Chalcogenide Hybrid Inorganic/Organic Polymer Resins: Amine Functional Prepolymers From Elemental Sulfur

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Dedicated to Professor Krzysztof Matyjaszewski on the occasion of his 70th birthday

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INTRODUCTION The concept of utilizing elemental sulfur (S_8) as an alternative feedstock for the synthesis of polymeric materials has been widely explored in the past decade.[1–3] Polymeric materials derived from the polymerization of elemental sulfur constitute an intriguing new class of sulfur-containing polymers and polysulfides, which have been referred to as chalcogenide hybrid inorganic/organic polymers (CHIPs).[4–12] One of the most widely used methods for preparing CHIPs has been the use of the *inverse vulcanization* process,[2–7,10,12] where liquid sulfur is employed as the solvent and monomer in a homolytic ring-opening copolymerization with organic comonomers. As the original report on the inverse vulcanization process used styrenic comonomers, this methodology has been expanded to a wide number of other organic comonomers, which include naturally occurring unsaturated compounds, benzoxazines, norbornenes, and a wide host of vinylic comonomers.[3,11,13] More recently, variations on the inverse vulcanization process have been developed to enable a wider range of comonomers to be utilized at lower reaction temperatures. Examples of these processes include *dynamic covalent polymerizations*[7,14] and accelerated,[10,12] or "catalytic"[15] inverse vulcanization processes.

Despite these numerous advances, a major challenge in this growing field is the introduction of useful and reactive functional groups into these materials to enable post-polymerization modifications, transformations to step-growth polymers and crosslinking to form thermosets. The introduction of orthogonal reactive moieties as side chain groups into CHIPs has been reported, as demonstrated by the inclusion of electropolymerizable thiophenes,[16] or alcohol groups[17] for post-polymerization modification. We recently demonstrated that amine functional CHIPs could be prepared by the inverse vulcanization of sulfur with 4-vinylaniline,[10] where the aniline moieties could be directly carried into the polymer without the need for protecting group chemistry. These amine functional CHIPs were then capable of post-polymerization modifications through reactions with acid chlorides and isocyanates. This report demonstrated the viability of using aniline-based units to prepare functional CHIPs; however, the high cost of the 4-vinylaniline comonomer limited the utility of this approach.

Herein, we report on a new chemical reaction to prepare reactive CHIPs resins via the unexpected reaction of liquid sulfur, or low glass-transition temperature (T_g) CHIPs (e.g., poly[sulfur-random-styrene], poly(S-r-Sty)) with 1,3-*meta*-phenylenediamine (PDA) to form amine functional prepolymers via a proposed electrophilic aromatic substitution mechanism. These oligomeric products carry the free aryl amine groups into the material and enable post-polymerization modifications with other reactive comonomers. In the current report, we report on the reaction of sulfur with PDA as well as demonstrate dynamic covalent polymerization (DCP) between poly(S-*r*-Sty) and PDA to afford an oligomeric product with improved solubility/miscibility with a wider range of organic solvents and comonomers. Using this approach, we report for the first time on using CHIP resins to prepare epoxide networks via the

Additional supporting information may be found in the online version of this article.

reaction of amine functional prepolymers with polyhedral oligomeric silsesquioxanes (POSS) functional epoxide comonomers.

RESULTS AND DISCUSSION

The central rationale for this report was the surprising reactivity of S_8 with 1,3-phenylenediamine in a single step to afford amine functional oligomeric products (S-PDA, Fig. 1). PDA was found to be miscible in liquid sulfur and rapidly reacted with liquid sulfur to afford an orange, glassy product that was soluble in organic solvents, such as tetrahydrofuran (THF), acetone. THF-size exclusion chromatography (SEC) of this material confirmed the formation of oligomeric sulfur products (M_n = 688 g/mol; M_w/M_n = 1.48), while ^{1}H NMR spectroscopy confirmed the incorporation of aromatic units to the amine functional sulfur oligomer (see Supporting Information Fig. S1).

