



Nonlinear optical properties of chalcogenide hybrid inorganic/organic polymers (CHIPs) using the Z-scan technique

MASOUD BABAEIAN,^{1,2,*} LILIANA RUIZ DIAZ,¹ SOHA NAMNABAT,¹ TRISTAN S. KLEINE,³ ALI AZARM,¹ JEFFREY PYUN,³ N. PEYGHAMBARIAN¹ AND ROBERT A. NORWOOD¹

¹College of Optical Sciences, University of Arizona, Tucson, AZ 85721, USA

²Department of Physics, University of Arizona, Tucson, AZ 85721, USA

³Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, USA

*Babaeian@physics.arizona.edu

Abstract: The linear and nonlinear optical behavior of novel sulfur based polymer materials are evaluated at the optical communication wavelength, 1550 nm. These polymers are attractive for near-IR (NIR) and mid-IR applications. The two photon absorption (TPA) coefficient (β) and second order refractive index (n_2) of chalcogenide hybrid inorganic/organic polymers (CHIPs) from poly(sulfur-random-(1,3-diisopropenylbenzen) (poly(S-*r*-DIB)) are measured via the Z-scan technique. In this study, we investigated the linear and nonlinear optical behavior of two types of CHIPs where the weight percentage of sulfur is varied (poly(S_{50%}-*r*-DIB_{50%}) and poly(S_{70%}-*r*-DIB_{30%})). The TPA coefficients for poly(S_{50%}-*r*-DIB_{50%}) and poly(S_{70%}-*r*-DIB_{30%}) obtained were 0.11 cm/GW and 0.063 cm/GW, respectively. The n_2 for poly(S_{50%}-*r*-DIB_{50%}) and poly(S_{70%}-*r*-DIB_{30%}) was measured and determined to be 2.45×10^{-15} cm²/W and 3.06×10^{-15} cm²/W, respectively, and are in good agreement with Miller's rule prediction. These materials exhibit low cost, low temperature processing, high transparency in the near to mid-IR range (except a few interval ranges) and relatively high refractive index, providing a unique set of properties for optics and photonics device applications.

© 2018 Optical Society of America under the terms of the [OSA Open Access Publishing Agreement](#)

OCIS codes: (190.4400) Nonlinear optics, materials; (160.5470) Polymers; (160.4330) Nonlinear optical materials.

References and links

1. S. A. Ray Hilton, *Chalcogenide Glasses for Infrared Optics*, 1st ed. (McGraw-Hill Professional, 2010).
2. V. F. Kokorina, *Glasses for Infrared Optics* (CRC Press, 1996).
3. A. B. Seddon, "Chalcogenide glasses: a review of their preparation, properties and applications," *J. Non-Cryst. Solids* **184**, 44–50 (1995).
4. A. Zakery and S. R. Elliott, *Optical Nonlinearities in Chalcogenide Glasses and Their Applications*, Springer Series in Optical Sciences (Springer Berlin Heidelberg, 2007).
5. A. Zakery and S. R. Elliott, "Optical properties and applications of chalcogenide glasses: A review," *J. Non-Cryst. Solids* **330**(1-3), 1–12 (2003).
6. W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y. E. Sung, K. Char, J. Pyun, A. Somogyi, P. Theato, M. E. Mackay, Y. Sung, K. Char, J. Pyun, Á. Somogyi, P. Theato, M. E. Mackay, Y. Sung, K. Char, and J. Pyun, "The use of elemental sulfur as an alternative feedstock for polymeric materials," *Nat. Chem.* **5**(6), 518–524 (2013).
7. J. J. Griebel, S. Namnabat, E. T. Kim, R. Himmelhuber, D. H. Moronta, W. J. Chung, A. G. Simmonds, K. J. Kim, J. van der Laan, N. A. Nguyen, E. L. Dereniak, M. E. Mackay, K. Char, R. S. Glass, R. A. Norwood, and J. Pyun, "New infrared transmitting material via inverse vulcanization of elemental sulfur to prepare high refractive index polymers," *Adv. Mater.* **26**(19), 3014–3018 (2014).
8. T. S. Kleine, N. Nguyen, L. E. Anderson, S. Namnabat, E. A. LaVilla, S. A. Showghi, P. T. Dirlam, C. B. Arrington, M. A. Manchester, J. Schwiegerling, R. S. Glass, K. Char, R. A. Norwood, M. E. Mackay, and J. Pyun, "High refractive index sulfur copolymers with improved thermomechanical properties: inverse vulcanization of sulfur with (1,3,5)-triisopropenylbenzene," *ACS Macro Lett.* **5**(10), 1152–1156 (2016).

