# ORMOCHALCs: Organically Modified Chalcogenide Polymers For Infrared Optics – Electronic Supplementary Information

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## Experimental

*Note:* It is important that all reactions be carried out in ventilated conditions (e.g. in a fume hood). It is also important that reactions be carried out while the researcher is wearing the proper personal protective equipment, including gloves, lab coat and proper eye protection. A respirator, to avoid inhaling any fumes, is also recommended.

**Materials:** Sulfur and selenium were purchased from All-Chemie Ltd. and distilled four times each. 1,3-diisopropenyl benzene was purchased from TCI America and used as received. All polymers were fabricated with a S-Se precursor:DIB comonomer weight ratio of 70:30.

**Analysis Instrumentation:** FT-IR data was obtained using an Analect Diamond-20 FT-IR. SWIR images of polymers were taken using an FJW Industries FIND-R-SCOPE. MWIR images of human subjects through the polymers were taken using a Sofradir-EC camera (model IRE-640BB) that had a spectral response range of 1.5 – 5.1 µm, using a 50 mm focal length lens with a 3 – 5 µm spectral range. The differential scanning calorimetry (DSC) experiments were conducted using a Q200 DSC (TA Instruments) under a nitrogen purge with Tzero® DSC pans. The weight of each sample was between 5 mg and 15 mg. The analysis was done using Universal Analysis (TA Instruments) software. Each sample was heated at 5 °C/min, cooled to 40 °C and then reheated across the previous range at the same rate. The sulfur precursor was heated up to 200 °C because of the known transitions. The $S_{95}Se_5$ and the $S_{90}Se_{10}$ precursors were heated beyond 200 °C, to 300 °C, in order to investigate the potential for ring openings and unreacted selenium. The ORMOCHALC polymers were heated up to 210 °C. The polymers were not heated beyond 210 °C to prevent decomposition within the DSC pan and cell.

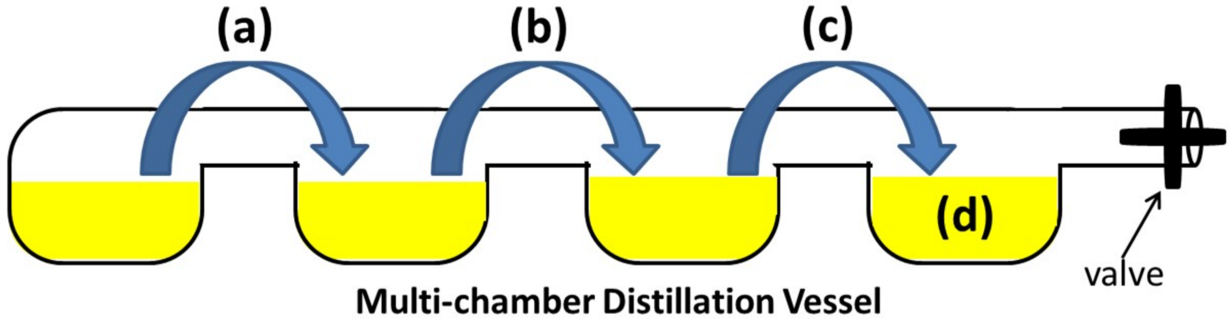


**Figure S1.** Distillation diagram for sulfur and selenium. (a), (b) and (c) are distillation steps. (d) represents the final, pure crystalline product.

Both sulfur and selenium were purified in a multi-step process using a multi-chamber glass vessel. Figure S1 depicts the chamber, and each step is designated in the specific details for each element below. The subscript values given for sulfur and selenium within the precursor compounds represent atomic percentages.

**Sulfur Purification:** High purity sulfur powder was loaded into the chamber farthest from the valve. The chamber glassware was placed inside a furnace, and attached to a vacuum pump. The furnace temperature was increased from 20 °C to 140 °C and held for 5 hrs under vacuum to remove physiadsorped $OH^-$ and $H_2O$ species (Figure S1a). Next the furnace temperature was increased to 240 °C for 10 hours for dynamic distillation (Figure S1b). This step eliminated the chemiadsorped $OH^-$, $H_2O$, $SH^-$, C, and heavy metals. The furnace temperature was ramped down to 20 °C (Figure S1c), and the high purity sulfur (Figure S1d) was retrieved and stored inside a nitrogen atmosphere glove box.

