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Article

Utilizing Reclaimed Petroleum Waste to Synthesize Water-Soluble Polysulfides for Selective Heavy Metal Binding and Detection

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Cite This: ACS Appl. Polym. Mater. 2022, 4, 1110−1116

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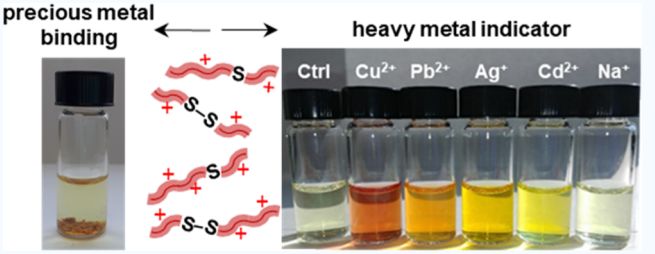
ABSTRACT: Many industrial processes produce waste with toxic and precious metal pollutants. Current remediation strategies lack the selectivity needed to effectively eliminate heavy metals. Thus, materials are needed to effectively treat waste streams and contaminated waterways. Sulfur is well known for its ability to selectively bind heavy metals. Additionally, excess sulfur is produced on large scales during petroleum refinement making it inexpensive and abundant. Inverse vulcanization enables surplus sulfur to be repurposed into high sulfur content materials without the need for solvents. These polysulfides have demonstrated many beneficial applications including heavy metal binding. However, they are plagued by low solubility and dominated by hydrophobic monomers. Here, elemental sulfur and charged monomers, including diallyl dimethylammonium chloride (DADMAC), were combined for the first time in a one-step reaction forming water-soluble polysulfides. The water solubility allows for complete interaction of dissolved metal ions with the polymer, rather than surface-level interaction as is the case for traditional inverse vulcanized polymers. Additionally, the charged polysulfides exhibit enhanced solubility in organic solvents, making solution-based characterization such as NMR more accurate. Poly(S-DADMAC) has demonstrated selective binding to gold and silver inducing the formation of a macromolecular complex that precipitates from solution. Additionally, these polymers interact with other heavy metals including lead and copper demonstrating a visible color change at low concentrations that may be used to detect the presence of these metals in wastewater. The low cost, ease of preparation, and scalability make these polysulfides practical as well as functional.



KEYWORDS: *inverse vulcanization, sulfur, heavy metal binding, lead detection, selective gold removal, charged polymer, water-soluble polymer*

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INTRODUCTION

Heavy metals occur naturally as ores, but most heavy metal accumulation in the environment is from anthropogenic sources, such as mining, metal plating, surface finishing, and power production.[1−5] Because heavy metals cannot be broken down or degraded naturally in the environment, waste streams are highly regulated to limit the threat to aquatic ecosystems and human health.[4,6,7] Currently, chemical precipitation and adsorption by activated carbon filters are two of the most common wastewater treatment methods. Each of these methods is hindered by the lack of selectivity leading to rapid clogging of carbon filters and the generation of large quantities of sludge that must undergo further treatment.[7−9] Therefore, selective, cost-effective materials are needed to treat those waste streams before the water is released into the environment.

Elemental sulfur (S_8) is known to have a high affinity for heavy metals, but limited solubility and processability make it challenging to use in metal-binding systems.[10−12] Additionally, S_8 is produced on vast scales during petroleum refinement, leading to the annual production of ∼70 billion kg of sulfur byproduct.[13] Although there are a variety of industrial uses, still ∼7 million tons of excess sulfur is produced annually.[14] Inverse vulcanization offers an efficient, solvent-free path to turn this reclaimed S_8 into functional polysulfides.[14] Cross-linking polymeric sulfur with a monomer adds stability and processability, allowing sulfur to be crafted into useable materials.[14] Because sulfur acts as the solvent, initiator, and monomer, these reactions retain high atom economy utilizing a variety of green chemistry principles.[15] Previously, inverse vulcanization has been carried out on the ton scale, with a recent report showing that 500 kg of one product is produced commercially.[16,17] This class of polymers typically vary from 20 to 90% sulfur content.[10] Because inverse vulcanized polymers (IVPs) increase the workability of sulfur while retaining its metal binding ability, they offer an inexpensive, scalable strategy for the remediation of industrial waste streams.

