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Perspective

Polymerizations with Elemental Sulfur: From Petroleum Refining to Polymeric Materials

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ABSTRACT: The production of elemental sulfur from petroleum refining has created a technological opportunity to increase the valorization of elemental sulfur by the synthesis of high-performance sulfur-based plastics with improved optical, electrochemical, and mechanical properties aimed at applications in thermal imaging, energy storage, self-healable materials, and separation science. In this Perspective, we discuss efforts in the past decade that have revived this area of organosulfur and polymer chemistry to afford a new class of high-sulfur-content polymers prepared from the polymerization of liquid sulfur with unsaturated monomers, termed inverse vulcanization.

1. INTRODUCTION

Sulfur is an abundant element on Earth and found in minerals such as pyrite and gypsum and biological compounds including those essential for life such as proteins and redox agents.[1] Elemental sulfur (S_8) itself occurs as a yellow crystalline solid and has long attracted interest. Sulfur burns with a blue flame upon ignition, earning it the name brimstone. Since elemental sulfur is found in volcanoes, biblical associations of fire and brimstone with the underworld are rife.[2] This flammability of sulfur led to its early use in gunpowder.[3] More recent uses are in vulcanization of rubber[4−6] and oxidation to sulfuric acid, which is crucial in isolating phosphate from apatite and other rocks for use in agriculture.[7] Sulfur itself is used as a fertilizer and pesticide in agriculture;[8−10] sulfur is also used in dermatology.[11] Sulfur-containing functional groups play centrally significant roles in hundreds of approved pharmaceuticals.[12,13] Sulfates are also valued additions to asphalt and concrete.[14] A recent review of the reactions of elemental sulfur with organic compounds has been published.[15] The enormous global production of elemental sulfur by hydrodesulfurization of petroleum and natural gas,[16,17] and to a lesser extent by the Claus process,[18] is on the order of 70 million tons yearly, which has prompted greater use of this abundant substance. Over 70% of this 70 million metric tons of sulfur is produced from the refining of petroleum from conventional or tar sand reservoirs, with only 1% being generated from the Frasch processing of naturally occurring sulfur reserves.[19,20] There are no practical advantages or sustainability-driven motivations to use mined vs recovered elemental sulfur for conversion to base chemicals; hence, S_8 recovered from petroleum refining is the primary source of this reagent due to lower costs for S_8 production versus other methods.[2] New uses of elemental sulfur would help remedy this situation—alternatively said, elemental sulfur is a widely available and cheap potential starting material for industrial applications.

Serendipitous addition of elemental sulfur to natural rubber and heating led to a dramatic improvement of the natural polymer's property. The transformed natural product, dubbed vulcanized rubber, initiated a new and impactful material which formed the basis of a new industry, namely, vulcanized rubber for tires. The chemical basis for the transformation of natural rubber by treatment with modest amounts of elemental sulfur on heating involves several key steps.[4−6] Among these are the thermal cleavage of the S−S bond in elemental sulfur, which consists of an eight-membered cyclic ring, to generate reactive sulfur radicals. The chemistry of sulfur radicals is known and broad in scope,[15] including addition reactions to carbon−carbon double bonds. Thiol−ene addition via thiyl radicals to alkenes and alkynes (i.e., thiol−ene, thiol−yne additions) is arguably the most impactful sulfur radical chemistry for materials synthesis as a "click chemistry" type of reaction exploited in biological systems and polymers.[21−23] Furthermore, S_8 has long been used as an inexpensive chain-transfer agent for free radical polymerization of vinylic monomers,[24] which was a conceptual predecessor to other, more advanced organosulfur chain-transfer agents, such as thiocarbonyl reagents now used in reversible-addition−fragmentation chain transfer (RAFT) polymerization.[25−28] The significance of these sulfur radical chemistries in organic synthesis and polymerization has been reviewed elsewhere[15,29] and is beyond the scope of this Perspective.

The concept of inverse vulcanization incorporates the generation of sulfur radicals and their addition to carbon−carbon double bonds of low-molecular-weight alkenes.[30−34] However, it posits the use of large amounts of elemental sulfur relative to the alkene in contrast to classical vulcanization. Two

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question are raised by this supposition: (1) will stable polymers be produced, and (2) will the polymers have useful properties? An additional motivation for these studies is that elemental sulfur is cheap and readily available. This is due, in large part, to the hydrodesulfurization of petroleum products,[16−18] although naturally occurring deposits of elemental sulfur are known as well. These and related aspects of the "green chemistry" of inverse vulcanization have recently been reviewed.[32,33]

To increase the valorization of elemental sulfur obtained from petroleum refining, further chemical conversion to higher value products has long been pursued.[2] Sulfuric acid (H_2SO_4) remains the largest commodity chemical made from S_8, using a three-stage process to produce SO_2 and SO_3 gases via combustion of elemental sulfur to produce oleum (i.e., "fuming sulfuric acid"), which is then reacted with water.[35] Sulfuric acid is then widely used to prepare phosphoric acid via reaction with phosphate rock salts, which is eventually used to produce ammonium phosphate fertilizers. The use of S_8 to prepare sulfur-based concretes or polymerized sulfur concretes has also been explored but remains largely underdeveloped due to chemical stability concerns and environmental regulatory issues.[14] Of course, prior to the generation of sulfur from petroleum refining was the use of elemental sulfur and polymerized sulfurs as cross-linking agents for the vulcanization of rubber for tires, as invented by Charles Goodyear and developed into a billion dollar chemical industry, as alluded to previously.[4−6]

The concept of using elemental sulfur as a feedstock monomer to produce polymers has been an attractive technological aim of the petroleum industry to both garner increased financial returns from refined S_8 and create chemical products to consume the large volumes of sulfur generated annually. This particular enterprise has proven challenging due to both the paucity of polymerization chemistry methods available for elemental sulfur and the absence of clear value propositions identified from high-sulfur-content polymeric materials. A pioneering demonstration in this field was the anionic ring-opening copolymerization of S_8 with propylene sulfide.[36,37] This example pointed to both the potential and the challenges of polymerizing elemental sulfur as a comonomer, as noted by the low solubility of this reagent in organic media, the low ring-strain of S_8 (which limited the rate of propagation), and the dynamic nature of S−S bonds in the copolymer which can result in chain transfer or depolymerization. Alternatively, it has long been known that S_8 can homolytically undergo equilibrium ring-opening polymerization (ROP) in liquid sulfur melts to form linear polymers with diradical chain ends, which subsequently reversibly polymerize into a high-molecular-weight form of polymeric sulfur which exhibits a deep red color and vitrifies the reaction medium (Figure 1).[29−34,38] Stabilization of the polymeric sulfur can be achieved by quenching of the sulfur radical chains via copolymerization with dienes, such as dicyclopentadiene (DCPD), which chemically stabilizes the polymer but still affords a brittle crystalline material. This type of approach has been widely utilized for production of "insoluble soluble" products, such as Crystex (produced by Eastman Chemical) for vulcanization of rubber.[4−6] However, the concept of using liquid sulfur as a comonomer and reaction medium for polymer chemistry had not been widely explored. Thus, a new methodology for polymerization and access to new stable high-sulfur-content polymers was developed, which is the subject of this Perspective. However, these developments are believed to be just the beginning of a new and exciting area of polymer chemistry, and it is hoped that these initial breakthroughs will provide the impetus for further research. The concept of sulfur polymerization has been more rigorously reviewed by our group and other leading researchers in this emerging field.[30−34] Herein, we will discuss the most impactful areas explored in the past decade and highlight the important chemical and materials advances to date, with an emphasis on our own contributions since 2011.

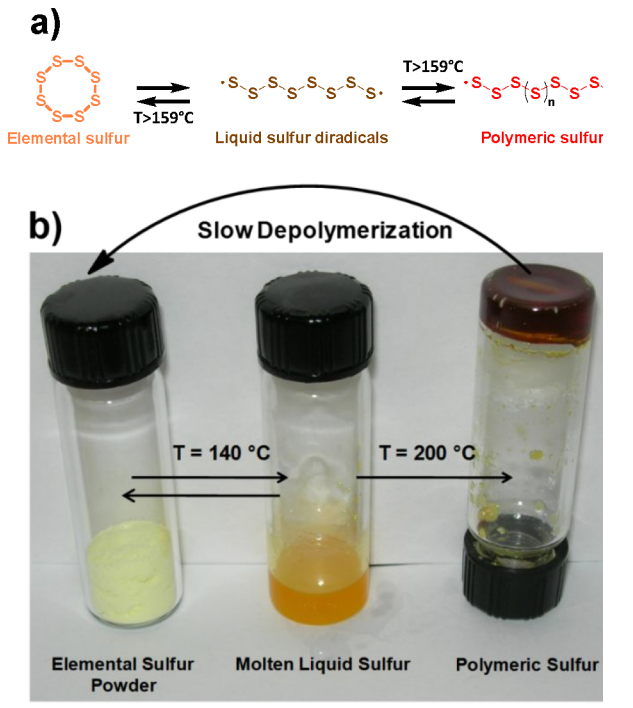

Figure 1. (a) Thermally induced homolytic ring-opening and polymerization of cyclooctasulfur (S_8). (b) Photograph of elemental solid, molten liquid, and polymeric sulfur. Reproduced with permission from ref 51. Copyright 2013 Nature Publishing Group.