The amine groups on PDA both nucleophilically activate S_8 to form reactive sulfobetaine intermediates and electronically activate the aromatic ring for electrophilic aromatic substitution (S_EAr). This reaction proceeded under optimal conditions without the need for protecting groups on the free amines as indicated by ^{1}H NMR spectroscopy (Supporting Information Fig. S1). The substitution reaction of sulfur on the aromatic rings of 1,3-phenylenediamine (Fig. 1) is a remarkable and unexpected finding in the organosulfur literature and has not been explored (to our knowledge) as a new polymer forming reaction.

While the exact mechanism for this polymerization is still being investigated, we propose a partial mechanism for the creation of C—S bonds via base-induced electrophilic aromatic substitution processes. The activated sulfur species formed in this reaction [Fig. 2(B)] is especially interesting because the sulfur directly bonded to the positively charged nitrogen may be electrophilic and capable of affecting electrophilic aromatic substitution on highly activated aromatic rings such as PDA. Such enhancements of electrophilic character by Lewis bases in organic synthesis have been reviewed.[18] Activation of elemental sulfur for aromatic substitutions and polymerizations is unprecedented and provides a new opportunity for inverse vulcanization. While this would represent a new reaction for elemental sulfur, previous, similar mechanisms have been proposed in the literature for the formation of electropositive sulfur bound to nitrogen, which subsequently activates the sulfur toward alkylation followed by cleavage of the S—N bond affording new RS+ species [Fig. 2(A)].

In this work, we propose that a similar activation mechanism makes sulfur sufficiently electropositive to undergo nucleophilic attack by the highly activated PDA comonomer/nucleophile either via an intramolecular (shown) or intermolecular (not shown) reaction pathway; re-aromatization is proposed to proceed via deprotonation from the ring opened thiolate species [Fig. 2(B)]. A second equivalent of PDA could then attack the linear polysulfane liberating —SH (a known leaving group), which would also act as the base required to re-aromatize the second PDA ring, affording the proposed oligomer shown in Figure 2 (B), as well as explain the evolution of H_2S observed during the course of this reaction. Products from this reaction were only low-molecular-weight species as noted by SEC but despite this, definitive interpretation of the NMR spectra could not be made

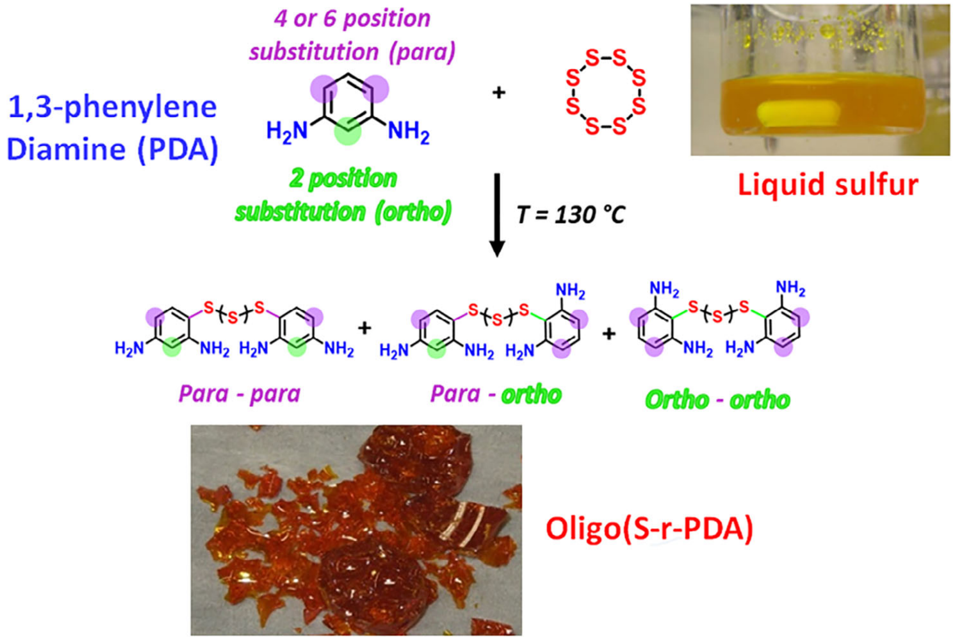

FIGURE 1 Synthetic scheme for the reaction of liquid sulfur with 1,3-phenylenediamine to form amine functional oligomers (S-*r*-PDA). The three bonding motifs shown for the product oligomers are the three most likely species observed via size exclusion chromatography, with further additions of sulfur chains at the highlighted positions leading to broader molecular weight distributions and contribute to the structural heterogeneity of the mixture which complicated the NMR analysis [Color figure can be viewed at wileyonlinelibrary.com]