9. J. J. Griebel, N. A. Nguyen, S. Namnabat, L. E. Anderson, R. S. Glass, R. A. Norwood, M. E. Mackay, K. Char, and J. Pyun, "Preparation of dynamic covalent polymers via inverse vulcanization of elemental sulfur for healable infrared optical materials," *ACS Macro Lett.* **4**, 862–866 (2015).
10. L. E. Anderson, T. S. Kleine, Y. Zhang, D. D. Phan, S. Namnabat, E. A. LaVilla, K. M. Konopka, L. R. Diaz, M. S. Manchester, J. Schwiegerling, R. S. Glass, M. E. Mackay, K. Char, and R. A. Norwood, "Chalcogenide hybrid inorganic/organic polymers: ultrahigh refractive index polymers for infrared imaging," *ACS Macro Lett.* **6**(5), 500–504 (2017).
11. S. Namnabat, M. Babaeian, L. E. Anderson, M. S. Manchester, J. Pyun, and R. A. Norwood, "Nonlinear refractive index of sulfur copolymer materials," *Conference on Lasers and Electro-Optics, OSA Technical Digest*, Optical Society of America, paper SW1K.3 (2017).
12. J. G. Liu and M. Ueda, "High refractive index polymers: fundamental research and practical applications," *J. Mater. Chem.* **19**(47), 8907–8919 (2009).
13. S. Namnabat, J. J. Gabriel, J. Pyun, and R. A. Norwood, "Optical properties of sulfur copolymers for infrared applications," *Proc. SPIE* **8983**, 89830D (2014).
14. M. Sheik-bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, "Sensitive measurements of optical nonlinearities using a single beam," *IEEE J. Quantum Electron.* **26**(4), 760–769 (1990).
15. M. Sheik-Bahae, A. A. Said, and E. W. Van Stryland, "High-sensitivity, single-beam $n(2)$ measurements," *Opt. Lett.* **14**(17), 955–957 (1989).
16. E. W. V. Stryland, H. Vanherzeele, M. A. Woodall, M. J. Soileau, A. L. Smirl, S. Guha, and T. F. Bogges, "Two photon absorption, nonlinear refraction, and optical limiting in semiconductors," *Opt. Eng.* **24**, 613 (1985).
17. R. C. Miller, "Optical second harmonic generation in piezoelectric crystals," *Appl. Phys. Lett.* **5**(1), 17–19 (1964).
18. W. Boyd, *Nonlinear Optics* (Academic Press Inc., 2003).
19. T. Wang, X. Gai, W. Wei, R. Wang, Z. Yang, X. Shen, S. Madden, and B. Luther-Davies, "Systematic z-scan measurements of the third order nonlinearity of chalcogenide glasses," *Opt. Mater. Express* **4**(5), 1011–1022 (2014).
20. H. Ticha and L. Tichy, "Semiempirical relation between non-linear susceptibility (refractive index), linear refractive index and optical gap and its application to amorphous chalcogenides," *J. Optoelectron. Adv. Mater.* **4**, 381–386 (2002).
21. G. Lenz, J. Zimmermann, T. Katsufuji, M. E. Lines, H. Y. Hwang, S. Spälter, R. E. Slusher, S.-W. Cheong, J. S. Sanghera, and I. D. Aggarwal, "Large Kerr effect in bulk Se-based chalcogenide glasses," *Opt. Lett.* **25**(4), 254–256 (2000).
22. C. C. Wang, "Empirical relation between the linear and the third-order nonlinear optical susceptibilities," *Phys. Rev. B* **2**(6), 2045–2048 (1970).
23. J. M. Harbold, F. Ö. Ilday, F. W. Wise, J. S. Sanghera, V. Q. Nguyen, L. B. Shaw, and I. D. Aggarwal, "Highly nonlinear As-S-Se glasses for all-optical switching," *Opt. Lett.* **27**(2), 119–121 (2002).
24. A. Zakery, Y. Ruan, A. V. Rode, M. Samoc, and B. Luther-Davies, "Low-loss waveguides in ultrafast laser-deposited As₂S₃ chalcogenide films," *J. Opt. Soc. Am. B* **20**(9), 1844–1852 (2003).
25. A. A. Major, F. Yoshino, J. S. Aitchison, P. W. Smith, I. T. Sorokina, and E. Sorokin, "Ultrafast nonresonant third-order optical nonlinearities in ZnSe for photonic switching at telecom wavelengths," *Appl. Phys. Lett.* **85**(20), 4606–4608 (2004).
26. A. Boskovic, S. V. Chernikov, J. R. Taylor, L. Gruner-Nielsen, and O. A. Levring, "Direct continuous-wave measurement of $n(2)$ in various types of telecommunication fiber at 1.55 μm ," *Opt. Lett.* **21**(24), 1966–1968 (1996).
27. K. Ikeda, R. E. Saperstein, N. Alic, and Y. Fainman, "Thermal and Kerr nonlinear properties of plasma-deposited silicon nitride/ silicon dioxide waveguides," *Opt. Express* **16**(17), 12987–12994 (2008).
28. M. Dinu, F. Quochi, and H. Garcia, "Third-order nonlinearities in silicon at telecom wavelengths," *Appl. Phys. Lett.* **82**(18), 2954–2956 (2003).
29. S. J. Madden, D.-Y. Choi, D. A. Bulla, A. V. Rode, B. Luther-Davies, V. G. Ta'eed, M. D. Pelusi, and B. J. Eggleton, "Long, low loss etched As₂S₃ chalcogenide waveguides for all-optical signal regeneration," *Opt. Express* **15**(22), 14414–14421 (2007).
30. A. S. Mayer, A. Klenner, A. R. Johnson, K. Luke, M. R. E. Lamont, Y. Okawachi, M. Lipson, A. L. Gaeta, and U. Keller, "Frequency comb offset detection using supercontinuum generation in silicon nitride waveguides," *Opt. Express* **23**(12), 15440–15451 (2015).
31. R. Salem, Y. Okawachi, M. Yu, M. R. E. Lamont, K. Luke, P. Fendel, M. Lipson, and A. L. Gaeta, "Octave-Spanning Supercontinuum Generation in a Silicon Nitride Waveguide Pumped by a Femtosecond Fiber Laser at 1.9 μm ," in *CLEO: 2015, OSA Technical Digest* (online) (Optical Society of America, 2015), paper STu1I.7.
32. P. S. Donvalkar, F. A. S. Barbosa, X. Ji, Y. Okawachi, R. McNally, A. Farsi, A. Klenner, M. Lipson, and A. L. Gaeta, "Broadband Frequency Comb Generation in the Near-Visible using Higher-Order Modes in Silicon Nitride Microresonators," in *Conference on Lasers and Electro-Optics, OSA Technical Digest* (online) (Optical Society of America, 2017), paper STu4J.5.
33. Y. Okawachi, K. Saha, J. S. Levy, Y. H. Wen, M. Lipson, and A. L. Gaeta, "Octave-spanning frequency comb generation in a silicon nitride chip," *Opt. Lett.* **36**(17), 3398–3400 (2011).