2. THE ORIGINS OF SULFUR FROM PETROLEUM REFINING

The refining of natural gas and crude oil, particularly for the removal of sulfur containing compounds, is a critical process for production of fossil fuels for global energy supply. Among these processes are the hydrodesulfurization and Claus processes to convert organosulfur compounds and hydrogen sulfide (H_2S) into elemental sulfur (S_8) (Figure 2).[16−18] The generation and accessibility of H_2S and S_8 from petroleum refining, in addition to other upstream sulfur products, such as carbon disulfide (CS_2), create a strong technological incentive for the petrochemical industry to create high-value products from these abundant chemicals of oil refining.[2,39−41] Due to the high volumes of H_2S, S_8, and CS_2 that are generated, the valorization of these materials by conversion into feedstocks for both commodity and specialty polymers has been identified as an attractive new revenue stream which would profoundly affect these industrial sectors. In our early publication with sulfur utilization for polymeric materials, we described S_8 generated from petroleum refining as a "waste byproduct" of these processes. However, after extensive education by experts from the oil and gas sector, we now know that this is an

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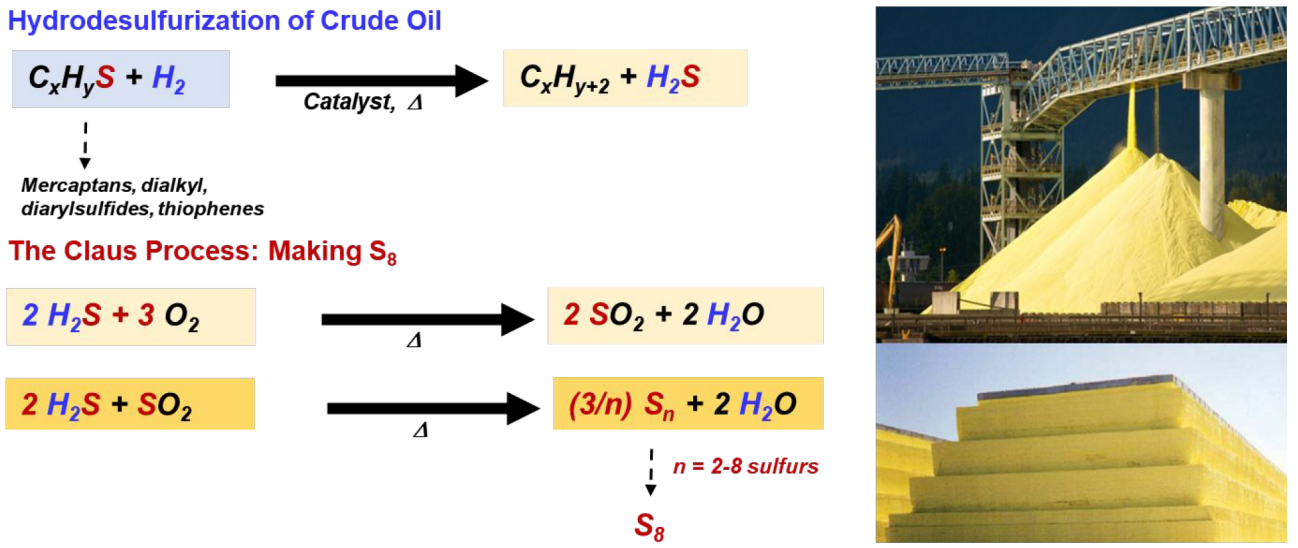

Figure 2. Examples of megaton above ground sulfur storage sites resulting from refining of petroleum via the Claus process. Adapted with permission from ref 31. Copyright 2016 Elsevier.

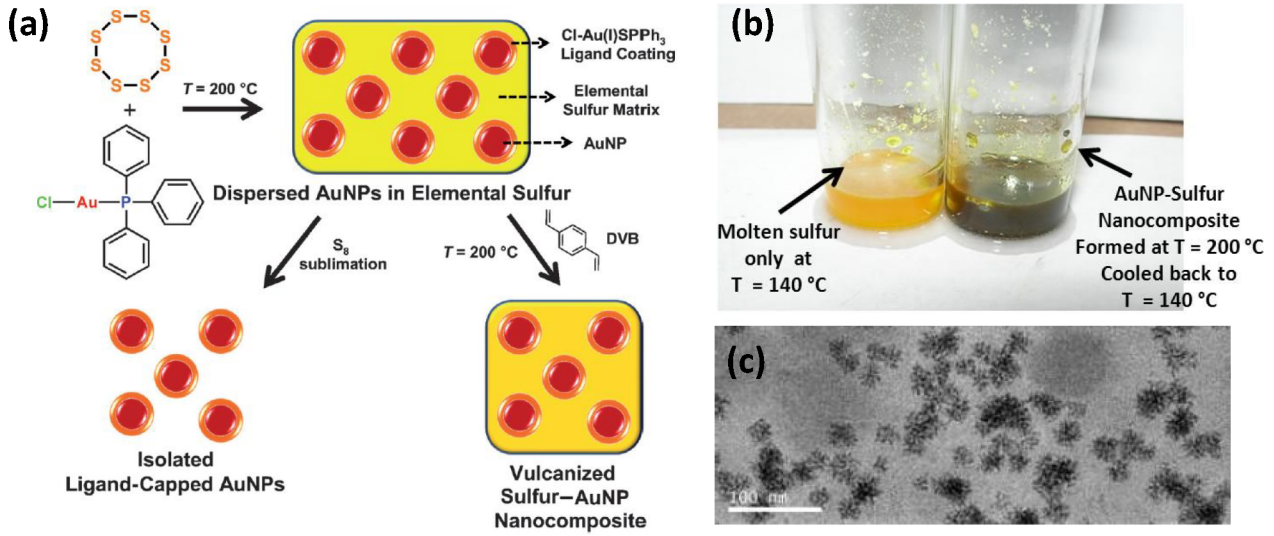

Figure 3. (a) Schematic illustration of the synthesis of gold nanoparticles in molten elemental sulfur followed by either removal of sulfur by sublimation or treatment with divinylbenzene (DVB) to form cross-linked sulfur nanocomposites. (b) Liquid sulfur at elevated temperature before and after formation in situ of gold colloids. (c) TEM of AuNP sulfur nanocomposite after cross-linking with DVB. Adapted with permission from ref 48. Copyright 2011 Wiley & Sons.

incorrect description, as the generation and sale of sulfur, along with sulfur-based chemical products (e.g., H_2SO_4), is calculated in the profitability of the entire petroleum discovery, refining, and distribution cycle for new candidate sites for oil and gas. Hence, if the price of sulfur and sulfur-derived products could be enhanced, particularly by the commercialization of new sulfur-derived plastics, this could potentially change the economics of which candidate oil and gas fields could be developed.

3. LIQUID SULFUR AS A NEW REACTION MEDIUM

A major breakthrough in polymerizing S_8 for the synthesis of high-sulfur-content polymers was the realization that liquid sulfur could be used as a bulk reaction medium and comonomer for free radical polymerizations. Early attempts using S_8 directly in the molten state or at elevated temperatures with other mixtures primarily afforded either oligomeric fluid resins, or intractable solids which were not usable in bulk form as thermoplastics, or thermoset materials.[42−44] Elemental sulfur melts at elevated temperatures ($T \approx 119$ °C) to form a low-viscosity liquid. Unfortunately, the molten sulfur form exhibits limited miscibility with conventional organic solvents or reagents. However, a limited range of chemical substances were found to be miscible with molten S_8, which include planar aromatic compounds, certain amines, carbon disulfide (CS_2), and, more recently, ionic liquids.[31,45−47]

In our initial report, we demonstrated that molten sulfur could be used as a reaction medium for the synthesis of gold nanoparticles (AuNPs, Figure 3).[48] It was observed that $AuCl(PPh_3)$ was soluble in liquid sulfur and was reduced to metallic AuNPs presumably by anionic sulfide species present in the melt phase. Furthermore, the liquid sulfur phase of the Au colloidal dispersion was cross-linked by the addition of divinylbenzenes to afford a freestanding Au−S polymer

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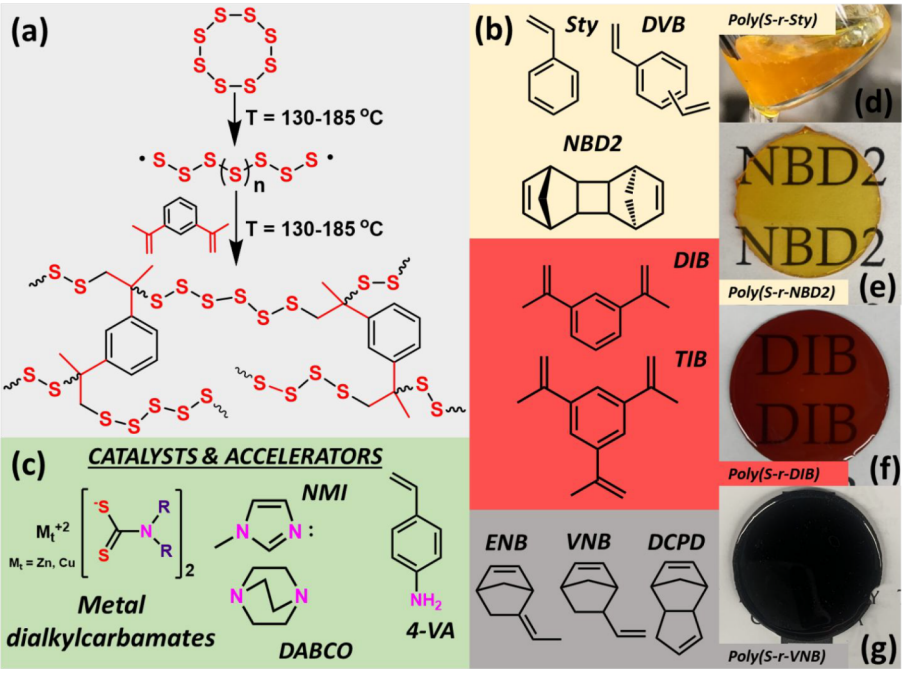

Figure 4. (a) Synthetic scheme for the inverse vulcanization of sulfur with 1,3-diisopropenylbenzene (DIB). (b) Monomers commonly used for inverse vulcanization. (c) Catalysts and nucleophilic accelerators used for inverse vulcanization. (d) Liquid form of p(S-*r*-Sty) and (e–g) melt process flat windows (50 mm in diameter, 1 mm thick) of sulfur copolymers of varying coloration depending on organic comonomer.

nanocomposite that did not revert to elemental sulfur as was the case with S_8 ring-opening homopolymerization. These findings demonstrated that multiple reactive species, in this case both ionic and free-radical, were present in the liquid sulfur medium, as noted by the ability of the molten sulfur medium to reduce Au(I) salts and copolymerize with divinylbenzenes. We were also able to prepare similar polymeric nanocomposites with sulfur and oleylamine containing PbS nanoparticles by *in situ* polymerization in molten sulfur.[49] Independently, Block et al. demonstrated the preparation of allylic sulfide-terminated oligomers using liquid sulfur as the solvent and comonomer.[9] Liquid sulfur was also found to be an excellent medium for the dispersion and partial exfoliation of molybdenum sulfide (MoS_2) particulate fillers, where simple addition and mixing in liquid sulfur at elevated temperature resulted in the formation of composite materials with dispersed MoS_2 inclusions on the order of 10 μm in the sulfur continuous phase.[50]