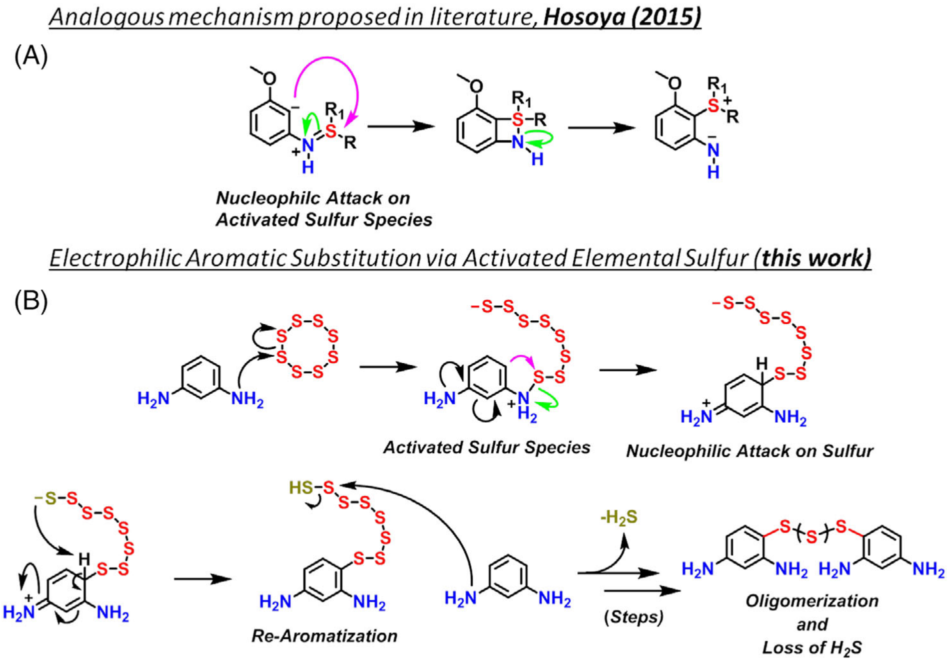

FIGURE 2 (A) Mechanism for precedence of electrophilic activation of sulfur via sulfilimine (modified from ref. 21 and (B) proposed mechanism for amine activation of elemental sulfur and the subsequent electrophilic aromatic substation reaction that produces S_n—1,3-PDA oligomers [Color figure can be viewed at wileyonlinelibrary.com]

due to the complexity of the spectra [Supporting Information Fig. S1(a)]. This was directly attributed to the vast number of possible products with similar molecular weights (Fig. 1) that can be formed from this reaction, which include mixtures of varying molar mass, sulfur rank and dangling thiol functionality. The chemistry of this process is akin to the condensation of phenolic and formaldehyde to form Bakelite, or Novolac resins,[19] where the polymer forming reaction is also an electrophilic aromatic substitution process that affords a wide distribution of possible products. The fact that high-molecular-weight species were not observed indicated that the reactivity of the aryl ring decreases upon the first addition of sulfur comonomer and that this new reaction would be dependent on electronic and resonance effects with regards to forming C—S bonds. It is important to note that model reactions of liquid sulfur and aniline did not proceed under these conditions (see Supporting Information), which supported an intra-molecular group-assisted electrophilic aromatic substitution mechanism as proposed in Figure 2(a). To investigate this effect further and attempt to elucidate the connectivity of the oligomeric products, model compound studies with small molecules were developed and characterized.

