

# On the Fundamental Polymer Chemistry of Inverse Vulcanization for Statistical and Segmented Copolymers from Elemental Sulfur

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**Abstract:** In this concept review, the fundamental and polymerization chemistry of inverse vulcanization for the preparation of statistical and segmented sulfur copolymers, which have been actively developed and advanced in various applications over the past decade is discussed. This concept review delves into a discussion of step-growth polymerization constructs to describe the inverse vulcanization process and

discuss prepolymer approaches for the synthesis of segmented sulfur polyurethanes. Furthermore, this concept review discusses the advantages of inverse vulcanization in conjunction with dynamic covalent polymerization and post-polymerization modifications to prepare segmented block copolymers with enhanced thermomechanical and flame retardant properties of these materials.

## Introduction

Polymerizations with elemental sulfur ( $S_8$ ) has recently been revitalized as a new field in polymer chemistry.<sup>[1–5]</sup> The development of copolymerization processes with  $S_8$ , particularly the invention of inverse vulcanization<sup>[6]</sup> and dynamic covalent polymerization (DCP)<sup>[7]</sup> methods, have been key synthetic methods to drive these advances. This new research area is at an intriguing nexus of petroleum, polymer and sustainability sciences, since  $S_8$  is generated in large volumes from petroleum refining and has limited utility for other chemical products. Additionally, high sulfur content polymeric materials have been recently demonstrated to exhibit useful optical, electrochemical, metal scavenging, adhesive and flame retardant (FR) properties prompting further development of this field.<sup>[8,9]</sup> However, the synthetic polymerization chemistry to convert  $S_8$  into well-defined homopolymers, statistical and segmented copolymers remains fairly narrow in scope, which has limited the preparation of enhanced sulfur derived polymeric materials. We recently reported on a new synthetic process to prepare for the first time segmented block copolymers from  $S_8$  which exhibited improved solubility, thermomechanical and FR properties.<sup>[10]</sup> However, the fundamental and polymerization mechanistic aspects of this approach were not discussed, particular in the context of classical polymer chemistry which is the focus of this

CONCEPT mini-review. Herein, we discuss the polymerization and monomer functionality of classical  $S_8$  homolytic ring-opening polymerization (ROP) and inverse vulcanization in the context of a homolytic step-growth process and describe how prepolymer approaches can be used to prepare segmented copolymers and the associated properties of these new materials.

## Homolytic $S_8$ Ring-Opening Polymerization

The homopolymerization of  $S_8$  via homolytic ROP has long been known and extensively studied to afford high molecular weight linear polymeric sulfur.<sup>[11–13]</sup> Due to the absence of ring-strain in  $S_8$  the ROP process is endergonic and hence requires high temperatures to induce polymerization. This form of sulfur, referred to as  $\mu$ -sulfur is insoluble and hence is not amenable to classical solution characterization for determination of molar mass and hydrodynamic volume (e.g, radii of gyration & hydrodynamic radii). Hence, rheological characterization of the melt viscosities of liquid sulfur and sulfur (co)polymers have been extensively investigated to interrogate the homolytic ROP process. Eyring et al. inferred that high molar mass forms of polymeric sulfur can be achieved using this process,<sup>[11]</sup> however, the presence of thiyl radical chain ends and the dynamic covalent nature of S–S bonds in the polymer backbone prompted depolymerization-polymerization reversibility. Tobolsky et al. extensively reported on the equilibrium polymerization aspects of  $S_8$  ROP and primarily described these processes in thermodynamic terms with respect to the equilibrium constants ( $K_{eq}$ ) of the reversible polymerization steps and ramifications on molecular weight, as tracked experimentally with polymeric sulfur melt viscosity.<sup>[12]</sup> However, in a modern polymerization chemistry context, the  $S_8$  ROP has not been explicitly discussed as either a step-growth, or chain growth polymerization process, with the exception of mention of the floor temperature of  $S_8$  at  $T_{floor} \sim 159^\circ\text{C}$ .<sup>[2,5,9]</sup> The free radical