4. INVERSE VULCANIZATION

Background and Mechanistic Aspects. Building on the success of early chemistry in liquid sulfur, Pyun and co-workers in 2013 developed the process termed "inverse vulcanization", which enabled the bulk copolymerization of molten elemental sulfur and vinylic comonomers without the need for externally added initiator or organic solvent.[51] As alluded to earlier, in classical vulcanization processes a very small feed ratio of insoluble sulfur (~1–5 wt%) is used to cross-link a majority feed of a polydiene to form cross-linked rubber.[4−6] Hence, this new polymerization method in liquid sulfur was termed inverse vulcanization since the comonomer feed ratios used a majority component of elemental sulfur to form high-sulfur-content polymers. In this first report, 1,3-diisopropylbenzene (DIB) was used as the organic comonomer for bulk copolymerization since this was an inexpensive monomer that was miscible with liquid sulfur, carried two vinyl moieties and possessed a higher boiling point than divinylbenzene. The inverse vulcanization process proceeded most efficiently, and with appreciable rate (on the order of minutes to hours), when conducted in the bulk at elevated temperature (T = 130–185 °C) in order to shift the equilibrium from S_8 (and other cyclic forms) to ring opened sulfur diradicals which drives the rate of polymerization. The degradation temperature of S–S bonds in many sulfur copolymers ranges from 200 to 300 °C, hence polymerizations should be conducted below 200 °C under ambient conditions to avoid other side reactions that can complicate structural characterization and mechanistic understanding of these reactions. Under these conditions, the inverse vulcanization process is essentially a thiol–ene type of polymerization in liquid sulfur where difunctional thiyl radical species were generated inexpensively by thermolysis of S_8 (Figure 4a). The addition of solvents or the use of lower temperatures shifts the position of this ring-opening equilibrium back toward cyclic sulfur species which lowers the global radical concentration and polymerization rate. In the inverse vulcanization reaction with DIB, elemental sulfur was heated in the molten state to 185 °C to initiate homolytic ROP of cyclic sulfur species (typically a mixture of ring sizes at elevated temperature[34,38]) followed by the addition of DIB (at a feed ratio of 10–50 wt%), which resulted in vitrification of the medium within minutes. The resulting red polymeric glass composed of a statistical copolymer was named poly(sulfur-*random*-1,3-diisopropenylbenzene), or poly(S-*r*-DIB), because of the high sulfur content (50–90 wt% S) and the polysulfide structure of the backbone of the polymer, poly(S-*r*-DIB). Using this process, the sulfur rank (x) of the copolymer (i.e., x = number of S–S units in the backbone) could be controlled on average around $x \approx 2$–8 units, which dramatically effects bulk properties as will be discussed. Despite the simplicity of this reaction and the great familiarity of the polymer chemistry

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J. Am. Chem. Soc. XXXX, XXX, XXX–XXX

community with the S_8 ROP process and with α-methylstyrene monomers (e.g., DIB), these particular comonomers were never paired, presumably because they were solely associated with discrete textbook concepts, namely the "floor temperature" for S_8 and the "ceiling temperature" for α-methyl styrenics.[24,52]

When we started this program in 2011, the prevailing perspective on S_8 ROP was that depolymerization of polymeric sulfur species back to S_8 and oligomers would suppress the preparation of chemically stable polymers. We confirmed this concern by the reaction of a mono-vinylic comonomer, α-methylstyrene, which added in situ-generated sulfur radicals to its vinylic groups but did not form high-molar-mass products under standard inverse vulcanization conditions.[51] In the case of the S_8 and α-methylstyrene, it is likely that a linear telechelic type of polymer is formed with sulfur diradical chain ends; however, depolymerization back to monomers proceeds faster than recombination of thiyl radicals to form stable cyclic polymers. Hence, we attributed the formation of stable sulfur copolymers when DIB was used as the comonomer as due to the branching of propagating sulfur radicals which could more easily recombine to form disulfide bonds. Furthermore, the possibility of chain transfer reaction of thiyl radicals with C−H bonds on aliphatic moieties on the copolymer backbone are likely, which would also afford thiol S−H end groups.[51]

Examples of Monomers. In principle, organic comonomers that are capable of undergoing thiol−ene or thiol−yne reactions are suitable for inverse vulcanization with the important caveat of being liquid sulfur miscible and possessing a sufficiently high boiling point. The full scope of unsaturated organic comonomers that have been investigated for inverse vulcanization has been comprehensively reviewed elsewhere, which include styrenics, α-methyl styrenics, cyclic olefins, numerous natural product olefins, allylics, alkynes, and benzoxazines.[31−34] A common problem in screening new organic comonomers is poor miscibility with liquid sulfur, which after increasing the reaction temperature affords heterogeneous polymeric materials often with significant amounts of residual elemental sulfur. Shown in Figure 4b are what can be considered "textbook examples" of commercially available or readily synthesized organic comonomers that can be melt processed in bulk form into reactive resins or free-standing windows with 50 wt% sulfur compositions from inverse vulcanization. High-sulfur-content copolymers made from styrenic comonomers (e.g., styrene (Sty), divinylbenzene (DVB), Figure 4) typically exhibit a deep yellow coloration as low-T_g resins or higher T_g glassy polymers under the appropriate conditions,[53−55] while sulfur copolymers made from α-methylstyrene-based monomers (DIB and 1,3,5-triisopropenylbenzene (TIB), Figure 4b,f) form transparent red glassy polymers.[51,56] Difunctional norbornenes, such as 5-ethylidene-2-norbornene (ENB), 5-vinyl-2-norbornene (VNB), and dicyclopentadiene (DCPD), afford dark-colored black materials when subjected to inverse vulcanization (Figure 4b,g).[57] A notable exception is the nickel-catalyzed dimer of norbornadiene (NBD2, Figure 4b,e), which affords yellow-orange-colored sulfur copolymers from inverse vulcanization.[58] The exact molecular causality of these different color effects of sulfur copolymers from Figure 4 are not yet determined, but yellow to red coloration has been correlated to the degree of sulfur cross-linking where lower sulfur rank afforded less coloration. Organic comonomer units that exhibit higher cross-linking densities as observed with NBD2 were also recently developed with vinyl ether comonomers when copolymerized with sulfur using a new chemical vapor deposition process termed, sCVD.[59] The dark coloration observed with certain norbornenes, such as ENB and VNB, may be attributed to partial carbonization and oxidation reactions which are known in reactions of sulfur with polybutadiene to undergo similar discoloration processes.

Organonucleophilic Activators and Catalysts. It has long been known in the rubber vulcanization and synthetic organosulfur literature that nucleophilic accelerators can be applied to increase reaction rate with elemental sulfur. These approaches have only recently been applied to inverse vulcanization reactions to accelerate the rate of polymerization, lower reaction temperature, and polymerize otherwise unreactive organic comonomers. Pyun and co-workers were the first to report two types of organic accelerators for S_8 that significantly increased the rate of inverse vulcanization. The first example utilized an activated monomer approach, where 4-vinylaniline (4-VA, Figure 4c) was observed to profoundly increase the rate of inverse vulcanization when copolymerized directly with S_8 or used as an organic accelerator (2 mol%) for the inverse vulcanization of sulfur with styrene.[60] Alternatively, nucleophilic activators such as *N*-methylimidazole (NMI, Figure 4c) are known to ring-open S_8 under various conditions to enhance the rate of inverse vulcanization reactions, namely with styrene since these copolymers were soluble and most amenable to polymerization kinetic studies.[61] Hasell et al. elegantly pioneered the use of metal dialkyldithiocarbamate complexes as catalytic accelerators for inverse vulcanization. Zn(II) and Cu(II) catalysts (Figure 4c) were found to be distinctive in both increasing reaction rate and allowing for polymerization of difficult unreactive olefinic comonomers, notably dimethacrylate monomers.[62] A comprehensive study on metal dialkyldithiocarbamate complexes, along with a wide range of conventional organocatalytic compounds evaluated for inverse vulcanization was recently reported.[63]

Peculiarities of Polymers Made from Inverse Vulcanization. High-sulfur-content copolymers made via inverse vulcanization have been referred to by a number of different names in the early stages of this field, such as thiopolymers, ORMCHALCS, and the term chalcogenide hybrid inorganic/organic polymers (CHIPs). It would appear that the scientific community has arrived on the term "inverse vulcanized polymers", which is certainly the most descriptive nomenclature term for polymers made via inverse vulcanization. This nomenclature issue will no doubt take some time to arrive at consensus, which the scientific community will ultimately adjudicate. For the purpose of this Perspective and to avoid confusion with our prior literature, we will refer to the term CHIPs for optical materials since this acronym was previously applied in our earlier publications and is a more familiar term in the optics community due to the prevalence of chalcogenide glasses (ChG's) as will be discussed in later sections. Regardless of these differences, the structural distinction of high-sulfur-content polymers made from inverse vulcanization is a statistical/random sequence and composition of -S_x- units bonded to organic comonomer units, where the sulfur units may be one, two, or multiple S−S bonds in the (co)polymer backbone.[34] There are also a number of other somewhat unique features of these polymers that complicate categorization of these materials in classical polymer science terms. For example, many of the reported high-sulfur-content polymers made are either insoluble or cross-linked, which