Toward this end, diphenyl disulfide replaced elemental sulfur as the electrophilic species with the idea that discrete adducts could be isolated and characterized. Furthermore, a 1:1 mole ratio of PDA to diphenyl disulfide was chosen in order to elucidate any differences in reactivity that might arise as a consequence of steric or electronic effect on the ring at any one of the three activated positions (Fig. 3), as well as if reactivity of the nucleophilic ring was affected by the addition of the first electrophile. This reaction was conducted by heating PDA and diphenyl disulfide in a vial with stirring at 150°C for 3 days; products from the reaction were purified and isolated by SiO_2—gel column chromatography. The major product from this reaction was the 4-position mono-sulfide adduct along with trace amounts of the 2-position mono-substituted and di-substituted addition product, which were confirmed by ^1H NMR spectroscopy, mass spectrometry (MS), and X-ray crystallography after isolation by column chromatography (see Supporting Information). These model reactions revealed that the first addition of S units to the PDA efficiently proceeded and essentially stopped at the mono-adduct as noted by the very low yields of the di-substituted product. In the absence of steric or electronic considerations, one would expect a

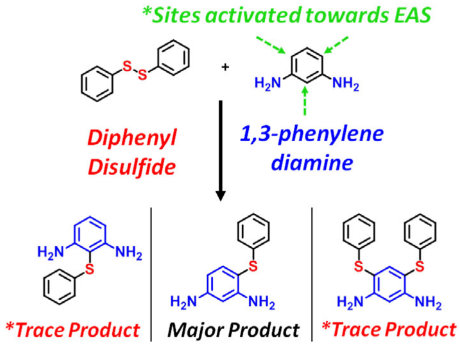

FIGURE 3 Model compound study used to investigate microstructure and reactivity of the electrophilic aromatic substitution reaction between elemental sulfur and PDA [Color figure can be viewed at wileyonlinelibrary.com]

statistical distribution of products for the various mono-, di-, and tri-substituted isomers; however, the sterically congested 2-position on the ring might explain why only trace amounts of product with the thiophenol moiety at that position was observed. Most importantly, it would appear that the addition of one thiophenol moiety dramatically reduced the activity of the ring toward further additions as only trace amounts of the di-substituted product were observed from this model reaction. This study provided chemical insights into the formation of the low-molecular-weight oligomers observed in the direct copolymerization of S_8 and PDA, because the polymerization processes were essentially terminated after the first addition of S-units to the PDA comonomer.

Both the S_EAr of S_8 and diphenyl disulfide reactions demonstrated an unexpected and potentially useful reaction for polymer synthesis. This S_EAr chemistry of PDA was also found to be applicable to pre-made CHIPs such as poly(sulfur-*random*-styrene) (poly(S-*r*-Sty)). Poly(S-*r*-Sty) (found 63 wt % S, 37 wt % Sty) was a low T_g copolymer (T_g = 0–2°C), we previously made via inverse vulcanization that exhibited improved miscibility with organic reagents and comonomers. Furthermore, the dynamic covalent S—S bonds in poly(S-*r*-Sty) could be thermally activated to form reactive sulfur radicals for post-polymerization modifications via a process termed *dynamic covalent polymerization*. We found that PDA (30 wt % initial loading) could also be directly added and reacted with molten poly(S-*r*-Sty) at T = 130–150°C to form amine functional sulfur oligomers. ^{1}H NMR spectroscopy of this product most readily confirmed the incorporation of PDA units as noted by the appearance of a well-resolved broad singlet at δ = 5.9–6.1 ppm, which corresponded to the protons d', d'' at **2** and **4** positions from the PDA units, while the proton d at the **5** position on PDA groups was overlapped with the aromatic protons from the styrenic units in the poly(S-*r*-Sty) resin (Fig. 4). SEC (Supporting Information Fig. S3) and elemental analysis (Supporting Information Table S2) confirmed that oligomeric products were formed (M_n = 768 g/mol; M_w/M_n = 1.46). These PDA-terminated poly(S-*r*-Sty) oligomeric prepolymers exhibited excellent solubility in organic solvents such as THF, dichloromethane, and acetone and were found to be miscible with a wide range of organic comonomers.