34. A. G. Griffith, R. K. W. Lau, J. Cardenas, Y. Okawachi, A. Mohanty, R. Fain, Y. H. D. Lee, M. Yu, C. T. Phare, C. B. Poitras, A. L. Gaeta, and M. Lipson, "Silicon-chip mid-infrared frequency comb generation," *Nat. Commun.* **6**(1), 6299 (2015).

1. Introduction

In the last few decades, there has been strong interest in the use of chalcogenide glass materials for mid-IR applications [1–3]. High transmissivity, low loss and high nonlinear refractive index in the IR optical range [4,5] compared to fused silica, make chalcogenide materials a viable option for photonics devices, particularly for 1550nm applications. However, chalcogenide glass materials have toxic constituent elements, such as arsenic (As). These materials also require high temperature to process ($\sim 300^{\circ}\text{C}$) and accordingly are more difficult and costly to use for photonics components. We have developed a novel sulfur-based polymer material where polymeric chains of elemental sulfur (S_8) are crosslinked with an organic monomer, 1,3-diisopropenylbenzene (DIB) through the "inverse vulcanization" technique [6,7] in order to realize a processable IR material. Chalcogenide (e.g., S, Se) containing macromolecules prepared from inverse vulcanization are polymeric analogs to ChG's, where organic comonomer moieties replace the Group 3,4, or 5 atomic unit in these network solids, the first generation examples of which being poly(sulfur-random-(1,3-diisopropenylbenzene))(poly(S-*r*-DIB) and selenium containing polymers. These high sulfur and selenium content materials are the first examples of chalcogenide hybrid organic/inorganic polymers (CHIPs), which we have demonstrated to exhibit among the highest refractive indices of any synthetic polymeric material ($n \sim 1.75\text{--}2.10$), excellent optical transparency and suitability for IR thermal imaging [6–11]. Poly(sulfur-random-1,3- (poly(S-*r*-DIB)) possesses a number of desirable material properties for use in IR optical and imaging applications, which include low cost, high IR transparency and favorable melt/solution processability. We have recently reported on the fundamental optical properties of CHIPs materials, however, investigation into the non-linear optical properties of these novel materials has not been explored. Herein, we present and discuss for the first time the linear and nonlinear optical properties of these polymers.

