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Functional Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) via Inverse Vulcanization of Elemental Sulfur and Vinylanilines

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Functionalized Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) via Inverse Vulcanization of Elemental Sulfur and Vinylanilines

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In this report, a new class of functional chalcogenide hybrid inorganic/organic polymers (CHIPs) bearing free aryl amine groups that are amenable to post-polymerization modifications were synthesized. These functional CHIPs were synthesized via the inverse vulcanization of elemental sulfur with 4-vinylaniline without the need for functional group protection of amines. This polymer is the first example of a polysulfide or CHIPs material to carry a useful primary amine functional group which can be successfully post functionalized with acid chlorides and isocyanates to improve the mechanical properties.

Sustainable chemical processes from naturally occurring and industrial waste materials have attracted increased attention due to growing environmental awareness. Sulfur is the thirteenth most abundant element in the earth's crust and is mined in its elemental form but also produced as a by-product of petroleum refining; together, these two sources of sulfur account for the approximately 70 million tons of sulfur is produced annually.[1] As demanding as all these applications combined might be, they actually consume only about 90% of the elemental sulfur that is generated as a by-product in other industrial processes, which is over 60 million tons per year.[2] Consequently, there is still an enormous excess of elemental sulfur, which is problematic and costly in terms of storage. However, utilizing surplus sulfur as an in expensive feed stock to be smartly exploited toward novel industrial applications is a convenient way to address the problem.[3, 4]

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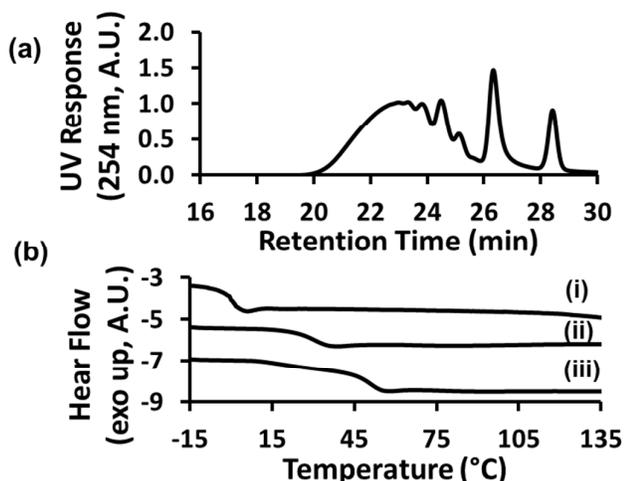
Figure 1. (a) SEC analysis for poly(S-*r*-VA) (Mn = 1038 g/mol. Mw/Mn = 1.4) (b) DSC analysis of of poly (S-*r*-Sty) and poly(S-*r*-VA) with (i) 30 wt% Sty (T$_g$ = 0.9 °C) (ii) 30 wt% VA (T$_g$ = 31 °C) and (iii) 50 wt% VA (T$_g$ = 50 °C)

In 2013, Pyun and *co-*workers developed a new process, termed, *inverse vulcanization*, which enabled the direct copolymerization of molten elemental sulfur with vinylic comonomers. The *inverse vulcanization* process has more recently been extended into a wider class of organic comonomers, which now include styrenes,[5-8] alkynes,[9-11] naturally occurring/commercial olefins,[12-14] allylics,[15]
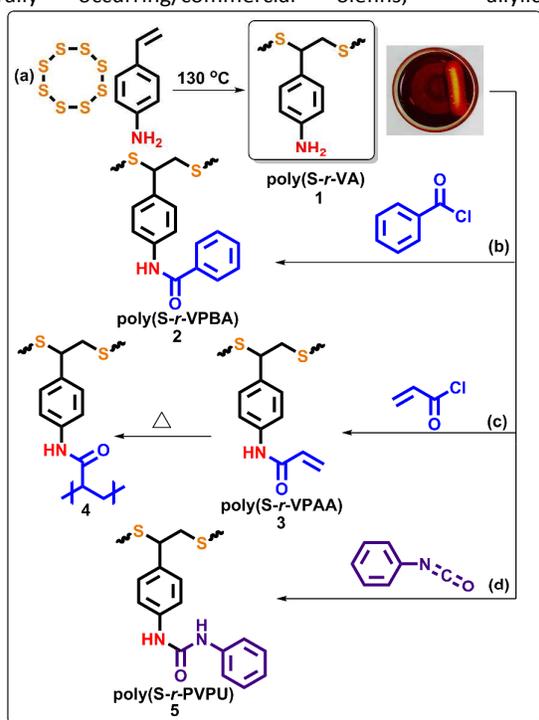
Scheme 1. Inverse vulcanization of sulfur and 4-vinylaniline and post polymerization functionalization of poly(sulfur-*random*-vinylaniline)