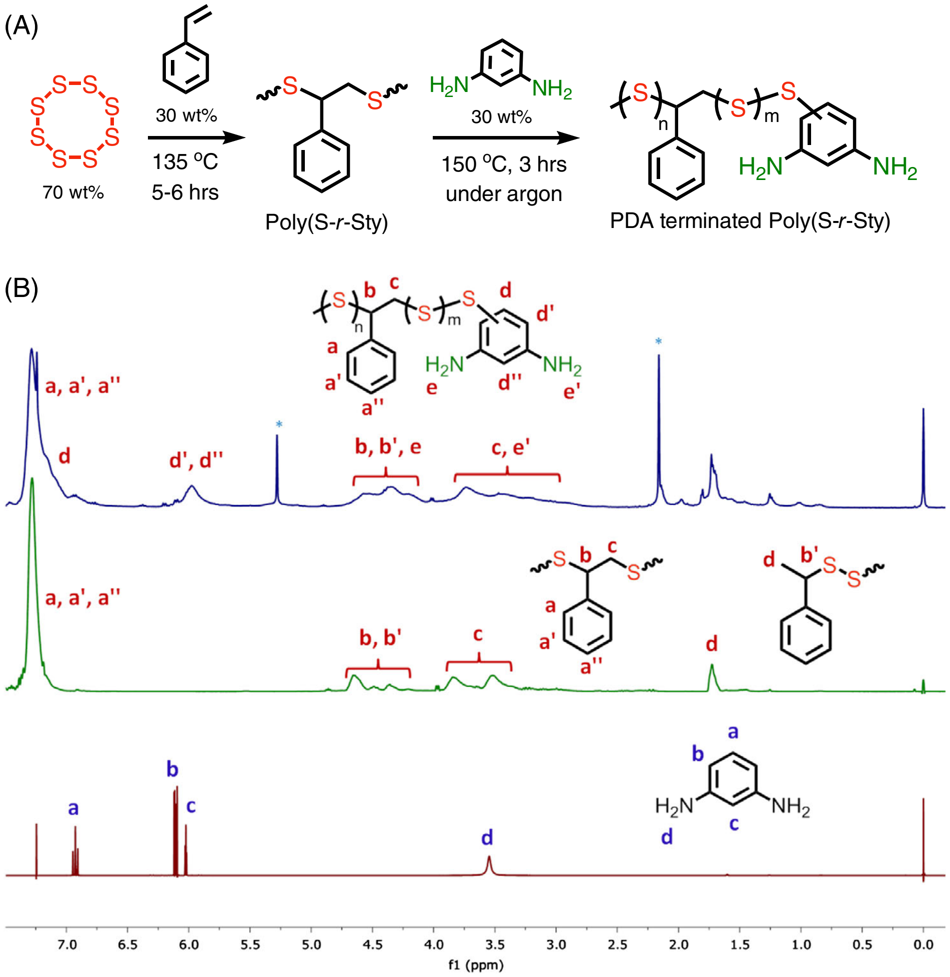

FIGURE 4 (A) Synthetic scheme for the preparation of PDA-terminated poly(S-*r*-Sty) terpolymer and (B) ^{1}H NMR spectra of PDA, poly(S-*r*-Sty), and PDA-terminated poly(S-*r*-Sty) in $CDCl_3$. * Solvent impurities [Color figure can be viewed at wileyonlinelibrary.com]

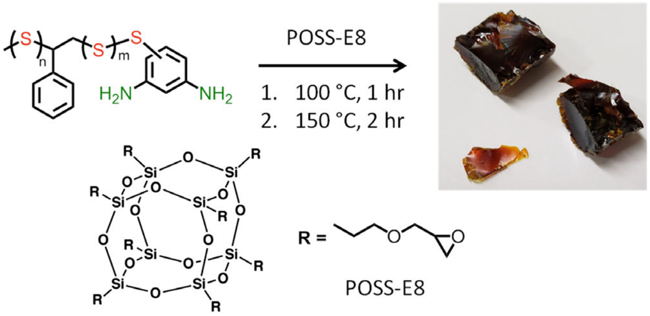

FIGURE 5 Reaction of PDA-terminated poly(S-*r*-Sty) prepolymer with glycidyl-POSS (ca. 15–20 wt % S in the final material) [Color figure can be viewed at wileyonlinelibrary.com]

Elemental analysis revealed that the total content of amines in the prepolymer calculated from % N was found to be 4.7 mmol —NH_2/g with 30 wt % initial PDA loading. We propose that the primary microstructure from this reaction afforded PDA fragments at the chain end(s) of the prepolymer via preferred mono-substitution of the PDA unit. This would afford primarily linear prepolymers with predominantly mono, or telechelic prepolymers bearing PDA end groups. These proposed microstructures are further supported by the model study findings of sulfur with diphenyldisulfide, which indicated that mono-substitution products are almost exclusively formed with negligible yields of di-substituted units. This microstructure is further supported by the elemental analysis of the PDA terminated poly(S-*r*-Sty) prepolymers with increasing PDA feed ratios (see Supporting Information Table S2).