2. Linear optical properties

The CHIPs used in this study are fabricated with an inverse vulcanization reaction of S_8 and DIB as described in our previous work [7,9]. Due to the high content of elemental sulfur, poly(S-*r*-DIB) compounds have been demonstrated to have interesting linear optical properties in the NIR (particularly $0.75\ \mu\text{m}$ to $1.65\ \mu\text{m}$ and $1.8\ \mu\text{m}$ to $2.1\ \mu\text{m}$) and mid-IR spectrum (specially $3.5\ \mu\text{m}$ to $5\ \mu\text{m}$) [7,10]. For this study, we focus on two copolymers where the weight percent (wt%) of sulfur is varied, poly($\text{S}_{50\%}$ -*r*-DIB $_{50\%}$) and poly($\text{S}_{70\%}$ -*r*-DIB $_{30\%}$). Both compositions have relatively similar transmittance but different ultra-high refractive index in the IR regime.

2.1 Sample preparation

Several fabrication methods were explored to assemble relatively flat thick samples. Due to the high melt viscosity of fully cured poly(S-*r*-DIB) materials, it was found to be ideal to fabricate substrate supported flats by casting a prepolymer resin of poly(S-*r*-DIB) onto the substrate and completing the curing process in an oven. To achieve relatively large area samples with proper thickness that have good optical quality flatness, a mold was fabricated using $100\ \mu\text{m}$ Corning Willow glass samples as shims attached to a glass substrate (also made of Willow glass) with double sided adhesive tape. The sulfur (0.70 g, 70 wt% and 0.50g, 50 wt% for poly($\text{S}_{70\%}$ -*r*-DIB $_{30\%}$) and poly($\text{S}_{50\%}$ -*r*-DIB $_{50\%}$), respectively) was melted in a vial at 180°C inside an oil bath until it turned orange. The DIB (0.30 g, 30 wt% and 0.50g, 50 wt%, respectively) was then added and stirred until a cherry red color was obtained (approximately 4 minutes). The resultant pre-polymer resin was poured into the mold which had been

allowed to thermally equilibrate in a 180°C oven. A second piece of Willow glass, coated with a thin layer of cured polydimethyl siloxane (PDMS) (applied via spin coating), was placed on top of the mold containing the resin. Homogenous minimum pressure was applied for 27 mins, then the mold containing the sample was removed from the oven and



Fig. 1. Poly(*S-r-DIB*) compounds: (a) Bulk sample of poly($S_{50\%}$ -*r-DIB*_{50%}). (b) and (c) images through two thin samples of poly($S_{50\%}$ -*r-DIB*_{50%}) and poly($S_{70\%}$ -*r-DIB*_{30%}) with 291 μm and 415 μm thickness, respectively. Both materials have low transmission in the visible spectrum.

allowed to reach room temperature before the PDMS coated top slide was removed. Figure (1a) shows poly($S_{50\%}$ -*r-DIB*_{50%}) bulk compound materials and Fig. (1b) and Fig. 1(c) denote two flat samples of poly($S_{50\%}$ -*r-DIB*_{50%}) and poly($S_{70\%}$ -*r-DIB*_{30%}) respectively. Both samples presented high orange coloration, characteristic of the CHIPs materials, which does not affect the IR transmission.

2.2 Transmittance and linear refractive index

Previous studies have shown that poly(*S-r-DIB*) copolymers have high transparency in the NIR (0.75 μm to 1.65 μm and 1.8 μm to 2.1 μm) and mid-IR range (3.5 μm to 5 μm) [7,11]. In Fig. 2(a), the optical transmittance of poly($S_{50\%}$ -*r-DIB*_{50%}) and poly($S_{70\%}$ -*r-DIB*_{30%}) is shown from 0.5 μm to 2.7 μm as measured with a Cary 7000 spectrophotometer. Figure 2(b) denotes the calculated attenuation in terms of dB/cm as the function of wavelength. Both compositions present excellent transparency in thin samples for the NIR and SWIR range. Strong absorption is observed below 0.5 μm in both cases. Compositions with higher sulfur wt% tend to be less transparent than those with lower values, however this difference is greatly reduced after correcting for Fresnel losses between the incident medium, the copolymer, and the substrate. At 1550 nm, the internal transmission is above 99.5% for 200 μm thick samples. The sulfur-containing polymers we have prepared, possess high refractive index ($n > 1.7$) due to the high content of S-S bonds and the large polarizability of the sulfur electrons [12]. In the case of poly(*S-r-DIB*) compounds, the refractive index can be increased as the wt% of sulfur is increased [7,13]. In Fig. 3, the refractive index is shown as a function of wavelength. At 1550 nm, the measured refractive indices for poly($S_{50\%}$ -*r-DIB*_{50%}) and poly($S_{70\%}$ -*r-DIB*_{30%}) are $n = 1.719$ and $n = 1.787$, respectively.