oleyamine,[16] aliphatic amines,[11, 17] allyl ethers,[18] maleimide,[19] nitriles [20] and benzoxazines.[21, 22] Furthermore, a number of different sulfur containing polymers have recently been prepared that use elemental sulfur as a key starting material. [11, 17] The sulfur copolymers generated from this approach, namely poly(sulfur-*random*-(1,3-diisopropenyl benzene)) (poly(S-*r*-DIB)), have also generated interest as a novel class of polysulfides with both intriguing electrochemical and optical properties.[23-25] High sulfur content materials are among a unique class of chalcogenide hybrid organic/inorganic polymers (CHIPs)[26] that are macromolecular analogs to amorphous chalcogenide glasses. However, due to the poor miscibility of elemental sulfur, the comonomers for inverse vulcanization are limited to high boiling point, relatively nonpolar molecules which makes it challenging to carry useful functional groups to sulfur materials and tune the properties by post polymerization modification. One notable exception has been our work with thiophene functional CHIPs from ProDOT Sty, which were used to improve the electrical properties of these insulating materials.[5]

Herein, we report on an amine functionalized CHIPs poly(sulfur-*random*-vinylaniline) (poly(S-*r*-VA)) synthesized via inverse vulcanization process with elemental sulfur and 4-vinylaniline. Functional CHIPs from this process were prepared where the retention of free amine groups in the sulfur copolymer was confirmed by IR and NMR spectroscopy. The aniline sites in Poly(S-*r*-VA) copolymers were further available for post-polymerization functionalization with a variety of acid
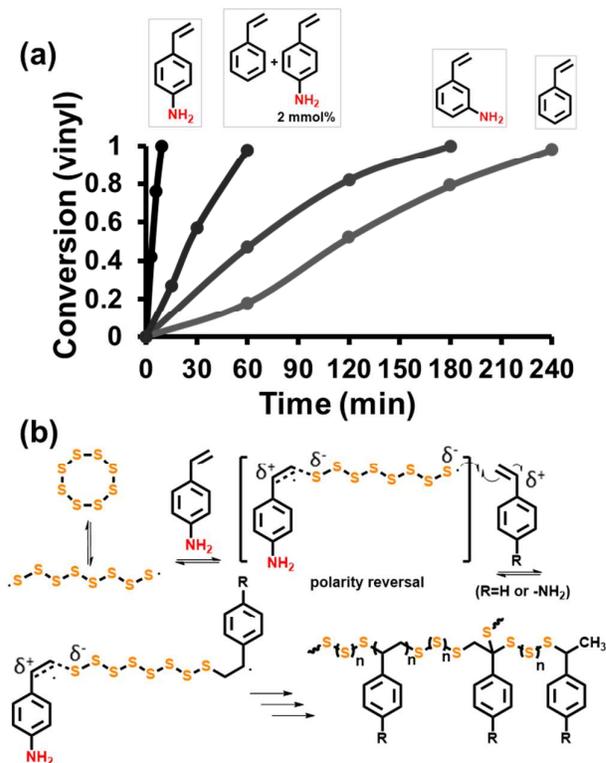
Figure 2. (a) kinetic study of sulfur-vinylaniline copolymerization (b) proposed mechanism for vinylaniline-sulfur activation

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chlorides and isocyanates (Scheme 1).