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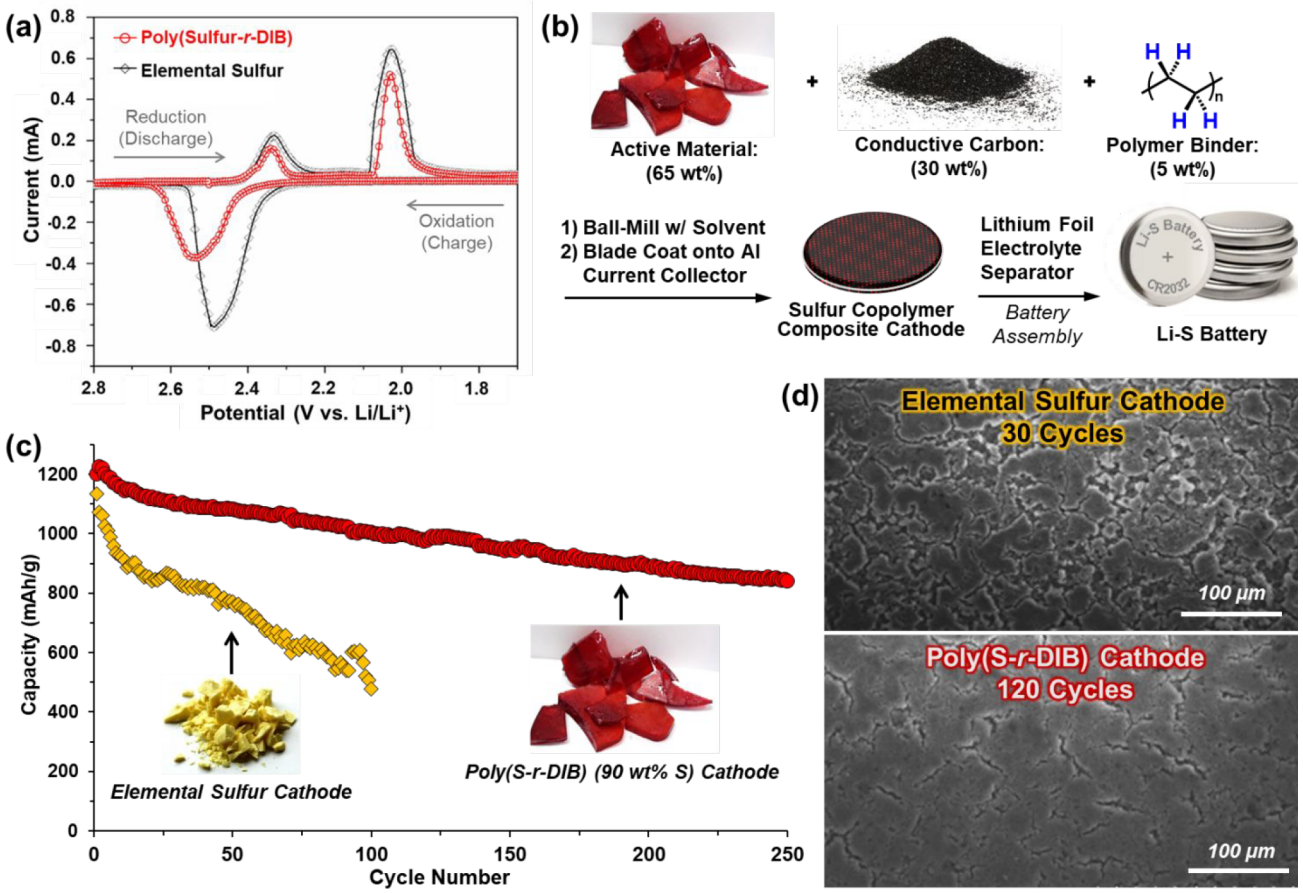

Figure 5. (a) Cyclic voltammetry comparing the electrochemical behavior of poly(S-r-DIB) (10 wt% DIB) prepared via inverse vulcanization and elemental sulfur (scan rate = 20 μV/s). Adapted with permission from ref 51. Copyright 2013 Nature Publishing Group. (b) Scheme for composite cathode preparation and Li−S battery fabrication. (c) Cycling performance of Li−S batteries with sulfur copolymer (poly(S-*r*-DIB) and elemental sulfur-based cathodes at a rate of C/10. Capacities shown are from the discharge cycle with specific capacity based on mass of sulfur contained in the cathode. Adapted with permission from ref 69. Copyright 2014 American Chemical Society. (d) SEM images of Li−S battery cathodes with elemental sulfur active material after 30 charge/discharge cycles and poly(S-r-DIB) active material after 120 charge/discharge cycles. Adapted with permission from ref 70. Copyright 2015 Materials Research Society.

has complicated structural and molecular weight determination of whether these polymers are true thermoplastics or thermosets. The architecture of many of these copolymers is a combination of branched and cyclic topologies if thermoplastic materials are targeted.[31] Polymers prepared from inverse vulcanization are primarily amorphous materials with glass transitions typically below 50 °C, as increasing sulfur content tends to lower T_g. Notable exceptions include co- and terpolymers made with comonomers with higher functionality (TIB, Figure 4b)[56] or that promote higher cross-linking density (NBD2, DCPD, Figure 4b) that can raise glass transition values above 100 °C.[57,58,64] Recent studies have demonstrated that DVB comonomers can also afford sulfur copolymers possessing T_g values around 100 °C by optimization of inverse vulcanization conditions.[54,55] Furthermore, high-sulfur-content copolymers made from inverse vulcanization may have dynamic covalent S−S bonds,[65] which may reorganize when subjected to melt or solution processing into free-standing films for rheological or mechanical property characterization.[66] These types of subtle distinctions can complicate structure−property correlation with molar mass of the polymeric material. In a general sense, the thermomechanical properties of high-sulfur-content copolymers made using inverse vulcanization are inferior to classical hydrocarbon-based polymeric materials. However, several unique electrochemical, optical, and mechanochemical properties arise from the high content of S−S bonds in the material. Hence, in the early stages of this research program, we explicitly chose to demonstrate the value of these bulk material properties, as will be discussed in the following sections.

5. CATHODES FOR Li−S BATTERIES

In electrochemical systems, the S−S bonds in copolymers prepared by inverse vulcanization exhibit redox reactivity comparable to elemental sulfur (Figure 5a). This motivated the investigation of these high-sulfur-content copolymers as a new type of electroactive cathode materials for Li−S batteries.[67] Li−S batteries have received a great deal of attention as a next-generation electrochemical energy storage system due to their high theoretical specific capacity (1672 $mAhg_{sulfur}$) which is nearly an order of magnitude higher than cathode materials in conventional Li-ion batteries.[68] This high specific capacity arises from the ability of each sulfur atom to accept two electrons and can be generally described in a theoretical Li−S cell by $S_8 + 16\ Li^+ + 16e^- \rightarrow 8\ Li_2S$. However, the intrinsic electrical conductivity of elemental sulfur is extremely low ($\sim 10^{-16}$ S/cm), which necessitates the addition of conductive

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

carbon adjuncts and processing with a polymer binder into a composite before it can be integrated as an operational cathode (Figure 5b). Further issues are presented by the intractability of S_8 in conventional solvents, which complicates the composite formulation and impedes ideal solution processing conditions used for device fabrication. In addition to these problems with device fabrication, the fundamental electrochemical operation of a Li−S cell presents a number of challenges toward optimal battery performance.[67] During the conversion reactions between S_8 and Li_2S_x, the different Li−S redox products exhibit varied solubility and undergo significant volume changes. Ultimately, as the battery is cycled, the repeated dissolution/precipitation and volumetric expansion/contraction of the redox products lead to deleterious battery operation with poor performance in terms of Coulombic efficiency, rate capability, cycle lifetime, and capacity retention.

Li−S batteries with cathodes using sulfur-DIB copolymers as the electroactive material achieved significantly better performance than elemental sulfur with longer cycle lifetimes and higher capacity retention (Figure 5c).[69,70] One significant advantage of replacing elemental sulfur with organosulfur copolymers made by inverse vulcanization is the preparation of superior composite cathodes. High-sulfur-content copolymers have been shown to exhibit enhanced compatibility and interfacial contact with the conductive carbon additives while producing more robust and compositionally homogeneous composite electrodes, as shown by rigorous electron microscopic and spectroscopic studies by Oleshko and Soles et al. (Figure 5d).[70−72] Further performance enhancement is garnered from the organic comonomer moieties that serve as anchors and help mitigate dissolution of the polysulfide redox products into the electrolyte and diffusion away from the cathode.[69,73] An additional benefit of utilizing sulfur copolymers prepared via inverse vulcanization is the relatively facile large-scale production compared to many other enhanced Li−S cathode materials which often rely on multi-step synthesis and nanochemistry. This was exemplified with the kilogram-scale synthesis of poly(S-*r*-DIB) that provided Li−S cathodes with equivalent performance to sulfur copolymer batches synthesized at typical lab scale (∼10 g).[74]

The promising Li−S battery performance coupled with the straightforward, scalable synthesis of poly(S-*r*-DIB) spurred investigation of a variety of comonomers for new high-sulfur-content copolymers and the integration of sulfur copolymers into novel materials for Li−S batteries. Since the initial report on poly(S-*r*-DIB)-based cathodes, sulfur-rich materials prepared by direct reaction of S_8 under thermal ring-opening conditions with aryl alkynes,[75] trithiocyanuric acid,[76] allyl-terminated poly(thiophene),[77] bismaleimide,[78] diallyl disulfide,[79] terpenes,[79,80] divinylbenzene,[53] unsaturated fatty acids,[81] eugenol,[82] styrene,[83] quinones,[84] triazine,[84] benzoxazines,[85,86] ionic liquids,[87] and vinylphosphonic acid[88] have been explored as electroactive cathode materials in Li−S batteries. Additionally, sulfur copolymers have been used to prepare composites with inclusion of filler materials targeted at augmenting Li−S battery performance including graphene[89−93] and MoS_2.[50] Notably, Li−S batteries from sulfur-MoS_2 composites exhibited high C-rate capability (500 mAh/g at 5C) and cycle lifetimes to 1000 cycles.[50] In addition to Li−S cathode materials prepared with S_8 under homolytic ring-opening conditions (∼180 °C), the field has expanded to beyond the use of inverse vulcanization chemistry to prepare cathode materials. New methods include the use of nucleophilic aromatic substitution (S_NAr) have been developed to prepare sulfur-rich covalent triazine frameworks,[94−96] hydroquinone-based networks,[97] and phthalocyanine copolymers.[98]

The utility of a diverse array of sulfur copolymers for enhancing Li−S battery performance has been demonstrated with notable advancements of cycle lifetimes and rate capability. Long device lifetimes of ≥1000 cycles have been realized using sulfur copolymers of divinylbenzene,[53] styrene,[83] and polybenzoxazine.[85] Furthermore, high rate capability has been demonstrated with sulfur-rich copolymers of trithiocyanuric acid[76] and markedly tetra(allyloxy)benzoquinone (>800 mAh/g at 10C).[84] In addition to improved electrochemical performance, there have been recent advances toward improved device safety through the use of copolymers with flame retardant phosphazine-based comonomers[99,100] and all-solid-state devices with ionically conducting polyether comonomers.[101]

While inverse vulcanization has allowed for a facile way to chemically modify sulfur for use in the cathode, there remain fundamental questions as to the structure *in operando* of the sulfur copolymers and a more complete structure−activity relationship of the various organic comonomer inclusions.[102−104] Moving forward, substantial development and optimization are still needed before Li−S batteries can become a practical energy storage solution.[105] High-sulfur-content copolymers are a promising contribution toward development of advanced Li−S cathodes, but ultimately realization of commercially viable system will require adopting high-sulfur-loading cathodes[91,106] and further improvement of the many different components of a cell (anode, separator, electrolyte, etc.).[104,107]