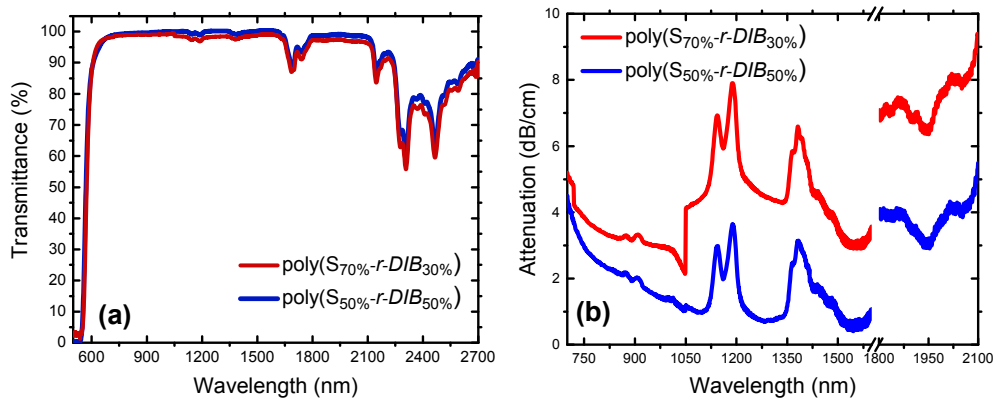


Fig. 2. Copolymer optical properties: (a) Transmission spectrum for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}). These transmittance values have been normalized to correct for Fresnel reflections between the incident medium, the poly(S-r-DIB), and the glass substrate. (b) Attenuation spectrum of the materials in terms of dB per centimeter (dB/cm).

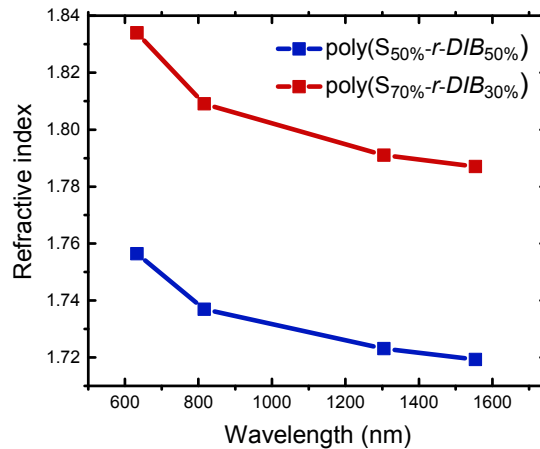


Fig. 3. Refractive index as function of wavelength for both materials.

3. Nonlinear optical properties

The nonlinear optical behavior of sulfur copolymer materials, and in particular the third order nonlinear optical susceptibility ($\chi^{(3)}$), were determined using the Z-scan technique [14,15]. A simultaneous closed and open aperture Z-scan set-up was used in order to obtain the nonlinear refractive index ($\text{Re}[\chi^{(3)}]$), n_2 , and two photon absorption (TPA) coefficient ($\text{Im}[\chi^{(3)}]$), β , respectively (Fig. 4). These nonlinear coefficients were measured in the optical communication band at a wavelength of 1550 nm. The coherent source was an optical parametric amplifier (OPA) producing micro joules range energy per pulse with pulse widths of 187 femtoseconds (fs) at full width half maximum (FWHM) of the intensity profile. The OPA was pumped by a chirped pulse amplification (CPA) system including a regenerative amplifier (Spectra Physics, 800 nm, 100 fs, 1 kHz repetition rate) and the amplifier was also seeded with a mode-locked Ti:sapphire laser (Spectra Physics, Tsunami). The closed and open aperture transmissions in the far field were monitored as a function of sample position along the optical beam waist after the focusing lens using two photodiodes (PDs). The reference input laser beam was recorded by PD1 in order to capture the pulse-to-pulse fluctuations for normalization of closed and open aperture transmittances.