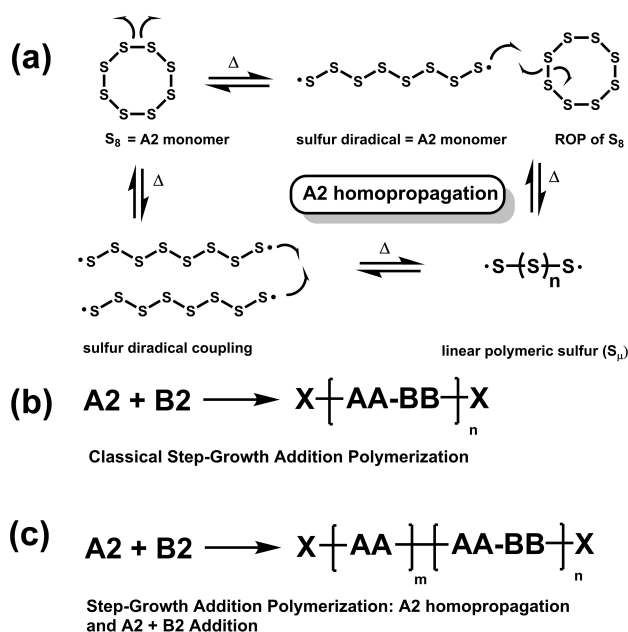
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nature of homolytic  $S_8$  ROP further confounds this categorization of polymerization classification, since free radical polymerizations are associated with chain growth processes.

The  $S_8$  ROP processes can be mechanistically described as a step-growth polymerization that proceeds by either homolytic ring-opening of dithiyl radical species to  $S_8$  or other  $S_x$  rings, or at sufficiently high thiyl radical concentrations by thiyl radical coupling to form high molar mass polymeric sulfur (Figure 1), where both  $S_8$  and ring-opening dithiyl radical species can be thought of as difunctional "A2" monomers (Figure 1a). This particular system can be deemed an unconventional step-growth polymerization since the A2 monomers can homopropagate, while classical step-growth polymerizations require two discrete difunctional "A2+B2" monomers (e.g., diol+diacid, diamine+diacid) that can only polymerize via selective bond formation between the A and B functional groups (i.e., A2, or B2 homopropagation does not proceed) (Figure 1b).<sup>[14]</sup> Hence, due to the homolytic nature of  $S_8$ /dithiyl radical species, copolymerizations with organic comonomers, typically with olefinic groups, could be characterized as a non-classical step-growth polymerization, where A2 homopropagation within a copolymer chain to form A–A rich segments will be accompanied by A2+B2 polymerized units (Figure 1c). Anionic polymerizations of  $S_8$  with sodium sulfide and difunctional alkyl halide monomers can proceed via classical A2+B2 step-growth condensation polymerization (with NaCl byproducts) since thiolate anions do not self-terminate.<sup>[15,16]</sup>



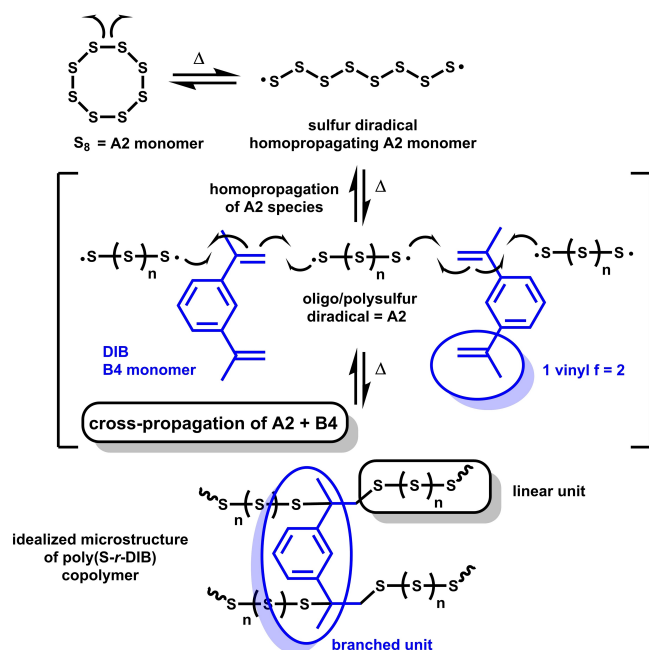
**Figure 1.** (a) Chemical scheme for both ring-opening and homolytic coupling pathways for the polymerization of  $S_8$  (b) simplified representation of classical step-growth addition polymerization of A2 + B2 monomers to form linear polymers (c) non-classical A2 + B2 step-growth polymerization with additional possibility of A2 homopropagation to form linear copolymers.