6. HIGH REFRACTIVE INDEX POLYMERS FOR INFRARED OPTICS

Chalcogenide hybrid polymers prepared via inverse vulcanization possess unusually high refractive index (RI) and infrared (IR) transparency relative to conventional optical polymers due to the presence of a high content of S−S bonds in the material.[108,109] This combination of useful optical properties has prompted investigation of these chalcogenide hybrid polymers (CHIPs) as the first class of high RI plastic optics for IR optical applications. IR optical technology has been widely utilized in imaging and sensing systems in the civil, medical, and military sectors. Since many objects and organisms (e.g., humans) emit IR radiation via black body radiation, IR thermal imaging and sensing are attractive systems for monitoring human activity and motion in near or total darkness with high resolution. Currently, IR-transmissive materials used for fabricating lenses and windows are prepared from inorganic materials, such as germanium or amorphous chalcogenide glasses, since these materials are chemically stable and thermomechanically robust while also possessing very high RI ($n \approx 2-4$) and excellent IR transparency. However, since these materials are expensive to acquire and fabricate into optical elements, there has been a long-standing technological opportunity to develop low-cost, melt-processable IR plastics, particularly since IR optical systems are a critical aspect of U.S. national security.[109]

High Refractive Index CHIPs. The RIs of high-chalcogenide-content hybrid polymers prepared via inverse vulcanization are significantly higher than conventional organic polymers, such as PMMA ($n \approx 1.45$), or classical high

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

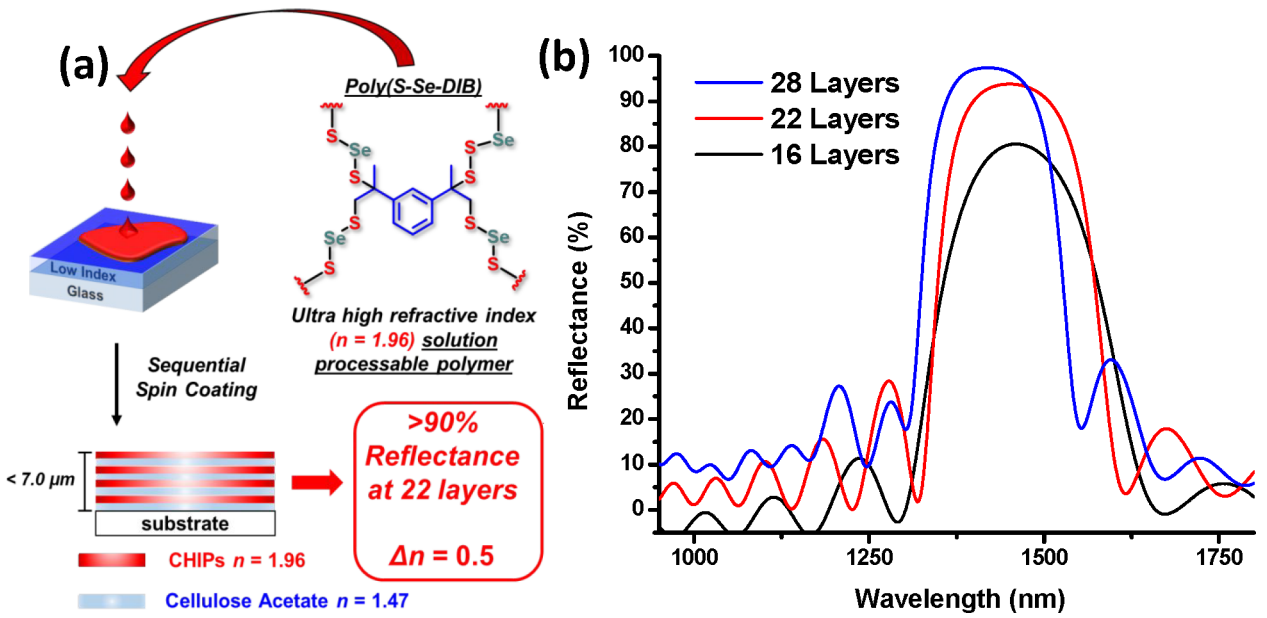

Figure 6. (a) General scheme for the fabrication of highly reflective all-polymer 1-D photonic crystals from CHIPs materials that possess tunable reflectance across the NIR and SWIR (1.0−2.0 μm). (b) ~ 2 cm^2 Bragg reflectors with 16, 22, and 28 layers each, with reflectance values at 1450 nm. Adapted with permission from ref 119. Copyright 2018 American Chemical Society.

refractive index polymers (HRIPs, $n \approx 1.6-1.7$).[110] Achieving high refractive indices in plastic optics is essential for IR optics to reduce the gravimetric and volumetric footprint of optical elements in imaging systems (i.e., high n = small and thinner lenses); furthermore, state of the art IR imaging systems are designed for high RI materials. The use elemental sulfur as the majority feed comonomer in polymerization inherently allows for an unusually large volume of highly polarizable sulfur units to be introduced into polymeric materials. Hence, sulfur copolymers possessing RI values in the range of $n \approx 1.75-1.86$ in the visible and IR spectrum could be obtained by simply controlling feed ratios of S_8 and comonomers, such as DIB, over a range of 50−80 wt% sulfur.[108] Furthermore, we demonstrated for the first time the preparation of synthetic polymers with RI values exceeding n = 2.0 by introduction of gray selenium into the inverse vulcanization of S_8 and DIB to prepare CHIPs terpolymers of poly(S-*r*-Se-*r*-DIB), which to date is the highest RI synthetic polymer.[111] Similar efforts were reported from the U.S. Naval Research Laboratory using an iterative approach to prepare cyclic selenium sulfide precursors for use in inverse vulcanization.[112]

Highly Reflective Photonic Crystals from CHIPs. An attractive optical construct to demonstrate the benefit of high refractive index CHIPs was the fabrication of wholly polymeric one-dimensional photonic crystals (1-D PCs) from solution processing. 1-D PCs, also referred to as Bragg reflectors or dielectric mirrors, are composed of alternating multi-layered films that are designed to be highly reflective at certain targeted wavelengths.[113−119] The key to achieving high reflectivity is embedding a large RI contrast (Δn) between alternating layers, while using processing methods that can fabricate these periodic films without morphological defects which dramatically reduce reflectivity. The vast majority of engineering plastics typically exhibit refractive indices in the range of n = 1.45−1.65, which ultimately limits the RI contrast that can be generated for polymeric 1-D PCs. The limitations of low Δn with conventional synthetic polymers has led to the development of polymer engineering solutions, namely melt-extrusion of multi-layered films to fabricate hundreds of layers to create highly reflective films.[113,117] However, synthetic access to solution-processable high RI poly(S-*r*-Se-*r*-DIB) terpolymers (n = 1.96), the fabrication of highly reflective 1-D PC (>90% reflectivity) in the short-wave infrared (SWIR) spectrum (across 1−2.0 μm) was achieved by spin-coating 20−30 bilayer films with poly(cellulose acetate) (CA, n = 1.45), which achieved a large Δn = 0.5 for the first time with a wholly polymeric system (Figure 6).[119] Film thicknesses of individual layers of the poly(S-*r*-Se-*r*-DIB) and CA were around 200 and 300 nm, respectively, to achieve reflectivity in the SWIR. The advantages of using a high RI polymer are evident in the reduced number of spin-coating steps required to achieve high reflectivity, which would require high precision engineering and processing methods to create much thicker multi-layered films when working with smaller RI contrast.

The Problem with Organic Polymers for Mid- and Long-Wave Infrared Optics. The desirable IR optical properties found in germanium and amorphous ChG semiconductors arise from the nature of their constituent atoms and bonds. Specifically, the large mass of their atoms shifts the vibrational energies of their bonds to outside the MWIR and LWIR spectral windows. RI values for these materials are also typically very high (n > 2.0−4.0), again due to the presence of large, highly polarizable atoms. The use of conventional polymeric materials for IR optics would at first sight be precluded by the presence of a high fraction of covalent carbon bonds (e.g., C−C, C−H, or C−heteroatom), leading to stretching and bending vibrations in the MWIR and LWIR regions.[109] This intrinsic limitation is illustrated for the FTIR spectra of polystyrene in Figure 7, where the MWIR and LWIR bands are highlighted in yellow. Absorptions in the MWIR are dominated by C−H stretching vibrations around 3000 cm^{-1} (~3.3 μm). Hence, the guiding principle in the design of MWIR transparent plastics is the omission of C−H moieties in the material without sacrificing other desirable material properties. A pioneering demonstration of MWIR imaging through CHIPs was conducted with melt-processed and

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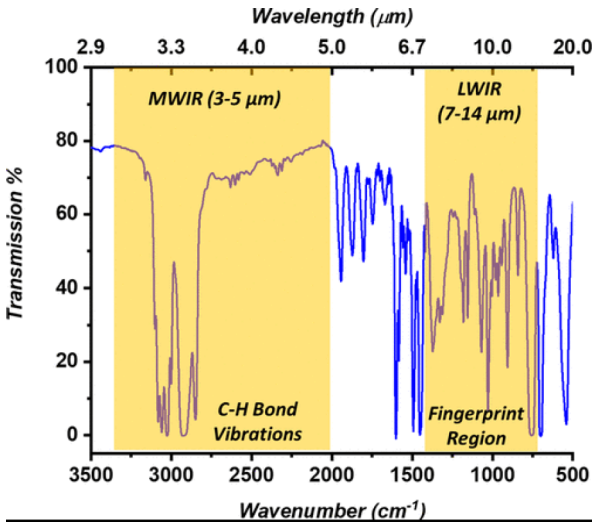

Figure 7. IR spectrum of a polystyrene film; the spectral windows in the MWIR and LWIR regions used for IR thermal imaging are highlighted in yellow. Adapted with permission from ref 109. Copyright 2020 American Chemical Society.

molded windows of poly(S-*r*-DIB) in 2014. These experiments confirmed that the high content of S−S bonds and the dramatic reduction in C−H bonds profoundly improved MWIR transparency, particularly when high-sulfur-content hybrid copolymers were used (70−80 wt% sulfur).[108] Improvments in MWIR transparency and quality of MWIR thermal imaging with high T_g poly(S-*r*-TIB) copolymers were also demonstrated,[56] along with the concept of "scratch and heal" CHIPs using poly(S-*r*-DIB), where reorganization of dynamic covalent S−S bonds could be used to remove scratches on the surface of molded windows.[66]