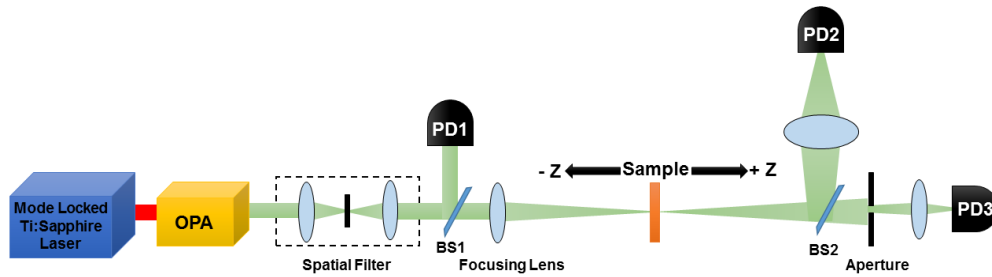


Fig. 4. Experimental set-up of the Z-scan measurement. The output wavelength was tuned to 1550nm by the OPA. A spatial filter was installed to clean up the output beam from the OPA. Beam splitter 1 (BS1) and beam splitter 2 (BS2) were used to monitor the reference input beam and open aperture transmission, respectively. An aperture was used in order to collect the closed aperture transmission by PD3. The focal length of the focusing lens was + 30 cm and the input collimated beam radius was 1.6 mm, as determined using the knife-edge technique.

Consider the second order nonlinear absorption model:

$$\frac{dI}{dz'} = -\alpha_0 - \beta I^2 \quad (1)$$

Here I is the peak irradiance, α_0 is the linear attenuation coefficient (including both scattering and absorption contributions), β is the TPA coefficient and z' is the propagation depth in the sample [16]. Using the Z-scan technique the normalized transmission for the open aperture configuration can be written as:

$$T = \sum_{m=0}^{+\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad (2)$$

where $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2 / z_R^2)$, $L_{\text{eff}} = (1 - e^{-\alpha_0 L}) / \alpha_0$, I_0 is the peak irradiance at the focal point, L is the thickness of the sample and z_R is the beam's diffraction length [14,15]. The z_R in our case is much larger than thickness of the samples, which is a required condition for this Z-scan analysis. The linear attenuation coefficients at 1550 nm wavelength are measured to be $\alpha_0 = 0.17 \text{ cm}^{-1}$ and $\alpha_0 = 1.23 \text{ cm}^{-1}$ for poly($\text{S}_{50\%}$ - r - $\text{DIB}_{50\%}$) and poly($\text{S}_{70\%}$ - r - $\text{DIB}_{30\%}$) concentration sulfur copolymer materials respectively. Figure 5(a) and Fig. 5(b) denote the normalized transmissions for the open aperture measurement of the two samples and the nonlinear curve fit with Eq. (2). The TPA coefficients are determined to be $\beta = 0.11 \text{ cm} / \text{GW}$ and $\beta = 0.063 \text{ cm} / \text{GW}$ for poly($\text{S}_{50\%}$ - r - $\text{DIB}_{50\%}$) and poly($\text{S}_{70\%}$ - r - $\text{DIB}_{30\%}$) concentration sulfur copolymer materials respectively. No damage was observed on the samples up to $98 \text{ GW} / \text{cm}^2$.

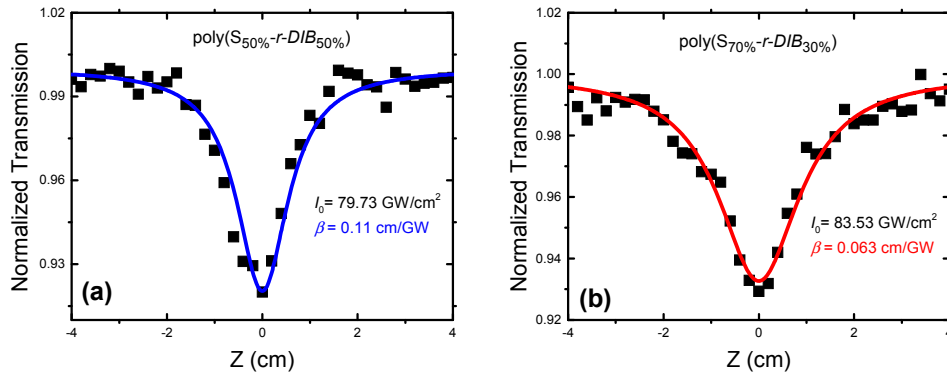


Fig. 5. Z-scan open aperture measurements. (a), (b) Measured normalized transmissions versus sample position for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}), respectively, with TPA nonlinear fits. The TPA coefficients were calculated to be $\beta = 0.11$ cm/GW and $\beta = 0.063$ cm/GW for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}) respectively. The transmissions were measured by taking the ratio of the optical powers from P_{PD2} / P_{PD1} . The peak irradiance at the focal point was roughly ~ 80 GW/cm².