The poly(sulfur-*r*-4-vinylaniline) (poly(S-*r*-VA)) copolymer was synthesized by the inverse vulcanization method wherein sulfur was heated above its melting points (T_m = 108-120 °C) to 130 °C followed by the addition of 4-vinylaniline to the liquid sulfur phase in a dropwise fashion. The reaction mixture vitrified rapidly to form a red, transparent glass (Fig. 1). It is worth noting that the evolution of hydrogen sulfide (H_2S) was not observed under these conditions as confirmed by purging the reaction mixture throughout the polymerization with argon into $Pb(Ac)_2$ aqueous solution, which affords lead sulfide precipitates in the presence of H_2S. Monomer conversions of 4-vinylaniline and S_8, were determined using a combination of ^{1}H NMR spectroscopy and silica gel based chromatography. ^{1}H NMR spectroscopy of these reaction mixtures confirmed the complete consumption of 4-vinylaniline and size exclusion chromatography (SEC) analysis showed the product of this reaction was oligomeric in nature (M_n = 1038 g/mol, M_w/M_n=1.4) (Fig. 1). The residual sulfur could be removed from the poly(S-*r*-VA) copolymer via silica gel column chromatography with hexanes followed by THF to elute the polymer (61% yield for 70 wt% S feed ratio). The DSC analysis of these materials confirmed the formation of true copolymers as noted by a single glass transition temperature (Tg) for poly(S-*r*-VA) (T_g = 30-50 °C for copolymers of 30-50 wt% pVA) which was significantly higher than poly(S-*r*-Sty) copolymers of comparable composition due to the amine group in the polymer backbone and the Tg increased with higher feed ratio of organic comonomer 4-vinylaniline (Fig. 1b).

The copolymerization of sulfur and 4-vinylanilne were observed to proceed with a dramatic increase in rate, based on the consumption of vinyl peaks in the ^{1}H NMR spectrum, compared with sulfur-styrene inverse vulcanization reactions. We have conducted kinetic studies for a series of sulfur copolymerizations at 130 °C with 70 wt% sulfur feed ratios on a 0.5 g reaction scale. The conversion of vinyl monomers was determined by ^{1}H NMR spectroscopy of aliquots removed from the reaction mixture at different time points while the sulfur conversion is determined gravimetrically from the residual sulfur isolated from flash chromatography. For the copolymerization of sulfur with styrene, styrene was consumed after 4 h while 62 % sulfur was consumed at this point. In contrast, the copolymerization of sulfur and 4-viynlaniline only took 9 min to achieve full conversion of 4-vinylaniline and comparable conversion of sulfur which suggested a different, more efficient polymerization mechanism that emerges when aryl amines are present in comparison to classical inverse vulcanization reactions with styrene or DIB.

The polar effects[27] in the addition reaction of free radicals to carbon-carbon double bonds have been studied with Hammett-type linear free-energy treatments. In those studies, the rate constants for the addition reactions of the benzenethiyl radicals to styrene and α-methylstyrene have been determined and higher rate constants were observed for the reaction of benzenethiyl radicals with styrenes with electron donating functional groups on the aromatic rings.

This rate enhancement could be interpreted by the polar nature of the transition state in the free-radical addition reaction and the electron donating groups, in this case $-NH_2$, increase the rate of reaction by contribution of the polar resonance structures in the transition state (Fig. 2b). This mechanism also accounts for the dramatic rate enhancement of styrene in the presence of only 2 mol% 4-VA in which 4-VA promotes reaction of styrene (see Fig. 2b R=H), and explains why the rate enhancement for 3-VA is not as significant, owing to the inability of 3-VA isomer (see Fig. 2a) to contribute to the polar resonance structure.

