dispersion and absorption coefficient) in the visible through LWIR wavelengths.

Overall, this study highlights the importance of comonomer choice when seeking to impart certain properties to polymers fabricated via inverse vulcanization. It also signals a caution against drawing broad conclusions about the origin of a material's properties based upon comonomer isomeric mixtures (e.g. DVB), unless the contributions of each isomer to the resulting material's properties are more explicitly detailed. Although this report focuses on sulfur-based polymers fabricated via inverse vulcanization, the use of comonomer isomers to develop polymers in other polymer reactions may result in drastically different optical properties in those systems as well. Furthermore, these general conclusions are likely not limited to the use of DVB in polymer fabrication, the development of polymers or observed optical properties, but are possibly applicable in other chemical reactions.

SUPPORTING INFORMATION

Associated Content: Extended FT-IR, Raman spectroscopy, thermal analyses and polymer densities are included.

AUTHOR INFORMATION

Corresponding Author

E-mail: darryl.boyd@nrl.navy.mil

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The views are those of the authors and do not represent the opinion or policy of the US Navy or Department of Defense.

REFERENCES

1. Boyd, D. A., Sulfur and Its Role In Modern Materials Science. *Angewandte Chemie International Edition* **2016,** *55* (50), 15486-15502.

2. Boyd, D. A., Schwefel in der modernen Materialwissenschaft. *Angewandte Chemie* **2016,** *128* (50), 15712-15729.

3. Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; SomogyiÁrpád; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J., The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nat Chem* **2013,** *5* (6), 518-524.

4. Kang, H.; Kim, H.; Park, M. J., Sulfur-Rich Polymers with Functional Linkers for High-Capacity and Fast-Charging Lithium–Sulfur Batteries. *Advanced Energy Materials 0* (0), 1802423.

5. Zhao, F.; Li, Y.; Feng, W., Recent Advances in Applying Vulcanization/Inverse Vulcanization Methods to Achieve High-Performance Sulfur-Containing Polymer Cathode Materials for Li–S Batteries. *Small Methods 0* (0), 1800156.

6. Liu, P.; Gardner, J. M.; Kloo, L., Solution processable, cross-linked sulfur polymers as solid electrolytes in dye-sensitized solar cells. *Chemical Communications* **2015,** *51* (78), 14660-14662.

7. Liu, P.; Kloo, L.; Gardner, J. M., Cross-Linked Sulfur–Selenium Polymers as Hole-Transporting Materials in Dye-Sensitized Solar Cells and Perovskite Solar Cells. *ChemPhotoChem* **2017,** *1* (8), 363-368.

8. Griebel, J. J.; Namnabat, S.; Kim, E. T.; Himmelhuber, R.; Moronta, D. H.; Chung, W. J.; Simmonds, A. G.; Kim, K. J.; van der Laan, J.; Nguyen, N. A.; Dereniak, E. L.; Mackay, M. E.; Char, K.; Glass, R. S.; Norwood, R. A.; Pyun, J., New infrared transmitting material via inverse vulcanization of elemental sulfur to prepare high refractive index polymers. *Adv Mater* **2014,** *26* (19), 3014-8.

9. Boyd, D. A.; Baker, C. C.; Myers, J. D.; Nguyen, V. Q.; Drake, G. A.; McClain, C. C.; Kung, F. H.; Bowman, S. R.; Kim, W.; Sanghera, J. S., ORMOCHALCs: organically modified chalcogenide polymers for infrared optics. *Chemical Communications* **2017**.

10. Boyd, D. A.; Nguyen, V. Q.; McClain, C. C.; Kung, F. H.; Baker, C. C.; Myers, J. D.; Hunt, M. P.; Kim, W.; Sanghera, J. S., Optical Properties of a Sulfur-Rich Organically Modified Chalcogenide Polymer Synthesized via Inverse Vulcanization and Containing an Organometallic Comonomer. *ACS Macro Letters* **2019,** *8* (2), 113-116.

11. Islam, M. D.; Kim, J. O.; Ko, Y.; Ku, Z.; Boyd, D. A.; Smith, E. M.; Nguyen, V. Q.; Myers, J. D.; Baker, C. C.; Kim, W.; Sanghera, J. S.; Czaplewski, D. A.; Urbas, A. M.; Genzer, J.; Ryu, J. E., Design of High Efficient Mid-Wavelength Infrared Polarizer on ORMOCHALC Polymer. *Macromolecular Materials and Engineering* **2020,** *305* (5), 2000033.

12. Islam, M. D.; Liu, S.; Boyd, D. A.; Zhong, Y.; Nahid, M. M.; Henry, R.; Taussig, L.; Ko, Y.; Nguyen, V. Q.; Myers, J. D.; Baker, C. C.; Kim, W.; Sanghera, J. S.; Smith, E. M.; Derov, J. S.; Ye, X.; Amassian, A.; Ade, H.; Genzer, J.; Ryu, J. E., Enhanced mid-wavelength infrared refractive index of

organically modified chalcogenide (ORMOCHALC) polymer nanocomposites with thermomechanical stability. *Optical Materials* **2020,** *108*, 110197.

13. Wu, X.; Smith, J. A.; Petcher, S.; Zhang, B.; Parker, D. J.; Griffin, J. M.; Hasell, T., Catalytic inverse vulcanization. *Nature Communications* **2019,** *10* (1), 647.

14. Zhang, B.; Gao, H.; Yan, P.; Petcher, S.; Hasell, T., Inverse vulcanization below the melting point of sulfur. *Materials Chemistry Frontiers* **2020,** *4* (2), 669-675.