**Selenium Purification:** High purity selenium pellets were loaded into the chamber farthest from the valve. The chamber glassware was placed inside a furnace, and attached to a vacuum pump. The furnace temperature was increased from 20 °C to 240 °C and held for 5 hrs under vacuum to remove physiadsorped $OH^-$ and $H_2O$ species (Figure S1a). Next the furnace temperature was increased to 420 °C for 10 hours for dynamic distillation (Figure S1b). This step eliminated the chemiadsorped $OH^-$, $H_2O$, $SeH^-$, C, and heavy metals. The furnace temperature was ramped down to 20 °C (Figure S1c), and the high purity selenium (Figure S1d) was retrieved and stored inside a nitrogen atmosphere glove box.

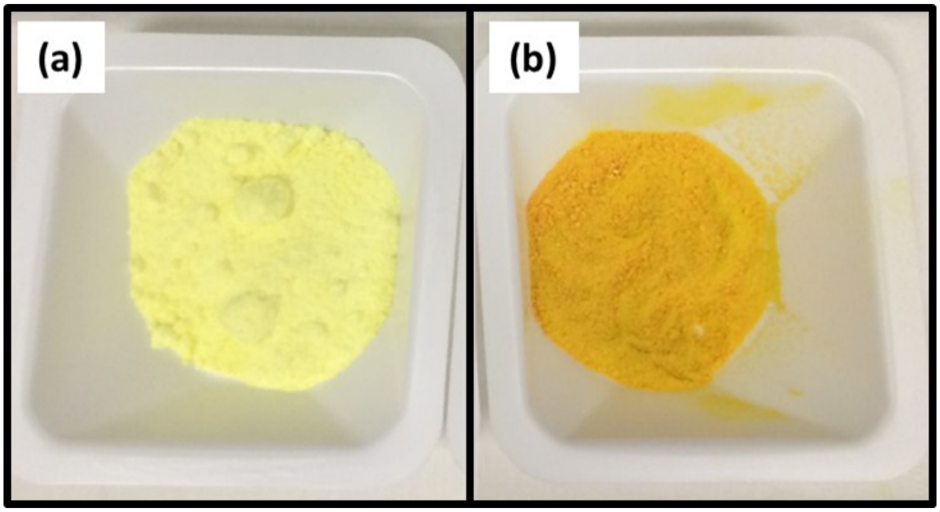


**Figure S2.** Images of (a) crystalline sulfur and (b) crystalline $S_{90}Se_{10}$ compound.

Figure S2 shows the difference in color between purified crystalline sulfur and purified crystalline $S_{90}Se_{10}$ ORMOCHALC precursor compound. The greater the amount of selenium within the precursor, the darker and more orange it appeared in comparison to sulfur.

**Preparation of crystalline sulfur-selenium compounds:** Purified elemental sulfur (S) and purified elemental selenium (Se) were loaded into an ampoule and placed under an inert nitrogen gas atmosphere in S to Se ratios of 95:5 and 90:10. The ampoule was connected to a vacuum pump and evacuated. The ampoule was then sealed and placed inside a rocking furnace. The furnace was slowly heated from 20 °C (room temperature) to 400 °C and held constant at 400 °C for 2 hours to form a melt; the furnace was rocked to facilitate mixing and homogenization of the S and Se elemental components. Rocking of the furnace was stopped and the ampoule was removed and quenched, forming a glassy solid compound. The ampoule containing the glassy compound was heated from room temperature to below the melting point of S to transform the S-Se compound from an amorphous to a crystalline phase. The ampoule was transferred inside a glove box and the crystalline S-Se compound was retrieved.