The retention of $-NH_2$ groups after the copolymerization in poly(S-*r*-VA) copolymers was confirmed by IR and ^{1}H NMR spectroscopy. In the IR spectroscopy, poly(S-*r*-VA) shows the primary amine N-H stretch from 3200~3500 cm^{-1} (Fig. S1). The ^{1}H NMR spectrum in DMSO shows a broad peak at 5.2~5.4 ppm and this broad peak was absent after adding 2% D_2O due to proton exchange (Fig. S2). This is the first example of synthesizing a sulfur polymer carrying unique functional groups which can be used for post polymerization modification. Earlier literature reported the reaction of sulfur compounds activated by amine compounds[28, 29] thus it is surprising to find that stable copolymers were formed via the reaction of sulfur and 4-vinylanilne and the possible reason could be that the aniline group is not as nucleophilic as aliphatic primary amine. The stability of the copolymer was tested by heating poly(S-*r*-VA) with elemental sulfur and in dichlorobenzene solution at 120 °C for 24 h and the SEC analysis for the product after heat treatment proved that the copolymer did not decompose through the reaction of sulfur and amine group (Fig. S3).

We also for the first time demonstrated the post polymerization modification of sulfur copolymer via the reaction of amine groups to tune the mechanical properties (Scheme 1). For example, poly(sulfur-*random*-1-phenyl-3-(4-vinylphenyl) urea) (poly(S-*r*-PVPU)) was synthesized with poly(S-*r*-VA) and isocyanatobenzene in THF solution at room
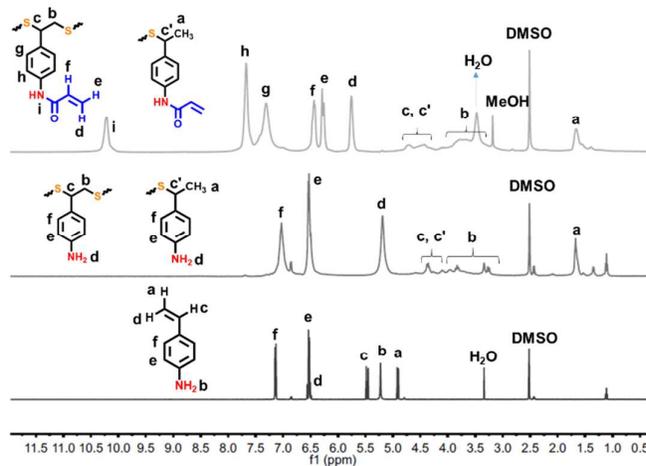
Figure 3. 1H NMR for 4-vinylaniline (bottom), poly(S-*r*-VA) (middle) and poly(S-*r*-VPAA) (top)

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temperature and isolated by precipitation in cold methanol. ^{1}H NMR (Fig. S5) confirmed the formation of (poly(S-*r*-PVPU)) and the SEC (Fig. S6) analysis shows comparable molecular weight of poly(S-*r*-PVPU) (M_n = 1349 g/mol, M_w/M_n = 1.4) with poly(S-*r*-VA).

The amine group could also be functionalized by amidation with acid chlorides. The model amidation reaction of poly(S-*r*-VA) was developed with benzoyl chloride. Poly(sulfur-*random*-(4-vinyl phenyl)benzamide) (poly(S-*r*-VPBA)) was synthesized with poly(S-*r*-VA) and benzoyl chloride in THF at 0 °C with K_2CO_3 as the proton sponge. ^{1}H NMR spectrum confirmed the formation of poly(S-*r*-VPBA) and SEC analysis (Fig. S4) shows comparable molecular weight of sulfur copolymer before (M_n = 1038 g/mol, M_w/M_n = 1.4) and after amidation (M_n = 1348 g/mol, M_w/M_n = 1.3), which suggested the sulfur backbone was intact during the amidation reaction.

Under the same reaction conditions, acryloyl chloride was used to synthesize a sulfur copolymer with crosslinkable acrylic groups. The ^{1}H NMR spectrum of poly(sulfur-*random*-(4-vinylphenyl) acrylamide) (poly(S-*r*-VPAA) is shown in Fig. 4. The absence of the broad peak at 5.2~5.4ppm suggested the consumption of -NH_2 group. The broad peaks at 5.75, 6.29 and 6.44 ppm represent the vinyl protons in the acrylic groups and the broad peak at 10.21 ppm corresponds to the amide proton.