## Inverse Vulcanization: Copolymerizations in Liquid Sulfur

A breakthrough discovery in  $S_8$  polymer chemistry was the use of liquid sulfur as a bulk reaction medium and comonomer for free radical polymerizations.<sup>[17]</sup> Pyun and co-workers in 2013 developed the process termed, inverse vulcanization,<sup>[6]</sup> which enabled the bulk copolymerization of molten elemental sulfur and vinylic comonomers without the need for externally added initiator or organic solvent. The scope of monomers and polymers made via this process have been reviewed extensively elsewhere.<sup>[2–5]</sup> For the purposes of this CONCEPT mini-review, we will explicitly discuss for the first time the monomer functionality and step-growth polymerization aspects of the inverse vulcanization process as an approach to statistical copolymers, followed by the development of sulfur prepolymers to prepare  $S_8$  derived segmented copolymers.

In the first report on inverse vulcanization, 1,3-diisopropenylbenzene (DIB) was used as the organic comonomer for bulk copolymerization since this was an inexpensive monomer that was miscible with liquid sulfur, where DIB carried two vinyl moieties for reaction with dithiyl radical monomeric and oligomeric species.<sup>[6]</sup> The inverse vulcanization process is mechanistically similar to the homolytic  $S_8$  ROP, where  $S_8$  and dithiyl radical species serve as homopropagating A2 monomers to form dithiyl oligo-, or polymeric sulfur radicals species that can then react via thiol-ene addition to the vinyl groups of DIB. In classical free radical chain growth polymerization, monovinylic monomers (e.g., styrene, propylene) afford linear polymers. In this case, each vinyl moiety in DIB can be considered a difunctional B2 moiety that can react with two thiyl radical moieties per olefin. Furthermore, since DIB (and  $\alpha$ -methyl styrenics) has a low ceiling temperature during free radical polymerizations, DIB units do not homopropagate in the inverse vulcanization process, as supported by  $^1H$  and  $^{13}C$  NMR spectroscopic studies of these copolymers as noted by the absence of C–C bonds between DIB units.<sup>[6]</sup> Hence, the monomer functionality (f) for the inverse vulcanization of  $S_8$  and DIB can be described as an "A2+B4" step-growth addition polymerization, since DIB carries two vinyl groups, along with A2 homopropagation of sulfur radical containing monomers and oligomers (Figure 2). Bis-olefinic comonomers, such as divinylbenzene (DVB),<sup>[18–21]</sup> ethylidene norbornene (ENB), vinyl norbornene, (VNB) dicyclopentadiene (DCPD),<sup>[22–24]</sup> dimeric norbornadiene monomers (e.g., NBD2),<sup>[25]</sup> or diallyl disulfides<sup>[26,27]</sup> would also be considered B4 monomers when paired with  $S_8$  for inverse vulcanization.

Copolymers prepared by the inverse vulcanization process have been described as statistical copolymers with stochastic chain lengths segments of S–S bonds between sulfur-organic comonomer units, and hence has been described as a statistical copolymer (i.e., also a "random copolymer"), unlike classical A2 + B2 step-growth polymerizations which are described as homopolymers of the  $[-AA-BB-]$  repeating unit (Figure 1b). In a typical polymerization, 70:30 wt% of  $S_8$  to DIB are employed, which corresponds to molar feed ratios of 92:8 mol%, respec-



**Figure 2.** Simplified chemical scheme for the inverse vulcanization of  $S_8$  with DIB described as an A2 + B4 step-growth addition polymerization with A2 homopropagation steps to afford poly(S-r-DIB) statistical copolymers, where DIB units represent branching points in the final copolymer.