**Fabrication of poly($S_xSe_y$-*r*-DIB) ORMOCHALC polymers:** In a fume hood, a beaker containing a magnetic stir bar and crystalline S-Se compound was placed in a silicon oil bath that was preheated to ~180 °C, covered with a watch glass and stirred on a magnetic stir plate. After the S-Se compound completely melted, 1,3-diisopropenyl benzene (DIB) was added to the beaker and the mixture stirred until it became viscous and red in color. The viscous material was poured from the beaker into a mold, and the mold was then placed into a furnace that was preheated to 200 °C and allowed to vitrify for 1 hr. The polymer was allowed to cool to room temperature and removed from its mold. All polymers in this study were made with 30 wt% DIB comonomer, while the subscript values given for sulfur and selenium within the precursor compounds represent atomic percentages.

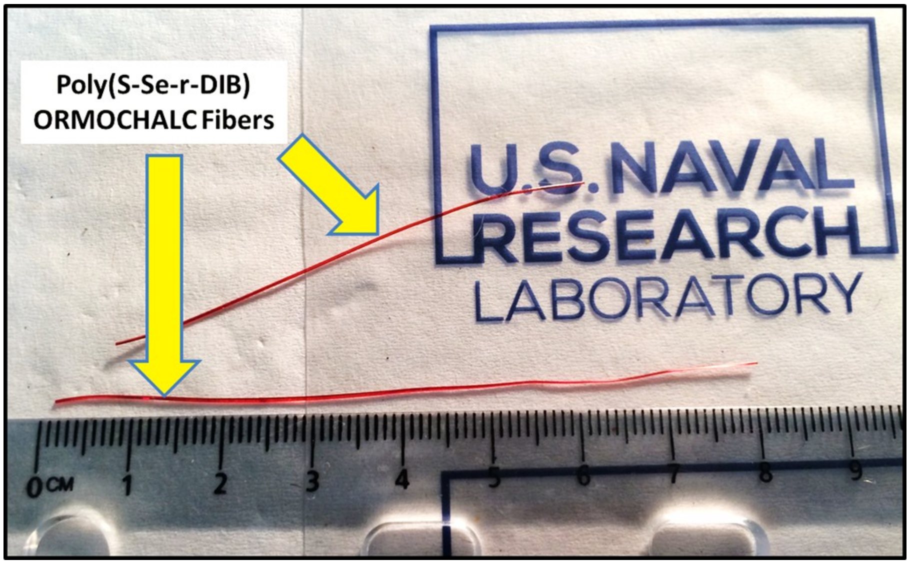
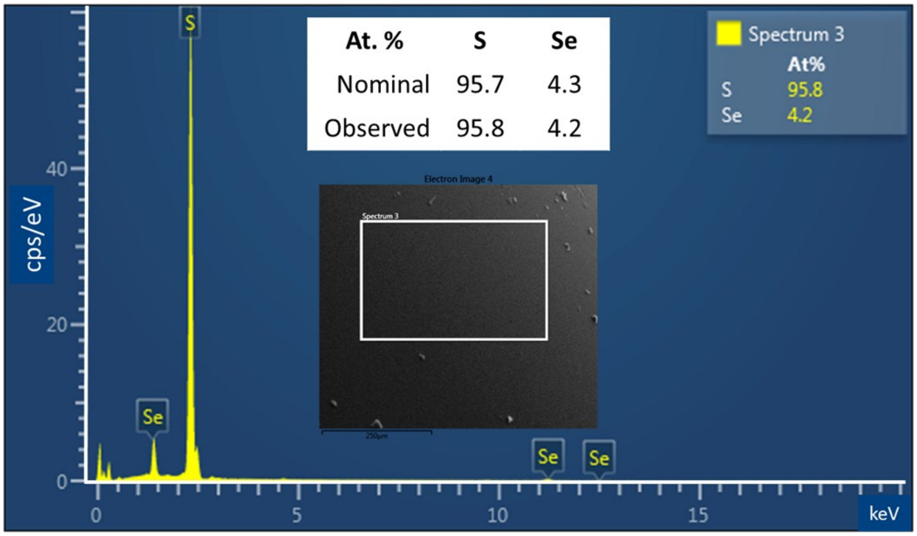