The mechanical properties of this material could be improved by thermally crosslinking the acrylic groups. At above 110 °C, the S-S bonds become thermally activated and undergo homolytic cleavage resulting in reaction with the vinyl bonds in the acrylamide side chains analogous to the dynamic covalent polymerization (DCP) mechanism we have reported on previously,[30] which precludes the homopolymerization of the acrylamide groups and does not result in a thermoset material. Thus the crosslinking reaction was conducted at a lower temperature to prevent the DCP process and promote crosslinking. When poly(S-*r*-PVAA) was heated to 100 °C and the dynamic shear properties were followed at a frequency of 1.0 s^{-1} and a strain amplitude of 3.0 %, the moduli crossing (i.e. the storage modulus becomes larger than the loss) was observed. This indicated the crosslinking ultimately resulted in

and formation of a gel according to ASTM Standard D4473-08 (Fig. 4). One could also plot inverse of the complex viscosity as a function of time, as shown in the inset, demonstrating another obeservation of a gel when the viscosity tends to infinity. Both techniques clearly show gelation and the formation of sulfur polymer networks due to crosslinking.

Conclusions

We demonstrate the synthesis of new functional CHIPs of poly(sulfur-*random*-vinylaniline) (poly(S-*r*-VA)) by the inverse vulcanization of elemental sulfur and 4-vinylaniline. A rapid rate enhancement in the copolymerization process to occur as a consequence of the amine groups on the styrenic comonomer. Furthemore, the free aniline groups can be carried into the sulfur copolymer without undesirable nucleophilic degradation of the S-S bonds in the backbone. This polymer is the first example of sulfur material proved to carry a useful primary amine functional group which can be successfully post functionalized with acid chlorides, isocyanates to improve the mechanical properties.

Notes

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.

Figure 4. Time dependent dynamic shear properties of poly(S-*r*-VPAA) at 100 °C

Notes and references

1 W. J. Chung, A. G. Simmonds, J. J. Griebel, E. T. Kim, H. S. Suh, I.-B. Shim, R. S. Glass, D. A. Loy, P. Theato, Y.-E. Sung, K. Char and J. Pyun, *Angew. Chem. Int. Ed.*, 2011, **50**, 11409-11412.
2 J. J. Griebel, G. X. Li, R. S. Glass, K. Char and J. Pyun, *J Polym Sci Pol Chem*, 2015, **53**, 173-177.
3 J. Lim, J. Pyun and K. Char, *Angew. Chem. Int. Ed.*, 2015, **54**, 3249-3258.
4 J. J. Griebel, R. S. Glass, K. Char and J. Pyun, *Prog. Polym. Sci.*, 2016, **58**, 90-125.
5 P. T. Dirlam, A. G. Simmonds, R. C. Shallcross, K. J. Arrington, W. J. Chung, J. J. Griebel, L. J. Hill, R. S. Glass, K. Char and J. Pyun, *ACS Macro. Lett.*, 2015, **4**, 111-114.

6 I. Gomez, D. Mecerreyes, J. A. Blazquez, O. Leonet, H. Ben Youcef, C. Li, J. L. Gómez-Cámer, O. Bondarchuk and L. Rodriguez-Martinez, *J. Power Sources*, 2016, **329**, 72-78.

7 T. R. Martin, K. A. Mazzio, H. W. Hillhouse and C. K. Luscombe, *Chem. Commun.*, 2015, **51**, 11244-11247.

8 Y. Zhang, J. J. Griebel, P. T. Dirlam, N. A. Nguyen, R. S. Glass, M. E. Mackay, K. Char and J. Pyun, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 107-116.

9 P. T. Dirlam, A. G. Simmonds, T. S. Kleine, N. A. Nguyen, L. E. Anderson, A. O. Klever, A. Florian, P. J. Costanzo, P. Theato, M. E. Mackay, R. S. Glass, K. Char and J. Pyun, *RSC Adv.*, 2015, **5**, 24718-24722.