Finally, with synthetic access to free amine functional PDA-terminated poly(S-*r*-Sty) resins, we demonstrated the ability to use these as reactive prepolymers for post-polymerization modifications with epoxides. Initial model reactions were conducted with PDA-terminated poly(S-*r*-Sty) resins (0.10 g, 0.47 mmol —NH_2) with benzyl glycidyl ether (15 μL, 0.2 mmol epoxides) in the melt at elevated temperature (T = 150°C) for an hour (Supporting Information Scheme S4) and the reaction between amine functional groups with epoxides was confirmed by ^{1}H NMR and IR spectroscopies of the soluble products (see Supporting Information Figs. S7 and S8). To demonstrate this concept of using amine functional sulfur prepolymers, PDA-terminated poly(S-*r*-Sty) (ca. 37 wt % S, 38 wt % Sty, 25% PDA) was reacted with a multifunctional epoxy comonomers as a route to form thermosetting networks. In this, a polyhedral oligomeric silsesquioxane compound containing eight glycidyl (epoxy) groups on each corner (POSS-E8) was chosen as a crosslinking agent, because this compound was multifunctional and miscible with the amine functional sulfur prepolymer. POSS-based polymers have historically been utilized to enhance the thermal properties of certain polymeric materials. POSS-based monomers were recently applied to inverse vulcanization processes in copolymerization with elemental sulfur to form novel organic/inorganic hybrid polymers.[20] In this post-polymerization reaction, PDA-terminated poly(S-*r*-Sty) prepolymer (ca. 37 wt % S) was first homogenously mixed in the melt with POSS-E8 (0.10 g, 0.075 mmol) at 100°C which, after 30–60 min, yielded a homogeneous, red, viscous mixture (Supporting Information Fig. S4). The temperature was then increased to 150 °C and the reaction was continued for additional 2 h in order to fully cure the epoxy network (ca. 15–20 wt % S in the final crosslinked sulfur polymers) (Fig. 5).

DSC analyses of the prepolymer resins and the final epoxy network were conducted to confirm efficiently crosslinking between amine functional sulfur prepolymers and epoxies occurred [Fig. 6(A)]. The initial poly(S-*r*-Sty) resin before reaction with PDA was observed to possess a low glass transition (T_g = 1°C), which was observed to increase over 30°C after reaction with PDA to form the prepolymer (T_g = 35°C) as determined by differential scanning calorimetry (DSC). Finally, after curing with POSS-E8, a new broad glass transition was observed ($T_g \sim 43$°C), which was consistent with the network formation. Furthermore, the red glassy materials were observed to be completely insoluble in organic solvents, such as THF, acetone or CH_2Cl_2, which were observed to be good solvents for the precursor materials. Thermogravimetric

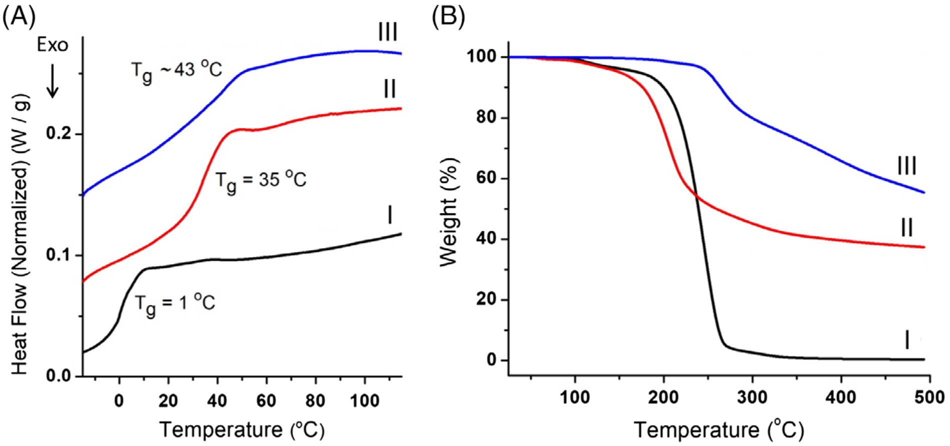

FIGURE 6 DSC thermograms (A) and TGA curves (B) of poly(S-*r*-Sty), PDA-terminated poly(S-*r*-Sty), and PDA-terminated poly(S-*r*-Sty) cured with POSS-E8 [Color figure can be viewed at wileyonlinelibrary.com]