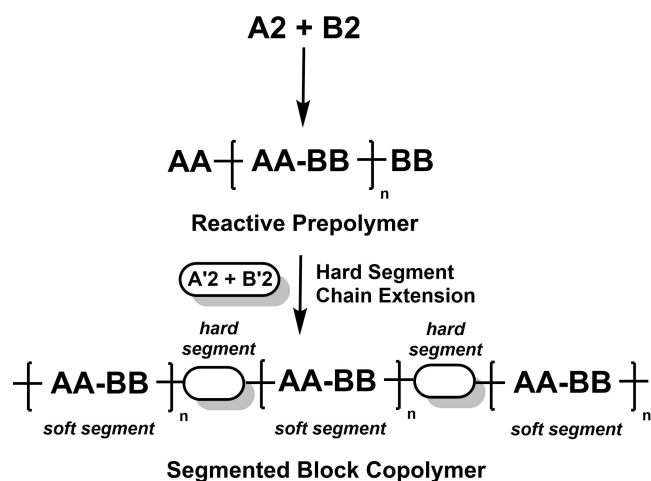
tively, to afford a statistical copolymer of poly(sulfur-*random*-(1,3-diisopropenylbenzene) (poly(S-*r*-DIB) composed of S–S units as linear fragments and S-DIB–S units as branching units, in the idealized microstructure (Figure 2). Unambiguous structural characterization of  $S_8$  derived copolymers is often challenging using standard techniques, such as,  $^1\text{H}$ , or  $^{13}\text{C}$  NMR spectroscopy due to the limited solubility of these materials with higher sulfur content.<sup>[6,9]</sup> Furthermore, these techniques do not report on the structure of sulfur catenation in the polymer backbone, or as end-groups. Unfortunately,  $^{33}\text{S}$  NMR spectroscopy is not a useful technique for structural characterization, since  $^{33}\text{S}$  nuclei have poor NMR sensitivity. Since inverse vulcanizations proceed as an addition-type step-growth reactions without byproduct formation, termination of end-functional thiyl radicals on sulfur copolymers can be presumed to undergo coupling with other thiyl radicals, or hydrogen abstraction from aliphatic moieties in the copolymer backbone.<sup>[6,28]</sup> A full survey of structural NMR characterization of inverse vulcanized polymers is in progress that details alternative microstructures for poly(S-*r*-DIB) and other widely investigated copolymers. Hence, the macromolecular architecture that is assigned as (hyper)branched polymers with some cyclic fragments formed from thiyl radical coupling.<sup>[2]</sup> Other organic comonomers for inverse vulcanization reactions based on bis-olefinic norbornenes (e.g., ethylidene norbornene, dicyclopentadiene, NBD2) are also prone to cross-propagation with thiyl radicals and hence do not homopropagate in these polymerizations, while divinylbenzenes have been proposed to undergo some homopropagation of vinylic groups to form C–C bonds in addition to thiol-ene cross-propagation reactions.<sup>[20–21]</sup>

In a general sense, high-sulfur content copolymers made by inverse vulcanization are either insoluble, or are crosslinked, although in certain cases, copolymers with higher organic content are amenable to solution characterization via NMR and SEC. Furthermore, inverse vulcanized polymers are primarily amorphous materials, or polymeric fluids with glass transitions typically below  $50^\circ\text{C}$  as increasing sulfur content tends to lower the glass transition and thermomechanical properties of these materials, although a few notable organic comonomers have been observed to afford sulfur copolymers possessing  $T_g$ 's exceeding  $100^\circ\text{C}$ .<sup>[9]</sup> While advances in the scope of monomers, nucleophilic and transition metal accelerators for inverse vulcanization have proceeded,<sup>[24,29–31]</sup> there remains a need to expand the synthetic variations and polymerization transformations with inverse vulcanization to prepare enhanced polymeric materials from  $S_8$ . These types of synthetic advances are challenging since the majority of single step inverse vulcanization processes tend to afford amorphous polymeric materials, which complicates the preparation of segmented block copolymers, or semi-crystalline (co)polymers as a route to enhance thermomechanical properties.

## Classical Prepolymer Approaches to Segmented Copolymers

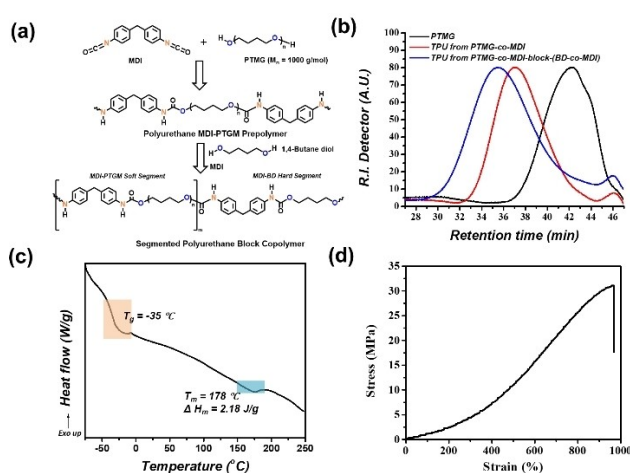
The preparation of block copolymers via step-growth polymerization classically utilizes a two-stage process for the growth of a prepolymer with reactive chains end, followed by chain extension step to link together the prepolymer units.<sup>[32]</sup> For the preparation of thermoplastic elastomeric materials, the prepolymer will comprise of flexible units to function as the “soft segment” followed by chain extension with monomers (A'2 + B'2) composed of aromatic, or hydrogen bonding moieties to introduce “hard segments” into the final copolymer.<sup>[33]</sup> Numerous variations on the prepolymer approach can be employed depending on the stoichiometric (im)balance between A2 and B2 functional groups and the desired end-group functionality (Figure 3). Furthermore, in the chain extension step to introduce hard segment units, variations have been developed using either one or two chain extending monomer(s) (e.g, B'2 only, or A2 + B'2). This type of multi-block copolymer is referred to as segmented copolymer which upon casting into solid state films forms phase separated morphologies via hydrogen bonding or crystallization of hard segments into discrete domains.