The nonlinear refractive index can be evaluated from the closed aperture transmission data using the following equation:

$$T = 1 + \frac{4(z/z_R)\Delta\phi_0}{((z/z_R)^2 + 9)((z/z_R)^2 + 1)} \quad (3)$$

where $\Delta\phi_0$ is the phase shift at the exit surface of the sample and is proportional to the nonlinear refractive index $n_2 = \lambda\Delta\phi_0 / 2\pi I_0 L_{eff}$ [14,15]. Figure 6(a) and Fig. 6(b) denote the normalized transmissions for the closed aperture measurement of the two samples and the nonlinear curve fit with Eq. (3). The nonlinear refractive indices are calculated to be $n_2 = +2.45 \times 10^{-15}$ cm²/W ($\pm 10\%$ of n_2) and $n_2 = +3.06 \times 10^{-15}$ cm²/W ($\pm 10\%$ of n_2) for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}) concentration sulfur copolymer materials respectively.

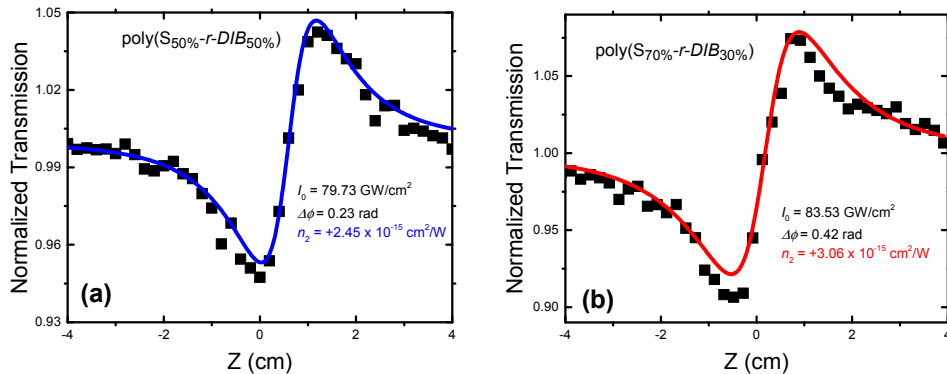


Fig. 6. Z-scan closed aperture measurements. (a), (b) Measured normalized transmissions versus sample position for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}) respectively with nonlinear refractive index fits. The n_2 coefficients were calculated to be $n_2 = +2.45 \times 10^{-15}$ cm²/W and $n_2 = +3.06 \times 10^{-15}$ cm²/W for poly(S_{50%}-r-DIB_{50%}) and poly(S_{70%}-r-DIB_{30%}), respectively. The transmissions were measured by dividing the optical powers from P_{PD3} / P_{PD2} . The peak irradiance at the focal point was roughly ~ 80 GW/cm².

4. Discussion

4.1 Comparison with Miller's rule prediction

The measured values for nonlinear refractive index conform very well to the semi-empirical Miller's rule relationship between the linear and nonlinear refractive index [17,18].

$$n_2 = \frac{\delta \times 0.0395}{n_0^2} \left(\frac{n_0^2 - 1}{4\pi} \right)^4 (\text{cm}^2 / \text{W}) \quad (4)$$

Here δ is the Miller's coefficient for chalcogenide glass and is equivalent to 2.7×10^{-10} [19]. The reported value for the Miller's coefficient is consistent with other reports for most of optical crystals, chalcogenide glasses, oxide glasses [20,21] and ionic crystals [22]. Table 1 denotes the summary of predicted values for n_2 based on Miller's rule and obtained experimental values using the Z-scan method.

Table 1. Comparison of n_2 between experimental and the predicted values, using Miller's rule

Material	n_0	Measured n_2 (cm^2/W)	Predicted n_2 (cm^2/W)
poly(S _{50%} -r-DIB _{50%})	1.72	2.45×10^{-15}	2.12×10^{-15}
poly(S _{70%} -r-DIB _{30%})	1.79	3.06×10^{-15}	3.14×10^{-15}