analysis (TGA) of these materials also confirmed changes in thermal stability after each reaction, as noted by the dramatic differences in weight loss thermograms of poly(S-*r*-Sty) versus PDA-terminated poly(S-*r*-Sty) (95% total mass loss for poly(S-*r*-Sty) at 267°C versus 57% mass loss for prepolymer. These were directly attributed to the presence of longer chain S—S bonds in the poly(S-r-Sty) resin, which lead to lower onsets of decomposition temperatures. The final crosslinked material from terpolymer and POSS-E8 did not undergo any thermal degradation up to 240°C with a final mass loss of less than 50% [Fig. 6(B)] which was attributed to the incorporation of the oligosiloxane-POSS moieties.

In conclusion, we report on a new chemical reaction with 1,3-phenylene diamine (PDA) with either elemental sulfur, or poly(S-*r*-Sty) to form amine functional sulfur prepolymers for post-polymerization processes with epoxies. To the best of our knowledge, this is the first example of using sulfur as the electrophilic substrate for electrophilic aromatic substitution reactions with an electron-rich arene to form these types of reactive oligomers. Due to the low cost of PDA and this process, this new approach provides an attractive alternative route to prepare aniline and aromatic amine functional sulfur polymers. We demonstrate for the first time the ability to use these materials as prepolymer resins for crosslinking of epoxies, with appreciable sulfur utilization content (15–20 wt % S in final material). These materials constitute a new class of reactive CHIP prepolymers resins, which we demonstrate are viable for use in step-growth polymerizations.

EXPERIMENTAL

General Procedure for Synthesis of Poly(S-*r*-Sty) Copolymer

To a 20 mL scintillation vial, elemental sulfur (7.0 g, 0.0273 mol) was added with a ½ inch Teflon-coated stir bar, and the flask was heated to 135°C. Uninhibited/purified styrene (3.0 g, 0.0288 mol) was added to molten sulfur dropwise. Then, the polymerization was run for 6 h at 135°C. The yellow/orange color polymer was dissolved in uninhibited (BHT-free) THF. The crude product was purified via silica column chromatography. All volatiles were removed under reduced pressure and the polymer was dried at high vacuum overnight (7.0–7.3 g, yield ca. 70%, conversion of styrene: > 99%, conversion of sulfur: ca. 60%).

General Procedure for Synthesis of PDA-Terminated Poly(S-*r*-Sty) Prepolymer

A 3-dram vial was loaded with purified poly(S-*r*-Sty) (0.70 g, 70:30 wt %), sublimed PDA (0.30 g, 2.77 mmol), and a Teflon-coated micro stir bar. The vial was sealed with a rubber septum and the sealed vial was vacuumed for 10 min and backfilled with argon total three times. The vial was placed in a pre-heated oil bath at 150°C and the reaction was run for 3 h. The resulting terpolymer was purified using the method discussed in the Supporting Information (60–70% yield).

General Procedure for Prepolymer—Glycidyl-POSS Reactions

A 3-dram vial was loaded with PDA-terminated poly(S-*r*-Sty) prepolymer (0.10 g), glycidyl-POSS (0.10 g, 0.075 mmol) and a Teflon-coated micro stir bar. The vial was placed in a pre-heated oil bath at 100°C and the reaction was run for 1 h. Then, the vial was placed in an oil bath at 150°C for additional 2 h.

Detailed procedures were shown in the Supporting Information.

CONFLICTS OF INTEREST

The authors declare the following competing financial interest(s): JP declares an actual or potential financial conflict of interest and is co-founder/equity holder in Innovative Energetics, a licensee of University of Arizona (UA) intellectual property. This relationship has been disclosed to the UA Institutional Review Committee and is managed by a Financial Conflict of Interest Management Plan.

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