This type of design has been notably applied for the synthesis of segmented polyurethane copolymers which when properly prepared can serve as a thermoplastic elastomer (i.e., a polymer with elastomeric properties while remaining melt or solution processable vs. lightly crosslinked elastomers). A classical example of which has been the step-growth polymerization of 4,4'-methylene diphenylisocyanate (MDI) with a diol terminated oligomer of poly(tetramethylene glycol) (PTGM) ( $M_n \sim 1000$  g/mol) to grow the a PTGM-MDI prepolymer ( $M_n \sim 15,000$  g/mol) which serves as the soft segment in the final copolymer.<sup>[34,35]</sup> Chain extension of this prepolymer with both a



**Figure 3.** Simplified representation of a two-stage pre-polymer approach to segmented multi-block copolymers using classical step-growth addition polymerization of A<sub>2</sub> + B<sub>2</sub> monomers to form linear polymers.

small amount of MDI and a short diol (1,4-butanediol, BD) links together the prepolymer segments with short hard segments units of MDI-BD, that exhibit greater capacity for hydrogen bonding since the carbamate groups are more closely associated vs. when spaced farther apart as in the prepolymer of MDI with PTGM. We present an illustrative example of which was synthesized using these monomers (Figure 4a). SEC of the prepolymer ( $M_n = 14,000$ ;  $M_w/M_n = 1.2$ ) and the final segmented copolymer ( $M_n = 44,000$ ;  $M_w/M_n = 1.8$ ) confirmed a progressive increase in molar mass, confirming successful chain extension to introduce hard segment moieties (Figure 4b). The ability of these copolymers to form phase separated domains of hard and soft segments in the solid state was most easily confirmed by DSC, as noted by two thermal transitions corresponding to



**Figure 4.** (a) Synthetic scheme for two-stage prepolymer approach to segmented polyurethanes using PTGM diols and MDI diisocyanates (b) SEC in DMF of PTGM diol, prepolymer and final segmented polyurethane (c) DSC of final segmented PU (d) Stress-strain profile for tensile properties of segmented polyurethane from Figure 4(a).

the T<sub>g</sub> (−35 °C) of the PTGM-MDI soft segment, and the T<sub>m</sub> (180 °C) of the MDI-BD hard segments (Figure 4c). Ultimately, the successful synthesis of the segmented PU into a TPE was confirmed by mechanical tensile testing, which exhibited high tensile strength (30 MPa) and excellent elongation at break (1000% strain, Figure 4d).

## Segmented polyurethane copolymers from elemental sulfur

The use of elemental sulfur as a monomeric component for conventional plastics is an attractive value proposition for consuming the large volumes generating from refining, while also imparting new emergent properties into the synthetic polymeric material.<sup>[2–5]</sup> The preparation of segmented sulfur based polyurethanes derived from S<sub>8</sub> was recently demonstrated toward this target that utilized both inverse vulcanization and post-polymerization modification to prepare for the first time soluble block copolymers and thermoplastic elastomers with improved flame retardancy.<sup>[10]</sup> The synthesis of S<sub>8</sub> derived thermoplastic elastomers was of particular interest, since these materials require both precision polymer synthesis to incorporate hard and soft segments to impart high tensile strength and elasticity. The preparation of polyurethanes using S<sub>8</sub> required the synthesis of alcohol containing oligomers via the inverse vulcanization of liquid sulfur with olefinic alcohols, followed by polymerization with aromatic diisocyanate monomers, such as, MDI. This approach was initially reported by BASF in 2014<sup>[36]</sup> and by Tsutsumi et al.<sup>[37]</sup> to form sulfur-based PU networks for Li–S cathode materials. Hasell et al. reported on a similar methodology to prepare sulfur based PU thermosets that demonstrated dynamic covalent healing properties.<sup>[38]</sup> However, the synthesis of soluble, thermoplastic segmented SPUs with improved thermomechanical properties remained elusive, which recently demonstrated using a classical prepolymer approach with a final chain extension to introduce hard segment units.