However, approaches for LWIR transparency are profoundly more complex due to the abundance of vibrational absorptions in this spectral window for organic-based materials, which is known as the "IR fingerprint region" (Figure 7).[58,109] Despite these significant challenges, the advantages of polymeric materials for this application (e.g., lower cost, moldability, use of Earth-abundant materials), call for more fundamental research into the synthesis and characterization of LWIR transmissive polymers. Furthermore, the chemical diversity available to organic compounds points to the potential to design polymeric materials that enable LWIR thermal imaging by reducing/eliminating vibrations in the technology relevant 7−14 μm LWIR spectral window. To accelerate materials design and synthesis, we exploited the use of computational chemistry (specifically, density functional theory (DFT) calculations) to simulate the IR spectra of candidate comonomers and CHIP materials for improved LWIR transparency.[58] The use of the EDF2 functional enabled accurate and rapid calculation of fundamental vibrational frequencies and absorption intensities, which were readily validated by comparing simulated vs experimental IR spectra of norbornane and norbornadiene (Figure 8a,b). Norbornadiene (NBD) was observed to have promising limited vibrational absorbances in the LWIR spectral region of interest (7−14 μm). Unfortunately, the boiling point of NBD (bp = 90 °C) was too low for use in liquid sulfur and inverse vulcanization. However, the dimeric form of norbornadiene ("NBD2") was observed to have a similar LWIR spectral profile, was presumably less volatile due to the higher molar mass and was readily synthesized in one step (Figure 8d). Furthermore, simulated IR spectra of a molecular model for the sulfurated polymeric form of NBD2 was designed where NBD2 units were linked by trimeric sulfur chains (Figure 8c). Copolymerization of these NBD2 with elemental sulfur afforded a yellow glassy, cross-linked network of poly(S-*r*-NBD2) (Figure 8d). These thermosets were observed to possess an enhanced glass transition ($T_g \approx 100$ °C) and excellent thermal stability until $T = 300$ °C, which were now comparable to poly(methyl methacrylate) (PMMA), which is one of the optical industry standards for plastic optics. Their thermomechanical features offered significant melt processing advantages for the fabrication of thicker optical elements (1−3 mm in thickness), i.e., windows; these were amenable, for the first time in the

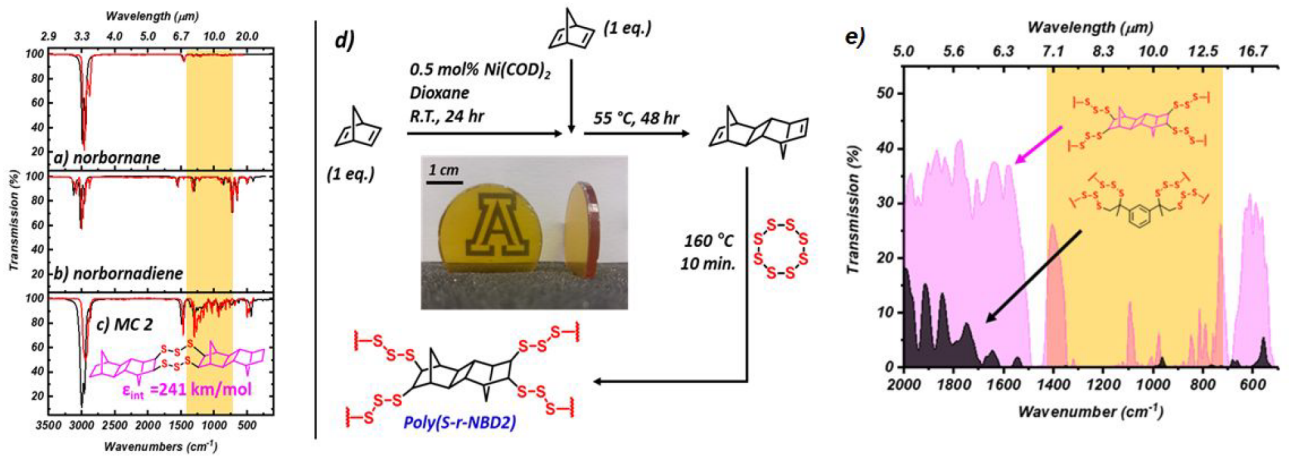

Figure 8. Comparison of the DFT-calculated FTIR spectra for equal concentrations of (a) norbornane, (b) 2,5-norbornadiene, and (c) a BD2-sulfide model compound (MC2) (black lines). The red lines indicate the experimental gas-phase spectra of (a) norbornane, (b) 2,5-norbornadiene, and (c) poly(S_{70}-*r*-$NBD2_{30}$). (d) Synthetic scheme for synthesis of NBD2 via the nickel-catalyzed [2+2] cycloaddition of 2,5-norbornadiene and the inverse vulcanization of NBD2 with elemental sulfur: the image shown consists of two 2.3 mm thick diamond polished windows of poly(S_{50}-*r*-$NBD2_{50}$). (e) Expanded region of the mid- to long-wave IR spectrum of 1 mm thick films of poly(S-*r*-NBD2) (pink) and poly(S-*r*-DIB) (black), both 70 wt% S, with the 7−14 μm regime shaded in yellow. Adapted with permission from ref 109. Copyright 2020 American Chemical Society.

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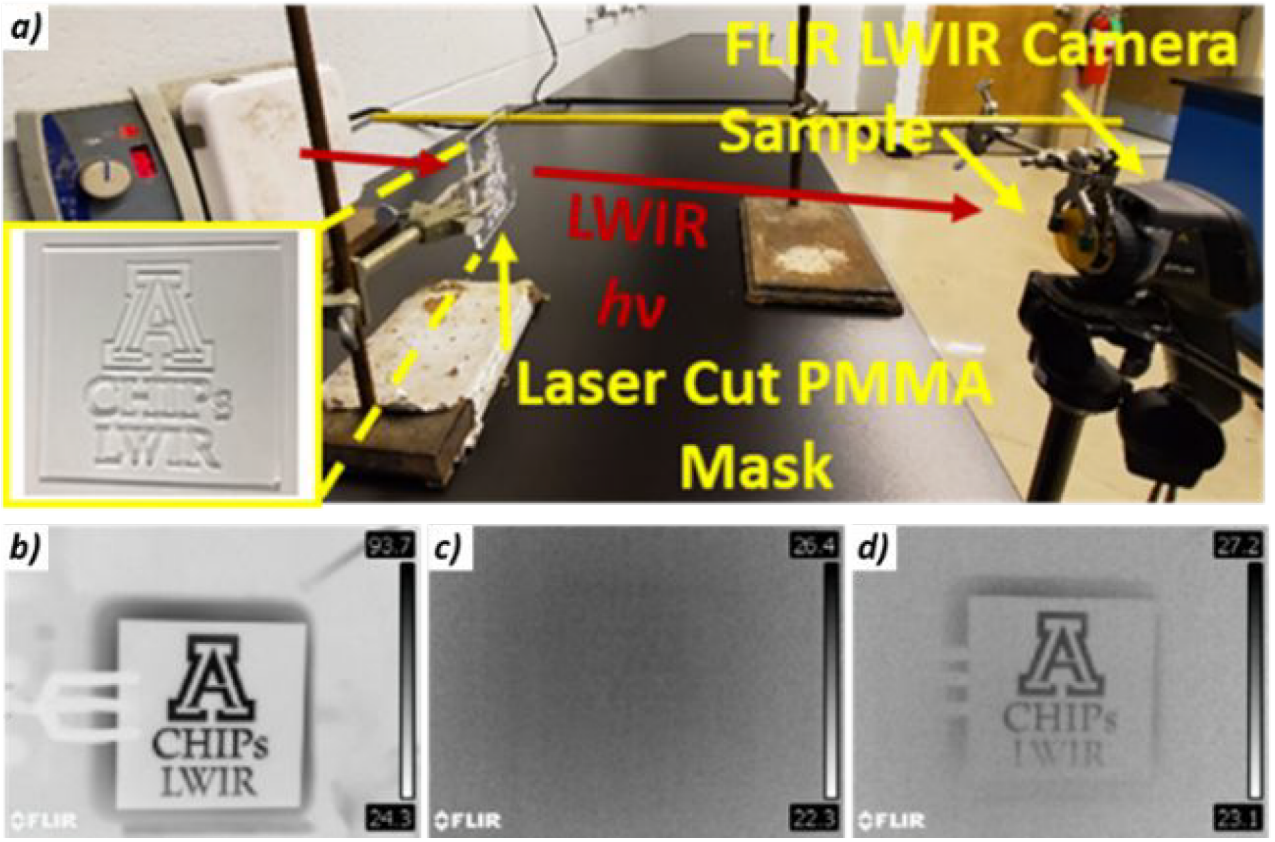

Figure 9. (a) Digital image of LWIR imaging set-up and LWIR images taken with a FLIR LWIR camera operating in the 7.5−13 μm regime in "black hot" mode with inset of patterned PMMA sheet (12 × 12 cm) used as mask for LWIR imaging. (b) No polymer window in front of the camera; (c) through a 1.3 ± 0.15 mm thick poly(S_{70}-*r*-DIB_{30}) window that is LWIR opaque; and (d) through a 1.3 ± 0.12 mm thick poly(S_{70}-*r*-$NBD2_{30}$) window. Adapted with permission from ref 109. Copyright 2020 American Chemical Society.

context of CHIP materials, to diamond turning to fabricate high-quality optical elements (Figure 8d).