**Figure S3.** Poly(S-Se-*r*-DIB) ORMOCHALC fibers formed via inverse vulcanization.

Figure S3 shows ORMOCHALC fibers. The fibers were readily formed by drawing them out of the molten ORMOCHALC material following the inverse vulcanization process.



| At. % | S | Se |
|---|---|---|
| Nominal | 95.7 | 4.3 |
| Observed | 95.8 | 4.2 |

| Spectrum 3 | At% |
|---|---|
| S | 95.8 |
| Se | 4.2 |

**Figure S4.** Representative EDAX spectrum of poly($S_{96}$-$Se_4$-*r*-DIB) ORMOCHALC polymer formed via inverse vulcanization.

Figure S4 shows energy dispersive X-ray spectroscopy (EDX) data indicating that sulfur and selenium are being incorporated into the final ORMOCHALC polymer at a ratio consistent with the composition of the precursor compound.

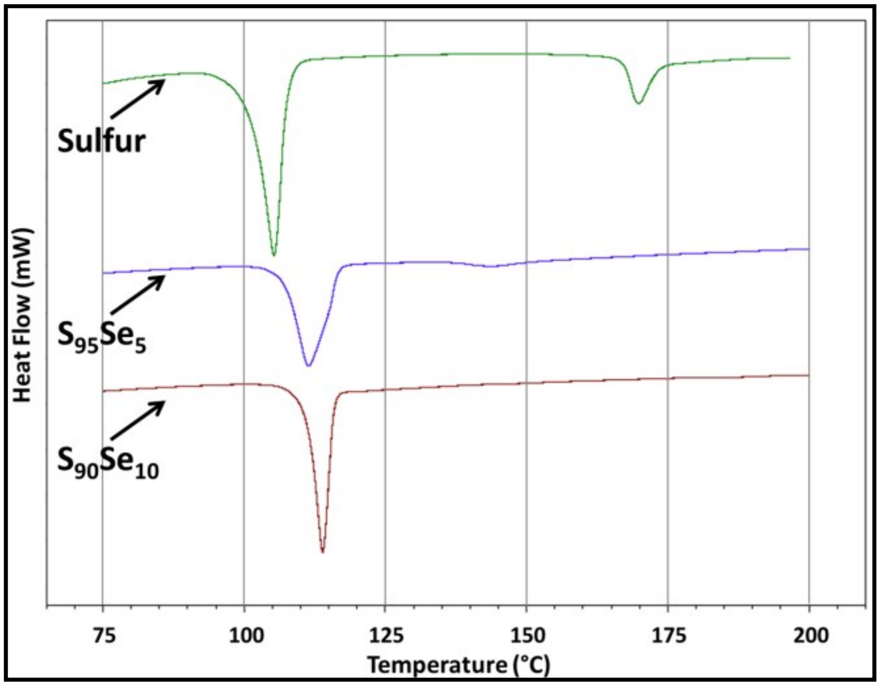


**Figure S5.** Differential scanning calorimetry data for crystalline ORMOCHALC precursors. Note: the DSC plots are offset along the Heat Flow (vertical) axis for clarity.

Figure S5 shows the 2nd heating ramp of three crystalline precursors with varied amounts of selenium. It is well known that sulfur undergoes a ring-opening process in which its $S_8$ rings are opened and can form chains at its radical ends at elevated temperatures. The floor temperature at which this process begins to occur is 159 °C. It was observed to occur anywhere between 160 °C and 175 °C in the present work (Figure S5). The nature of the S-Se precursor compounds presented in this work (i.e. whether the sulfur and selenium compounds form complex ring structures, or assume another conformation) is unclear. There is a slight dip in the 2nd DSC heating ramp for $S_{95}Se_5$ at ~145 °C (Figure S5). Similarly, sometimes there is a slight dip in the 2nd DSC heating for $S_{90}Se_{10}$ at ~130 °C (Figure 1), though it does not always appear (Figure S4). However, with the absence of a strong ring-opening transition in the DSC, it is clear that the overall character of the precursors is increasingly less sulfur-like as the percentage of selenium increases.