The key step in the synthesis of segmented sulfur based polyurethanes (SPUs) was the engineering of the polyol to introduce both sulfur units and organic comonomers to modulate solubility of the polyol and the thermomechanical properties of the final segmented copolymer. The first step in the synthesis of sulfur derived polyols was conducted by the inverse vulcanization of 10-undecen-1-ol (UnOH) which is an inexpensive, liquid sulfur miscible monomer and enabled facile scale up of the poly(sulfur-random-(10-undecen-1-ol)) (poly(S-*r*-UnOH; M<sub>n</sub> SEC = 1,300 g/mol) in 0.5 kilogram quantities. The poly(S-*r*-UnOH) polyol possessed around 3.7–4.4 OH groups per polymer ( $f_{\text{average}} \sim 4$ ) and was observed to exhibit excellent solubility in both non-polar (toluene, tetrahydrofuran, methylene chloride) and polar (methanol, ethanol) organic media. Hence, removal of unreacted S<sub>8</sub> from the sulfur polyol was readily conducted by extraction of poly(S-*r*-UnOH) with ethanol. The OH side chain moieties were found to be readily reactive with MDI isocyanate monomers, however, SPUs made from

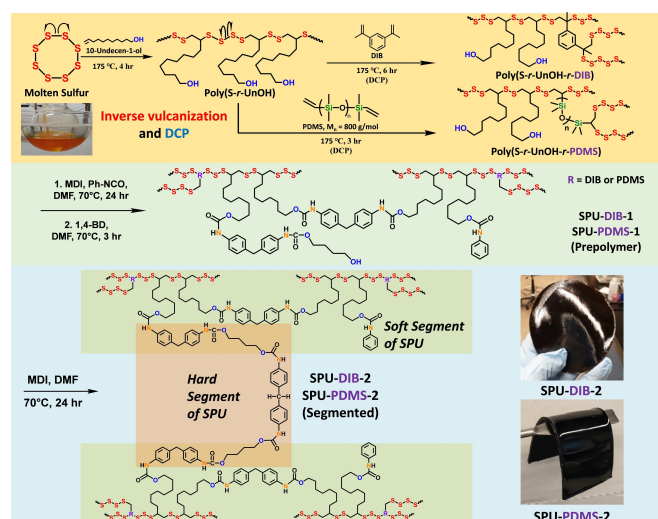
poly(*S-r*-UnOH) and MDI directly afforded low molar mass polyurethane prepolymers and segmented sulfur polyurethane due to the initial low molar mass of the poly(*S-r*-UnOH) polyol. Hence, the poly(*S-r*-UnOH) polyol was further modified accessing the dynamic covalent S–S bonds in these liquid sulfur resins to generate thiyl radicals that could add to externally added (di, or multi)vinyl comonomers, which is a process developed by Pyun et al., referred to as Dynamic Covalent Polymerization.<sup>[29]</sup> To prepare sulfur terpolyols, poly(*S-r*-UnOH) was chain extended with either 1,3-diisopropenylbenzene (DIB) or divinyl polydimethylsiloxane (PDMS,  $M_n=800$  g/mol) using DCP process with the neat materials at elevated temperature ( $T=175^\circ\text{C}$ ) to form new terpolyol materials, poly(*S-r*-UnOH-*r*-DIB) and poly(*S-r*-UnOH-*r*-PDMS)(Figure 5). This DCP step enabled the preparation of a more thermally and chemically stable higher molecular weight terpolymer to be formed which also enabled tuning of the hydrophilic/hydrophobic balance, which fortuitously enabled facile removal of unreactive oligomers by precipitation. Furthermore, the DCP step allowed for modulation of the sulfur terpolyol composition to introduce more rigid DIB units, or mechanically lossy PDMS moieties. Sulfur containing prepolymers (SPU-DIB-1, SPU-PDMS-1) were then prepared by polymerization of either sulfur terpolymer with MDI to serve as the soft segments in the final material. In the polymerization of SPU-DIB-1 with MDI, a small amount of a mono-isocyanate (Ph-NCO) was required to suppress crosslinking with MDI. The introduction of hard segment was then achieved by chain extension of either sulfur prepolymer with MDI and 1,4-butanediol (BD) was conducted to prepare the final segmented SPUs labeled as SPU-DIB-2 and SPU-PDMS-2 (Figure 5). Sulfur terpolyols, prepolymers and segmented SPUs were all soluble polymers and allowed for solution characterization by size exclusion chromatography (SEC), which demonstrated successful chain extension at each synthetic step and confirmed