We stress that IR spectroscopic and thermal imaging experiments that enable a truly comparative evaluation of the polymers as LWIR transmissive elements are a challenging but critical aspect of the optical characterization of these materials. IR spectroscopy is a central tool to determine the transparency windows and quantify transmittance in thicker polymer films. While thin-film samples on salt plates are sufficient to qualitatively access the fundamental IR absorptions from functional groups, it is required to conduct IR spectroscopic analysis of thicker free-standing films to assess the overall IR transparency of free-standing optical elements (Figure 8e) due to the exponential dependence of Beer's law. Thus, the evaluation of the LWIR transparency for different candidate materials calls for the development of robust processing protocols to prepare polymer films of identical film thicknesses (since even small thickness variations can lead to misleading interpretation of LWIR transparency). Figure 8e compares our first generation CHIPs for MWIR, poly(S-*r*-DIB) and poly(S-*r*-NBD2) films, using IR spectroscopy, which confirmed that the aromatic C═C bonds in poly(S-*r*-DIB) strongly absorb in the LWIR region.[58]

LWIR thermal imaging experiments with poly(S-*r*-NBD2) thermoset windows were conducted as a final assessment of optical transparency. Windows or films with a minimum thickness of 1 mm are required to conduct meaningful LWIR measurements. This criterion also indirectly requires the development of polymer processing and post-processing steps that enable high-quality optical elements with low scattering. To enable a systematic variation of imaging conditions, a straightforward system consisting of a LWIR camera and a temperature-controlled hot plate (as a blackbody radiator and IR source for imaging) was assembled, and imaging was demonstrated through a CO_2 laser-etched PMMA sheet with hollow cut-outs of an "A" and "CHIPs LWIR" (Figure 9a,b). The comparison between Figure 9c and 9d underlines the significantly higher quality of the poly(S-*r*-NBD2) vs poly(S-*r*-DIB) windows.[58] While the development of polymeric materials for LWIR optics is presently a daunting technical challenge, the use of computational methods will likely be an important tool to find novel molecular architectures to maximize LWIR transparency. Sulfur copolymers for LWIR imaging and characterization were independently reported using tetravinyltin[120] or diiodobenzene comonomers.[121]

7. FUNCTIONALIZATION AND POST-POLYMERIZATION MODIFICATIONS

Side-Chain Group Functionalization through Functional Monomers. There remains a need to develop versatile and robust methods to introduce functionality into sulfur-derived (co)polymers to improve the properties of this class of materials. As alluded to previously, the main obstacle to introducing new functionality into the main- or side-chain moieties of these polymers is the limited scope of organic comonomers that are miscible with liquid sulfur. Furthermore, the S−S bonds in the backbone of S_8-derived polymers are

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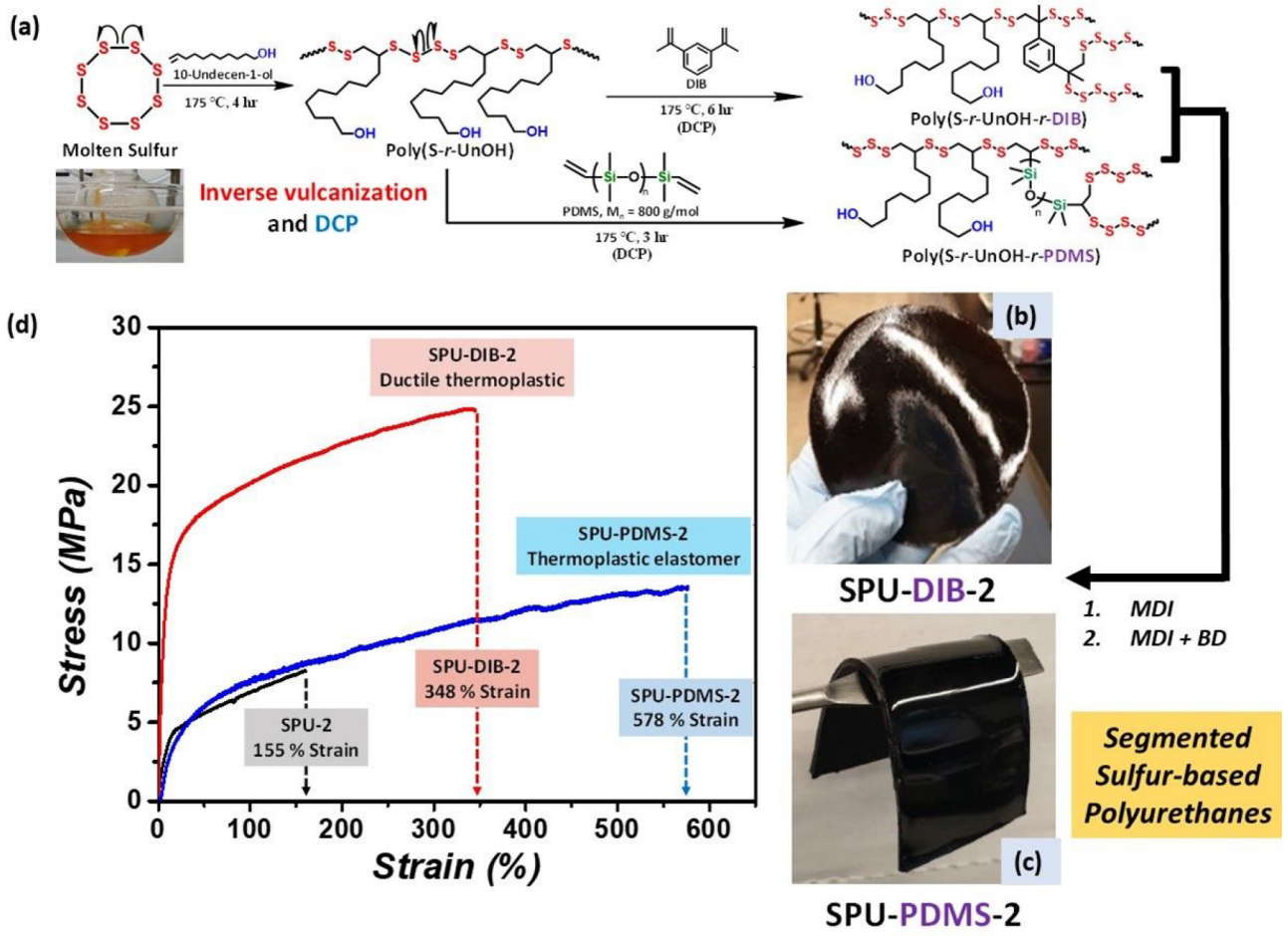

Figure 10. (a) Synthetic scheme for sulfur polyols, poly(S-*r*-UnOH-*r*-DIB) and poly(S-*r*-UnOH-*r*-PDMS), using a combination of inverse vulcanization and dynamic covalent polymerization and prepared from segmented SPUs, SPU-DIB-2 and SPU-PDMS-2. Digital images of (b) thermoplastic SPU-DIB-2 and (c) thermoplastic elastomer SPU-PDMS-2. (d) Tensile stress−strain curves overlaid for segmented block copolymers SPU-DIB-2 and SPU-PDMS-2. Adapted with permission from ref 129. Copyright 2021 John Wiley & Sons.

chemically sensitive to nucleophiles, bases, and a number of transition metal complexes or salts.[30−34] The most elegant and straightforward approach to introducing new functionality into sulfur-derived (co)polymers is the inverse vulcanization of S_8 with functional comonomers. To date, a few examples of direct copolymerization of functional comonomers have been successful, including that of 4-vinylaniline (4VA),[60] propylenedioxythiophenyl styrene,[122] 1,3-phenylenediamine,[123] 4-vinylbenzyl chloride,[124] and 10-undecen-1-ol (UnOH).[125,126] Using this approach, reactive side-chain functional groups were able to be carried into the sulfur copolymer chain without the need for protecting group chemistry and were successfully functionalized to form poly(ionic liquids),[124] cross-linked epoxy,[123] or methacrylamide networks.[60]

Main-Chain Functionalization. Alternatively, main chain modifications to sulfur-derived copolymers were also achieved by initially synthesizing liquid sulfur resins that possessed dynamic covalent S−S bonds in the copolymer backbone that could be thermally activated to generate thiyl radicals that could add to externally added (di- or multi-)vinyl comonomers. This process was referred to as dynamic covalent polymerizations (DCPs),[127] where liquid sulfur resins were initially prepared by the inverse vulcanization of S_8 with Sty to form a poly(S-*r*-Sty) low-T_g polymer fluid.[83] The poly(S-*r*-Sty) resin was found to be miscible with a wide range of acrylate, allylic, and vinyl ether[127,128] comonomers, where dynamic S−S bonds in the polysulfide backbones were accessible for thermally induced thiol−ene additions to acrylates and other functional vinyl monomers at elevated temperatures to introduce new termonomer units into the sulfur copolymer. This approach was recently extended to using poly(S-*r*-DVB) prepolymers for DCP with vinyl ethers to prepare new functional sulfur copolymers.[128] The generality of the DCP process approach with inexpensive vinyl comonomers significantly broadened the scope of monomer that could be used in comparison to direct inverse vulcanization of S_8.

Segmented Sulfur-Containing Polyurethanes. Recent work on the synthesis of segmented sulfur-based polyurethanes (SPUs) demonstrated the synergistic utility of inverse vulcanization, DCP, and post-polymerization modifications to prepare the first example of soluble block copolymers and thermoplastic elastomers derived from S_8.[129] This particular system also showcases the benefits of using efficient, low-cost chemistry in an iterative fashion to prepare useful polymer materials when direct one-step inverse vulcanization approaches are inaccessible. Integration of S_8 into polyurethane (PU)-based materials is of particular interest to the oil and gas sectors since this class of plastics can be used for both high-volume production applications and specialty high-performance materials. In particular, thermoplastic elastomeric polyur-

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

ethanes, also referred to thermoplastic polyurethanes (TPUs), are a target polymer product of interest for S_8, since precision polymer synthesis of segmented multi-block copolymers is necessary to ensure morphological microphase separation in bulk films to achieve high tensile strength and elasticity.[130] The incorporation of S_8 into polyurethane materials is most readily achieved by the copolymerization of liquid sulfur with vinylic comonomers bearing, OH groups, followed by polymerization of this sulfur-based polyol with diisocyanates. This approach was demonstrated by BASF in 2014,[125] and by Tsutsumi et al. in 2017,[126] to form sulfur-based PU networks for Li−S cathode materials. Hasell et al. reported on a similar methodology to form PU thermosets that demonstrated dynamic covalent healing properties.[131] However, the synthesis of soluble, thermoplastic segmented SPUs with improved thermomechanical properties remained elusive.