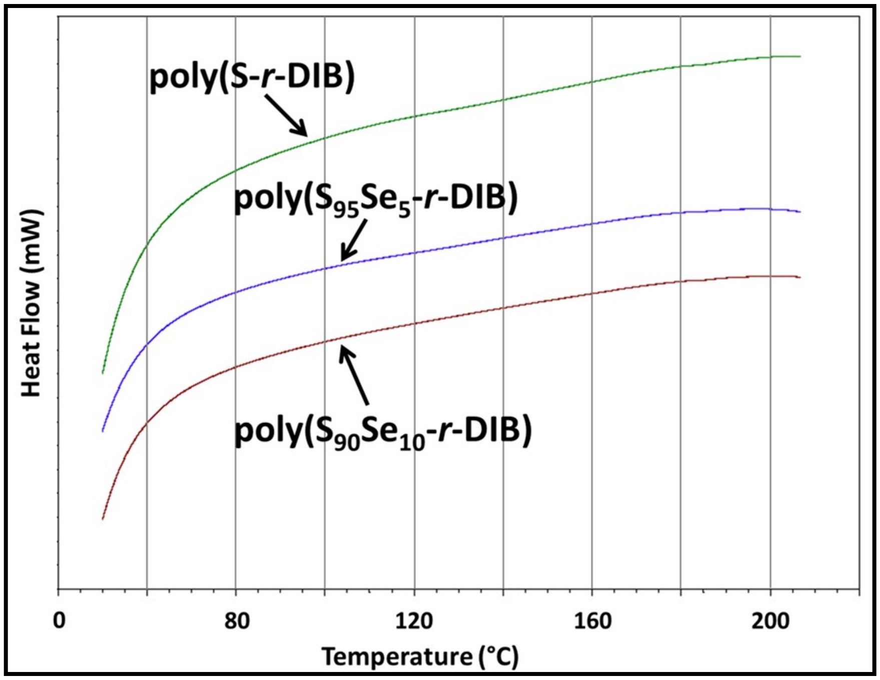


**Figure S6.** Differential scanning calorimetry data for ORMOCHALC polymers. Note: the DSC plots are offset along the Heat Flow (vertical) axis for clarity.

Figure S6 shows the 2nd heating ramp of three ORMOCHALC polymers with varied amounts of selenium. The lack of peaks, which would indicate that a phase transition has occurred, confirmed that the DIB was consumed during the inverse vulcanization process, and a single phase material was formed in each instance.