4.2 Comparison with other IR materials and applications

The sulfur copolymers and CHIPs materials have an intriguing set of optical properties, that occupies a unique range of refractive index ($n_0 \sim 1.7$ -2.1) which is a new regime of materials that are intermediary to classical inorganic IR transmitting materials (e.g., ChG's, germanium) and low index organic polymers. The refractive indices of CHIPs the sulfur copolymers are not as high as chalcogenide glasses and germanium (Ge) semiconductors, however, CHIPs still retain the low cost and processability of polymeric materials (Fig. 7). Conversely, CHIPs exhibit profoundly higher refractive index relative to conventional organic polymers while retaining high IR transparency. Thus, these materials have the potential for use in applications as antireflection coatings or index matching materials in infrared optics. In addition, it would be possible to make compact polymer based photonic devices for infrared applications, especially mid-infrared optics, as high index contrast waveguide structures can be made. In high index contrast platforms e.g. silicon photonics, the relatively high refractive index of these polymers with respect to silica is advantageous to introduce better mode matching for light coupling from single mode waveguides to optical fibers and vice versa. Additionally, their nonlinear optical properties are ten times higher than silica due to the highly polarizable sulfur atoms; the properties of the sulfur copolymers are, in fact, seen to match those of silicon nitride quite well with respect to both refractive index and n_2 (Table. 2). Especially, the low temperature processing for these polymers makes them attractive for fabricating compact all optical photonic devices, such as all optical signal processors, all optical switches, all optical signal regenerators [29], super-continuum generators [30,31] and frequency combs [32–34].

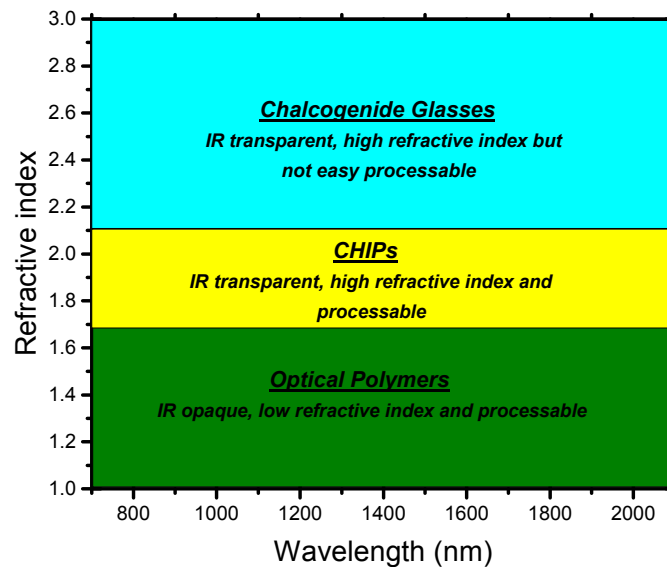


Fig. 7. Comparison of refractive index of CHIPs with conventional optical polymers and Chalcogenide glasses as the function of wavelength.

Table 2. Summary of optical properties for common infrared materials and sulfur copolymers.

Material	n_0	n_2 (cm ² /W)	β (cm/GW)	Reference
poly(S _{50%} - <i>r</i> -DIB _{50%})	1.72	2.45×10^{-15}	0.11	
poly(S _{70%} - <i>r</i> -DIB _{30%})	1.79	3.06×10^{-15}	0.063	
As ₂ S ₃	2.4	25×10^{-15}	0.03	[23,24]
ZnSe	2.7	1.1×10^{-15}	0.01	[25]
SiO ₂	1.44	0.21×10^{-15}	~0.0	[26]
Si ₃ N ₄	2.1	2.4×10^{-15}	~0.0	[27]
Si	3.4	45×10^{-15}	0.79	[28]

5. Conclusion

We have evaluated the linear and nonlinear optical properties of a recently developed sulfur-based polymers. The experimentally measured values for the nonlinear refractive index for both poly(S_{50%}-*r*-DIB_{50%}) and poly(S_{70%}-*r*-DIB_{30%}) are in good agreement with the Miller's rule prediction for chalcogenide glasses. These sulfur-based polymers can potentially be made into films and bulk optics using conventional polymer processing techniques at relatively low temperature. One of the key advantage of our polymers in contrast to chalcogenide glasses, as mentioned before, is their low cost of processing. In addition, their unique transmission properties can enable more affordable infrared spectrometers, gas sensors, infrared cameras, and etc.

Funding

National Science Foundation (NSF (DMR-1607971)); the Air Force Office of Scientific Research (AFOSR) Phase I & II SBIR contract (FA9550-15-C-0046, FA955017-C4005); NSF CIAN ERC and the Arizona TRIF program.

Acknowledgement

We would like to thank Laura E. Anderson and Sasaan A. Showghi assistance with sample preparation.

Disclosures

J.P. declares an actual or potential financial conflict of interest and is co-founder/equity holder in Innovative Energetics, a licensee of University of Arizona (UA) intellectual property. This relationship has been disclosed to the UA Institutional Review Committee and is managed by a Financial Conflict of Interest Management Plan. R.A.N. declares an actual or potential financial conflict of interest and is a consultant to TIPD, LLC.