To achieve this target, sulfur-containing polyols were prepared by the inverse vulcanization of S_8 with undecen-1-ol (UnOH) and chain-extended with either DIB or divinyl PDMS (M_n = 800 g/mol) using DCP to prepare sulfur terpolymers (i.e., sulfur terpolyols) of poly(S-*r*-UnOH-*r*-DIB) and poly(S-*r*-UnOH-*r*-PDMS). The DCP step proved to be an essential step to modify properties of the final segmented block copolymer SPU, as DIB-based terpolymers afforded higher mechanical strength, while the PDMS terpolymer imparted enhanced elasticity. Sulfur-containing prepolymers (SPU-DIB-1, SPU-PDMS-1) were then prepared by polymerization of either sulfur terpolymer with 4,4′-methylene diphenyl diisocyanate (MDI) to serve as the soft segments in the final material. Final chain extension with a hard segment of MDI and 1,4-butanediol (BD) was conducted to prepare the final segmented SPUs, labeled as SPU-DIB-2 and SPU-PDMS-2 (Figure 10a). Sulfur terpolyols, prepolymers, and segmented SPUs were all soluble materials that enabled unambiguous confirmation of block copolymer synthesis using size exclusion chromatography (SEC), which demonstrated that high-molar-mass SPUs were prepared ($M_w \approx 80\,000-100\,000$ g/mol). Phase separation in both SPUs was confirmed using both differential scanning calorimetry (DSC) and atomic force microscopy (AFM). Finally, mechanical properties confirmed the formation of segmented SPUs as noted by SPU-DIB-2 (Figure 10b) exhibiting thermoplastic characteristics with a high tensile strength (23 MPa) and strain-induced stiffening until 348% elongation at break (Figure 10d). Conversely, the segmented SPU-PDMS-2 (Figure 10c) sample exhibited significantly enhanced elongation at break (578% strain) and slightly lower tensile strength at 13 MPa (Figure 10d), where cycling tensile deformation to 100% strain confirmed that this material was reversibly elastic, and hence was a thermoplastic elastomer.[129] These findings demonstrate the versatility of this synthetic method that utilizes inexpensive reagents and facile synthetic processes while also affording soluble, high-molar-mass polymers with previously unattainable combinations of high tensile strength, ductility, and elasticity for S_8-derived polymers. Segmented SPUs were also found to exhibit excellent flame retardancy in the UL-94 vertical flame test in comparison to classical segmented thermoplastic elastomer polyurethanes made from poly(tetramethylene glycol) (PTGM) and MDI (Figure 11a,b). To our knowledge, these segmented SPUs were the first examples of intrinsically flame-retardant materials made using elemental sulfur, which is very surprising, given that S_8 is readily flammable.[129]

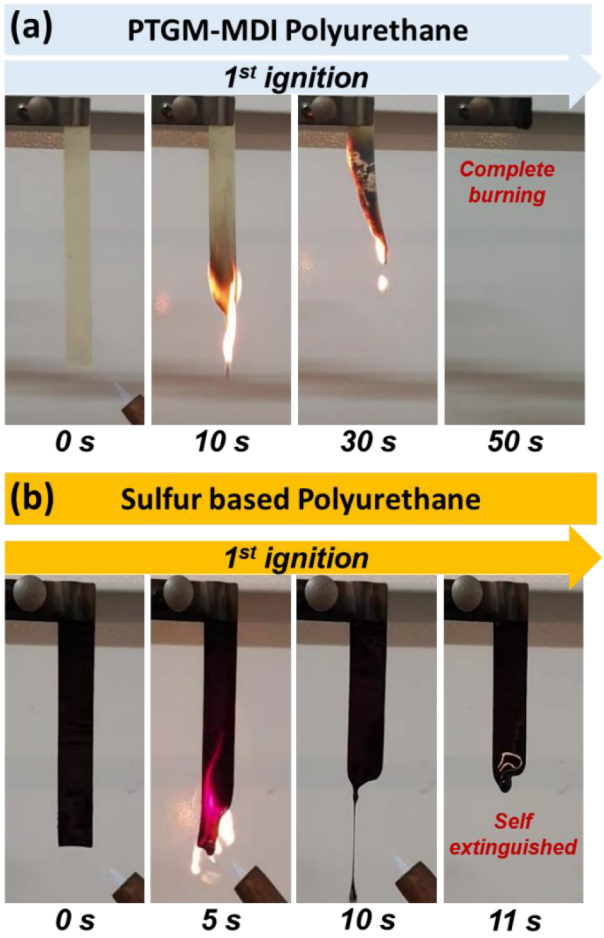

Figure 11. UL-94 vertical flame test for (a) PTGM-MDI segmented polyurethane, which completely burns after first ignition, and (b) segmented SPU-DIB-2, which self-extinguishes within 11 s and exhibited a V0 flame-retardant rating. Adapted with permission from ref 129. Copyright 2021 John Wiley & Sons.

8. EMERGING FIELDS OF USE FOR SULFUR-DERIVED POLYMERS

The development of emergent properties in high-sulfur-content polymers has spurred numerous new discoveries in the synthetic chemistry and material applications of sulfur-derived polymeric materials. Summarized below are notable novel reports in the field, with an emphasis on new reports since 2019 that are orthogonal to the areas discussed above:

Environmental Remediation. The use of high-sulfur-content copolymers from limonene and other naturally occurring olefinic comonomers has been elegantly pioneered by Chalker et al. for metal scavenging, oil remediation, and, more recently, agricultural fertilizers.[132−136] High-sulfur-content copolymers were observed to exhibit a high affinity for certain toxic metal ions, such as Hg^{2+} and Fe^{3+}, which points the potential of these sulfur plastics as low-cost alternative sorbent and sensor materials. Hasell et al. has pioneered foaming of sulfur-derived polymers to create porous materials for use in metal ion removal and separations,[137,138] along with other non-porous thermoset polymers.

Multi-component Polymerizations. Tang and Hu et al. have pioneered the incorporation of S_8 into multi-component reactions to prepare polythioamides, polythioureas, and poly(*O*-thiocarbamates) that also exhibit metal scavenging

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

affinities for Hg^{2+}, Au^{2+}, and Ag^{+} ions.[139,140] Chen et al. reported on the direct reaction of diamines with S_8 to prepare polythioamides.[141]

Rubber Vulcanization. The first example of the vulcanization of styrene−butadiene rubber (SBR) was reported by Wręczycki et al. using sulfur copolymers synthesized via inverse vulcanization as the cross-linking agent,[142] and independently Guo et al. recently reported the vulcanization of SBR using liquid-formed sulfur copolymer, poly(S-*r*-Sty), without toxic accelerator for the vulcanization.[143] Yagci et al. reported on the inverse vulcanization of sulfur and benzoxazines to cross-link polybutadiene as a route to dynamic covalent healable elastomers.[144]

Liquid Metal Composites. The preparation of liquid metal−sulfur copolymer composites was achieved by the inverse vulcanization of sulfur and DIB in the presence of gallium−zinc eutectic alloy fluids.[145]

Triboelectronics. Fluorination of poly(S-*r*-DIB) was conducted to afford a new class of extremely negative triboelectric material with a 3−6-fold increase in energy output relative to the state of the art negative triboelectronic polymer, PTFE.[146]

Antimicrobials. High-sulfur-content copolymers synthesized using inverse vulcanization were demonstrated by Theato et al. and Hasell et al. to exhibit antimicrobial activity toward certain bacterial strains (e.g., *Escherichia coli* and *Staphylococcus aureus*).[147,148]

Adhesives. The adhesive properties of S_8-derived polymers from inverse vulcanization have also been investigated, which point to future uses of these materials for self-adhesion of damaged polymers or interfacial adhesion promoters with inorganic surfaces.[149,150]

9. PERSPECTIVE AND FUTURE CHALLENGES

There remain numerous technical challenges and opportunities in this emerging field of sulfur polymer chemistry. Below are described a few potential areas of interest that remain impactful targets for future researchers to explore.

Controlled Polymerization Methods. A desirable target for S_8 polymerization is the prospect of achieving controlled or living polymerization processes that would afford control of molar mass and Poisson-type molar mass distributions. The current inverse vulcanization process can be described as a step-growth like process governed by the sulfur diradical concentration which dictates the overall rate of polymerization in the absence of additives or catalysts. This process would presumably afford a most probable molecular weight distribution[52] if not further complicated by chain-transfer reactions of sulfur- and carbon-centered radicals to polysulfide backbones. Transformation of this polymerization process to a controlled process would require the development of chain-growth initiators and mediators to allow for S_8 ROP at temperatures significantly lower than the known floor temperature for S_8.[34] The early work of Penczek on anionic S_8-thiirane ROP is the closest system to date that has achieved a true chain growth polymerization of S_8, but remains limited by equilibrium polymerization constraints on monomer conversion, along with chain transfer to S−S bonds in the polymer.[36,37] Suppression of chain transfer to polymer processes may be achieved by the discovery of reversible trapping agents for propagating sulfur species (radical, ionic), the concept of which is now ubiquitous in the field of controlled radical polymerization.[25,151,152] Our early work on the use of nitrone spin-trapping agents for thiyl radicals for EPR measurements may be informative here for future possibilities.[65]

Organic Comonomer Design Prospects. As demonstrated throughout this Perspective, appropriate design of the organic comonomer for inverse vulcanization profoundly affects the thermomechanical, electrochemical, and optical properties of the final chalcogenide hybrid material. We anticipate that computational chemistry and simulation will play significant roles to accelerate discovery of new monomers and polymers with targeted properties and performance. Our work with DFT simulations for LWIR transparency points to the potential of this approach when appropriately screened for synthetic viability.[58]

Toward Degradable and Circular Economical Chemistry. A major advantage of S_8-derived polymers is the presence of S−S bonds in the polymer backbone which in principle can be degraded by reducing agents, nucleophiles/bases, or transition metal salts. Thus, the development of new synthetic methods for the controlled degradation of these hybrid polymers into environmentally benign byproducts would be a compelling advance. Methods to recover monomers from these polymers is chemically feasible given that S_8 regeneration would be thermodynamically favorable given the low ring strain due to this sulfur allotrope.[38] The ability of sulfur bacteria to metabolize S_8 and other polysulfides[153] points to interesting possibilities for circular production, degradation, and reuse of S_8-derived polymers.

Prospects for Sulfur-Derived Polymers to Compete with Conventional Hydrocarbon-Based Plastics. Finding products or applications with a high-value proposition for sulfur-derived polymers over classical hydrocarbon-based plastics remains the key frontier to validate this emerging field of chemistry.[129] While new discoveries are no doubt in store, an attractive value proposition for this approach lies with the low cost of S_8 and other sulfur-derived base chemicals (e.g., CS_2) in comparison to many hydrocarbon-based specialty monomers. It is likely that hybrid polymers made from sulfur base chemicals derived from oil refining will provide a route to high-performance polymers that retain low cost due to the high-volume production of these reagents.

10. CONCLUSION

In the past decade, there has been a resurgence in the utilization of elemental sulfur as a new feedstock for polymerization chemistry and polymeric materials. The enormous volume of sulfur generated by the oil and gas industries has created a significant technological motivation for creating higher value chemical products for both commodity and specialty plastics. However, the paucity of synthetic methods to polymerize elemental sulfur into chemically stable, processable polymeric materials stifled advancement of this area. The simple but worthwhile use of liquid sulfur as an unconventional reaction medium was the key breakthrough that enabled a new class of organosulfur polymers to be developed and led to a new polymerization process, inverse vulcanization, which is the focus of this Perspective. As discussed, a number of important discoveries have been made in the scope of monomers and catalysts for the inverse vulcanization process. Furthermore, the useful electrochemical, optical, mechanochemical properties that emerge from high-sulfur-content polymers made from this process have been demonstrated to validate further work in this emerging area.

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

Moving forward, the development of improved sulfur-centered synthetic and catalytic methods holds the key to making commercially viable, advanced polymeric materials.

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Notes

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