10 Z. Sun, M. Xiao, S. Wang, D. Han, S. Song, G. Chen and Y. Meng, *J. Mater. Chem. A*, 2014, **2**, 9280-9286.

11 W. Li, X. Wu, Z. Zhao, A. Qin, R. Hu and B. Z. Tang, *Macromolecules*, 2015, **48**, 7747-7754.

12 M. P. Crockett, A. M. Evans, M. J. H. Worthington, I. S. Albuquerque, A. D. Slattery, C. T. Gibson, J. A. Campbell, D. A. Lewis, G. J. L. Bernardes and J. M. Chalker, *Angew. Chem. Int. Ed.*, 2016, **55**, 1714-1718.

13 A. Hoefling, Y. J. Lee and P. Theato, *Macromol. Chem. Phys.*, 2017, **218**, 1600303-n/a.

14 I. Gomez, O. Leonet, J. A. Blazquez and D. Mecerreyes, *ChemSusChem*, 2016, **9**, 3419-3425.

15 B. Oschmann, J. Park, C. Kim, K. Char, Y.-E. Sung and R. Zentel, *Chem. Mater.*, 2015, **27**, 7011-7017.

16 E. T. Kim, W. J. Chung, J. Lim, P. Johe, R. S. Glass, J. Pyun and K. Char, *Polym. Chem.*, 2014, **5**, 3617-3623.

17 Z. Sun, H. Huang, L. Li, L. Liu and Y. Chen, *Macromolecules*, 2017, **50**, 8505-8511.

18 A. Hoefling, D. T. Nguyen, Y. J. Lee, S.-W. Song and P. Theato, *Materials Chemistry Frontiers*, 2017, **1**, 1818-1822.

19 M. Arslan, B. Kiskan, E. C. Cengiz, R. Demir-Cakan and Y. Yagci, *Eur. Polym. J.*, 2016, **80**, 70-77.

20 S. N. Talapaneni, T. H. Hwang, S. H. Je, O. Buyukcakir, J. W. Choi and A. Coskun, *Angew. Chem. Int. Ed.*, 2016, **55**, 3106-3111.

21 M. Arslan, B. Kiskan and Y. Yagci, *Macromolecules (Washington, DC, United States)*, 2016, **49**, 767-773.

22 S. Shukla, A. Ghosh, P. K. Roy, S. Mitra and B. Lochab, *Polymer*, 2016, **99**, 349-357.

23 A. G. Simmonds, J. J. Griebel, J. Park, K. R. Kim, W. J. Chung, V. P. Oleshko, J. Kim, E. T. Kim, R. S. Glass, C. L. Soles, Y.-E. Sung, K. Char and J. Pyun, *ACS Macro. Lett.*, 2014, **3**, 229-232.

24 J. J. Griebel, S. Namnabat, E. T. Kim, R. Himmelhuber, D. H. Moronta, W. J. Chung, A. G. Simmonds, K.-J. Kim, J. van der Laan, N. A. Nguyen, E. L. Dereniak, M. E. Mackay, K. Char, R. S. Glass, R. A. Norwood and J. Pyun, *Adv. Mater.*, 2014, **26**, 3014-3018.

25 S. Zhuo, S. Huang, C. Liu, H. Wang and B. Zhang, *Chem. Commun.*, 2014, **50**, 11208-11210.

26 L. E. Anderson, T. S. Kleine, Y. Zhang, D. D. Phan, S. Namnabat, E. A. LaVilla, K. M. Konopka, L. Ruiz Diaz, M. S. Manchester, J. Schwiegerling, R. S. Glass, M. E. Mackay, K. Char, R. A. Norwood and J. Pyun, *ACS Macro. Lett.*, 2017, DOI: 10.1021/acsmacrolett.7b00225, 500-504.

27 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 1701-1703.

28 K. Mori and Y. Nakamura, *The Journal of Organic Chemistry*, 1971, **36**, 3041-3042.

29 T. B. Nguyen, *Adv. Synth. Catal.*, 2017, **359**, 1066-1130.

30 Y. Zhang, K. M. Konopka, R. S. Glass, K. Char and J. Pyun, *Polym. Chem.*, 2017, **8**, 5167-5173.

The first example of sulfur copolymer with amine groups poly(sulfur-*random*-vinylaniline) was synthesized and successfully post-functionalized to improve the thermomechanical properties of these materials