preparation of the target high molar mass SPUs ( $M_w \sim 80,000$ – $100,000$  g/mol). Both differential scanning calorimetry (DSC) and atomic force microscopy (AFM) confirmed in the solid state that phase separation of hard segments was observed. Tensile testing of both segmented SPUs were conducted with the SPU-DIB-2 exhibiting thermoplastic characteristics with a high tensile strength (23 MPa) and strain induced stiffening until 348% elongation at break. Segmented SPU-PDMS-2 sample was observed to exhibit enhanced elongation at break (578% strain) and slightly lower tensile strength 13 MPa, where cycling tensile deformation to 100% strain confirmed that this material was a thermoplastic elastomer.<sup>[10]</sup> The tensile properties of these sulfur derived segmented polyurethanes were found to be slightly inferior to classical segmented thermoplastic polyurethanes based on PTGM-MDI as shown in Figure 4c, are exhibit comparable tensile strength and elasticity to related segmented polyurethanes and other elastomers.<sup>[35]</sup> This approach to  $S_8$  derived segmented copolymers was the first demonstration of soluble block copolymers from elemental sulfur, where the ductility and elasticity of these copolymers were significantly enhanced relative to existing sulfur derived copolymers.<sup>[9,10]</sup>

## Flame Retardant Properties of Sulfur Derived Polymers

Synthetic plastics are a critical class of materials in modern society due to their low cost, excellent thermomechanical properties, and wide fields of use. However, an intrinsic hazard associated with plastics is the flammability of these materials, which is exacerbated by their proximity to ignitable consumer products in residential housing, transportation, and electronic packaging. To impart flame retardancy to plastics three primary approaches have been utilized: (a) addition of flame retardant (FR) additives to conventional plastics (b) protective coatings (c) the synthesis of novel intrinsically flame-retardant polymers.<sup>[39–45]</sup> Hence, from a chemical perspective, fire mitigation strategies in materials design have been directed at designing low heat release polymers, that rapidly carbonize to self-extinguish propagating flames (i.e., intumescent FR agents)<sup>[46–49]</sup> or generate species to quench  $\text{H}^\bullet$  or  $\text{OH}^\bullet$  radicals during combustion (i.e, vapor phase chemical FR agents).<sup>[45]</sup> While the preparation of novel FR monomers and polymers mitigate many of these issues the high cost of these monomers/reagents in comparison to conventional synthetic plastics is problematic for industrial translation.<sup>[50]</sup>

The use of disulfides molecules and elemental sulfur as FR additives was posited to be an alternative FR agent for flammable polymers.<sup>[51–52]</sup> In particular, these compounds are known for their propensity to under homolytic fragmentation reactions to generate thiyl radicals, which was posited to serve as a vapor phase retardant to intercept reactive radical species. The viability of disulfide (S–S) moieties as FR agents was recently demonstrated Gu et al., in the preparation of polymers from diallyloxydiphenylsulfide with bis-maleimides, that afforded polymers with significantly reduced heat release rate (3x



**Figure 5.** (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 & dynamic covalent polymerization and prepared of segmented SPUs, SPU-DIB-2 and SPU-PDMS-2. Adapted with permission from Ref. [10]. Copyright 2021 John Wiley & Sons.

lower) relative to the disulfide-free reference polymers.<sup>[52]</sup> However, one issue with this system is the relatively high cost associated with disulfide monomers and the utilized polymerization chemistry. Hence, the use of  $S_8$  derived polymers is one potential solution to lower the cost of new flame retardant polymers, where the presence of S–S bonds in the polymer backbone will likely exhibit vapor phase FR properties.