15. Westerman, C. R.; Jenkins, C. L., Dynamic Sulfur Bonds Initiate Polymerization of Vinyl and Allyl Ethers at Mild Temperatures. *Macromolecules* **2018,** *51* (18), 7233-7238.

16. Herrera, C.; Ysinga, K. J.; Jenkins, C. L., Polysulfides Synthesized from Renewable Garlic Components and Repurposed Sulfur Form Environmentally Friendly Adhesives. *ACS applied materials & interfaces* **2019,** *11* (38), 35312-35318.

17. Parker, D. J.; Jones, H. A.; Petcher, S.; Cervini, L.; Griffin, J. M.; Akhtar, R.; Hasell, T., Low cost and renewable sulfur-polymers by inverse vulcanisation, and their potential for mercury capture. *Journal of Materials Chemistry A* **2017,** *5* (23), 11682-11692.

18. Crockett, M. P.; Evans, A. M.; Worthington, M. J. H.; Albuquerque, I. S.; Slattery, A. D.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Bernardes, G. J. L.; Chalker, J. M., Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil. *Angewandte Chemie International Edition* **2016,** *55* (5), 1714-1718.

19. Worthington, M. J. H.; Kucera, R. L.; Chalker, J. M., Green chemistry and polymers made from sulfur. *Green Chemistry* **2017,** *19* (12), 2748-2761.

20. Hoefling, A.; Lee, Y. J.; Theato, P., Sulfur-Based Polymer Composites from Vegetable Oils and Elemental Sulfur: A Sustainable Active Material for Li–S Batteries. *Macromolecular Chemistry and Physics* **2017,** *218* (1), 1600303.

21. Hoefling, A.; Nguyen, D. T.; Lee, Y. J.; Song, S.-W.; Theato, P., A sulfur–eugenol allyl ether copolymer: a material synthesized via inverse vulcanization from renewable resources and its application in Li–S batteries. *Materials Chemistry Frontiers* **2017,** *1* (9), 1818-1822.

22. Arslan, M.; Kiskan, B.; Cengiz, E. C.; Demir-Cakan, R.; Yagci, Y., Inverse vulcanization of bismaleimide and divinylbenzene by elemental sulfur for lithium sulfur batteries. *European Polymer Journal* **2016,** *80*, 70-77.

23. Gomez, I.; Mecerreyes, D.; Blazquez, J. A.; Leonet, O.; Ben Youcef, H.; Li, C.; Gómez-Cámer, J. L.; Bondarchuk, O.; Rodriguez-Martinez, L., Inverse vulcanization of sulfur with divinylbenzene: Stable and easy processable cathode material for lithium-sulfur batteries. *Journal of Power Sources* **2016,** *329*, 72-78.

24. Salman, M. K.; Karabay, B.; Karabay, L. C.; Cihaner, A., Elemental sulfur-based polymeric materials: Synthesis and characterization. *Journal of Applied Polymer Science* **2016,** *133* (28).

25. Park, S.; Lee, D.; Cho, H.; Lim, J.; Char, K., Inverse Vulcanization Polymers with Enhanced Thermal Properties via Divinylbenzene Homopolymerization-Assisted Cross-Linking. *ACS Macro Letters* **2019,** *8* (12), 1670-1675.

26. Gracia, I.; Ben Youcef, H.; Judez, X.; Oteo, U.; Zhang, H.; Li, C.; Rodriguez-Martinez, L. M.; Armand, M., S-containing copolymer as cathode material in poly(ethylene oxide)-based all-solid-state Li-S batteries. *Journal of Power Sources* **2018,** *390*, 148-152.

27. Abraham, A. M.; Kumar, S. V.; Alhassan, S. M., Porous sulphur copolymer for gas-phase mercury removal and thermal insulation. *Chemical Engineering Journal* **2018,** *332*, 1-7.

28. Orme, K.; Fistrovich, A. H.; Jenkins, C. L., Tailoring Polysulfide Properties through Variations of Inverse Vulcanization. *Macromolecules* **2020,** *53* (21), 9353-9361.

29. Kleine, T. S.; Lee, T.; Carothers, K. J.; Hamilton, M. O.; Anderson, L. E.; Ruiz Diaz, L.; Lyons, N. P.; Coasey, K. R.; Parker Jr., W. O.; Borghi, L.; Mackay, M. E.; Char, K.; Glass, R. S.; Lichtenberger, D. L.; Norwood, R. A.; Pyun, J., Infrared Fingerprint Engineering: A Molecular-Design Approach to Long-Wave Infrared Transparency with Polymeric Materials. *Angewandte Chemie International Edition* **2019,** *58* (49), 17656-17660.

30. Calvez, L., Chalcogenide glasses and glass-ceramics: Transparent materials in the infrared for dual applications. *Comptes Rendus Physique* **2017,** *18* (5), 314-322.

31. Kleine, T. S.; Glass, R. S.; Lichtenberger, D. L.; Mackay, M. E.; Char, K.; Norwood, R. A.; Pyun, J., 100th Anniversary of Macromolecular Science Viewpoint: High Refractive Index Polymers from Elemental Sulfur for Infrared Thermal Imaging and Optics. *ACS Macro Letters* **2020,** *9* (2), 245-259.

32. Lee, J. M.; Noh, G. Y.; Kim, B. G.; Yoo, Y.; Choi, W. J.; Kim, D.-G.; Yoon, H. G.; Kim, Y. S., Synthesis of Poly(phenylene polysulfide) Networks from Elemental Sulfur and p-Diiodobenzene for Stretchable, Healable, and Reprocessable Infrared Optical Applications. *ACS Macro Letters* **2019,** *8* (8), 912-916.