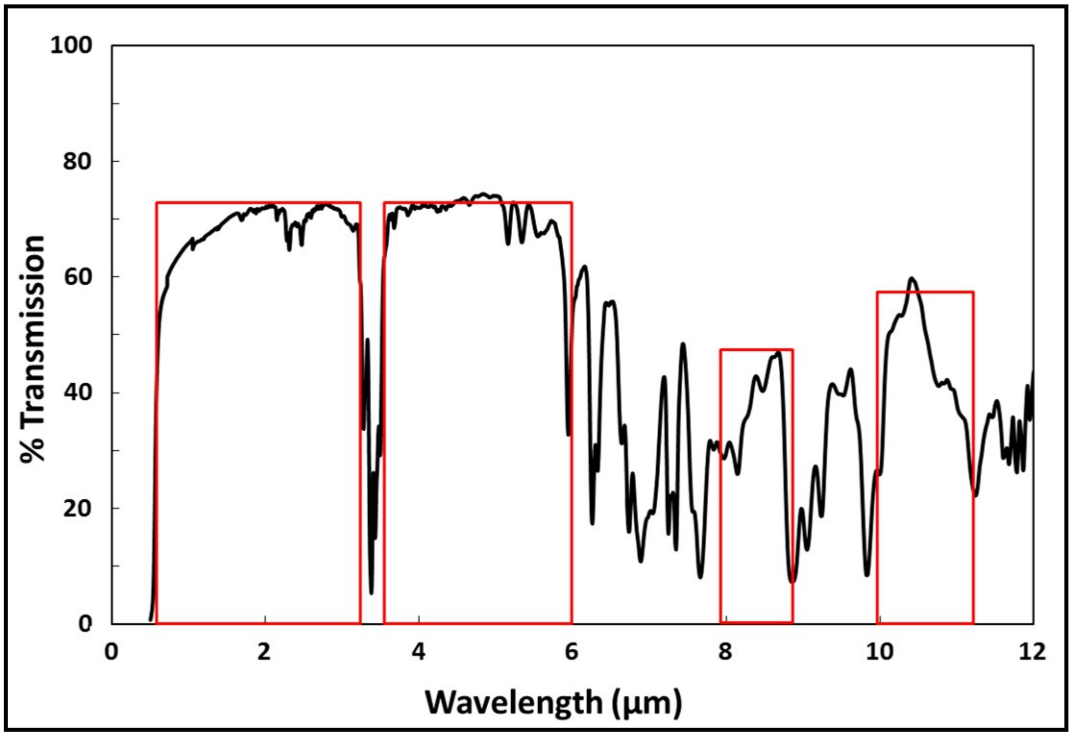


**Figure S7.** Representative poly(S-Se-*r*-DIB) infrared transmission spectrum with utilizable ranges highlighted (red boxes). FT-IR data shown is from a 150 µm thick poly(S-Se-*r*-DIB) film.

Figure S7 depicts the transmission window of a poly(S-Se-*r*-DIB) polymer, including regions of transmission in the long-wave IR (8 – 12 µm) range that may be useful in certain applications.

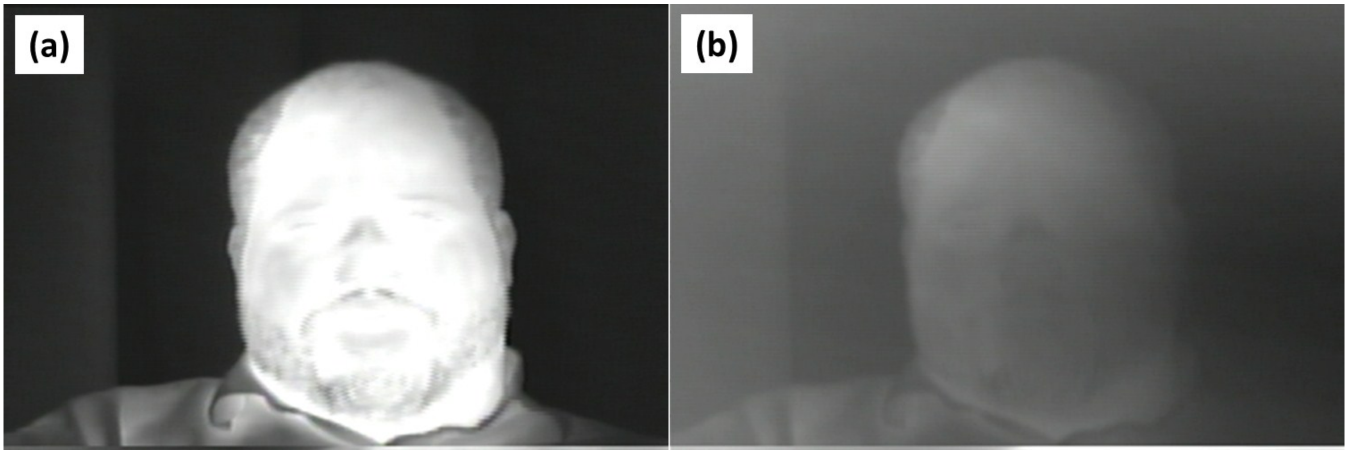


**Figure S8.** Image of a human subject visualized through a 3 – 5 µm MWIR camera lens with (a) no filter and (b) through a poly($S_{95}$-$Se_5$-*r*-DIB) ORMOCHALC polymer.

Figure S8 depicts a comparison of images taken using a 3 – 5 µm mid-wave infrared (MWIR) lens without any filter (i.e. open air), and through a poly($S_{95}$-$Se_5$-*r*-DIB) polymer. Figure S8b demonstrates that the S-Se ORMOCHALC polymers do indeed transmit into the MWIR.