Segmented SPUs derived from  $S_8$  were also found to exhibit flame retardancy in the UL-94 vertical flame test in comparison to sulfur-free, classical segmented thermoplastic elastomer polyurethanes which were readily flammable.<sup>[10]</sup> In the UL-94 flame test, a 12×1.3 cm strip of the polymer is fabricated via solution processing, ignited over a bed of cotton and timed for self-extinguishment. If the material rapidly self-extinguishes after a 2nd re-ignition and does not ignite the underlying cotton bed, a “V0” rating is observed which indicates flame retardancy.<sup>[45]</sup> UL-94 flame tests with classical segmented thermoplastic elastomeric polyurethanes (TPU) based on PTGM-MDI as shown in Figure 4 were found to completely burn in air within 50 seconds (Figure 6a), while the SPU-DIB-2 segmented copolymer rapidly extinguished within 1-second both in the initial and 2nd (re)ignition. Microcombustion calorimetry (MCC)<sup>[45]</sup> was conducted on small scale samples of the TPU and SPU-DIB-2 segmented copolymers to quantify differences in heat release upon combustion. The segmented sulfur based polyurethane with approximately 20-wt% sulfur in the copolymer exhibited a nearly 50% reduction in heat release capacity (351 J/g·K) relative to the control PTGM-MDI TPU sample, and higher char yield (Figure 6c). Slightly reduced total heat release for the SPU-DIB-2 (23.1 kJ/g) were also observed relative to the TPU control material. These initially findings were surprising, given how elemental sulfur is deemed highly flammable, but nevertheless confirmed that the incorporation of elemental sulfur imparted improved FR properties to polyurethane materials, which still retaining respectable thermomechanical properties. Future work points to the potential of enhancement

of FR properties by optimization of sulfur composition and  $T_g/T_m$  of the resulting polymers.

## Conclusion

Recent interest in the use of elemental sulfur as a monomer and reaction medium for polymer chemistry has spurred new developments in copolymerization processes using  $S_8$ , particular by the inverse vulcanization and dynamic covalent polymerization processes. In this mini-review, we discuss the fundamental polymerization aspects of the classical ROP of  $S_8$  and the inverse vulcanization process as means to prepare high sulfur content statistical copolymers. We define the monomer functionality in these processes as a homopropagating A2 polymerization for the ROP of  $S_8$  and a homopropagation A2 + B4 step-growth processes, where diene comonomers are defined as B4 monomers. Approaches to prepare sulfur prepolymers and segmented block copolymers using post-polymerization processes are then discussed in a fundamental context to explain recent efforts to prepare sulfur derived segmented copolymers. Synthetic methods to prepare segmented copolymers from elemental sulfur access to novel materials with improved thermomechanical and flame retardant properties, which are discussed in this report. These collective findings point to an exciting realm of possibilities for novel polymeric materials derived from sulfur as low cost, high performance plastics and elastomers with emerging promise for green chemistries.<sup>[53]</sup>

## Acknowledgements

We gratefully acknowledge the NSF (DMR-1607971, CHE-1807395, CHE-1920234, PFI-1940492), the RII Research Advancement Grant program, the College of Science from the University of Arizona, TRIF/University of Arizona, the AFOSR Phase II STTR Contract (FA9550-17-C-005), ENI s.P.A. and ExxonMobil for support of this work.

## Conflict of Interest

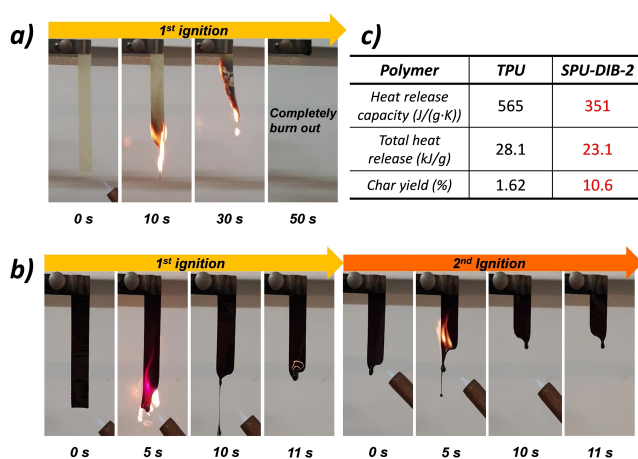
The authors declare no conflict of interest.

## Data Availability Statement

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

**Keywords:** elemental sulfur · flame retardants · inverse vulcanization · ring-opening polymerization · segmented polyurethanes

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**Figure 6.** Flame retardancy testing of (a) PTGM-MDI control TPU which was observed to completely burn and (b) SPU-DIB-2 sample which rapidly self-extinguished affording a V0 rating in the UL-94 V vertical flame test. Adapted with permission from Ref. [10]. Copyright 2021 John Wiley & Sons.

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Manuscript received: January 13, 2022

Accepted manuscript online: March 31, 2022

Version of record online: May 12, 2022