Received: November 4, 2021
Accepted: December 28, 2021
Published: January 15, 2022

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https://doi.org/10.1021/acsapm.1c01536
ACS Appl. Polym. Mater. 2022, 4, 1110−1116

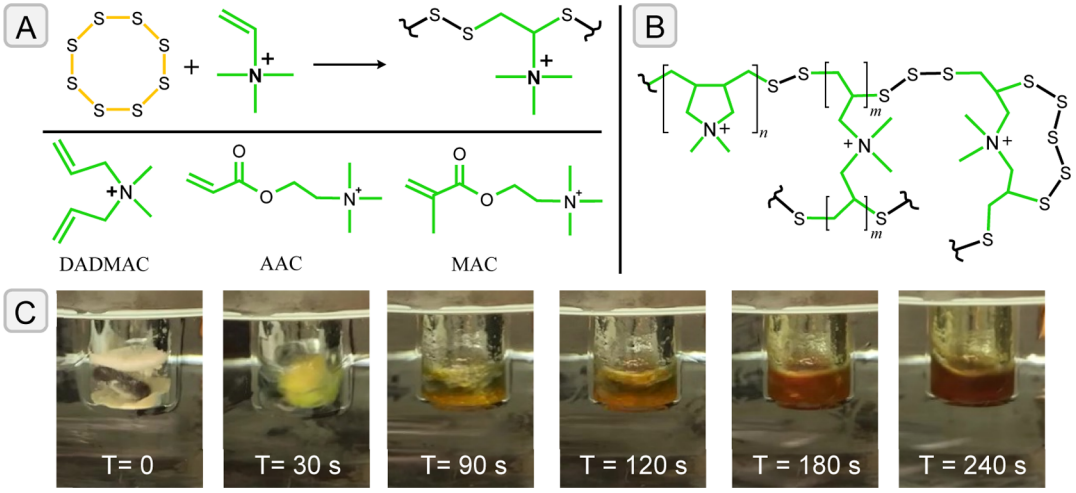

Figure 1. (A) General reaction of S_8 with trimethylammonium-containing monomers (top) and the monomers used to form polysulfides (bottom). (B) Possible structures formed by DADMAC. Chloride counterions have been removed for clarity. (C) Reaction of aqueous DADMAC with S_8 over time. Monomer solution transitions from immiscible with S_8 to fully miscible as water evaporates during the reaction progression yielding poly(S-DADMAC).

Although many IVPs have been used in metal binding, most focus on the removal of mercury whereas a few others demonstrate binding to Au, Pd, and Fe.[10−12,18−29] However, limited binding is observed for polymers formed by typical IV methods. To create more available metal binding sites, various methods to increase the surface area of IVPs have been investigated. Higher porosity has been obtained through the use of supercritical CO_2,[12] the production of CO_2 in situ,[22] the incorporation of NaCl during synthesis,[18,20,25,30] carbonization,[26,31] and electrospinning.[19,27] All of these processes increased the polymer surface area, which led to increased metal uptake when compared to the unaltered polymers.[12,18,19,26] Further details on how altering the surface area can specifically impact mercury binding have been expanded upon elsewhere.[17] Without a highly porous material, these polymers, have very limited interactions with water and the metal ions dissolved within.

Typical IVPs demonstrate limited solubility in most organic solvents and are absolutely insoluble in water.[14,15,30,32] Currently, the only published method to create a water-soluble IVP uses a solvent-based synthesis and requires a multiday post-polymerization process.[33] Here, IVPs with enhanced solubility were created by using charged monomers in a one-step, solvent-free synthesis. These charged polysulfides exhibit enhanced solubility in both water and organic solvents, making solution-based characterization more representative of the material as a whole. The development of water-soluble polymers enabled them to interact fully with aqueous metal ions rather than relying solely on surface interactions. These materials selectively bind precious metals causing them to precipitate from solution for easy removal. These polymers offer both chemical coagulation and flocculation by providing specific chemical interactions and a physical support, thus improving selectivity and limiting additional waste production. Furthermore, these IVPs exhibit a visible color change in the presence of heavy metal ions such as lead demonstrating their utility as inexpensive detectors.

RESULTS AND DISCUSSION

Synthesis and Characterization. Polysulfides formed by inverse vulcanization often demonstrate limited solubility, especially in water due to their high sulfur content and the common use of hydrophobic monomers. In order to improve solubility, charged monomers were combined with S_8 (Figure 1A) and subjected to inverse vulcanization. The high temperature requirements of this process led to the selection of commercially available charged monomers with boiling points above 160 °C including diallyl dimethylammonium chloride (DADMAC), [2-(acryloyloxy)ethyl]-trimethylammonium chloride (AAC), and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MAC). Additionally, all three of these monomers have been used to form cationic flocculants.[34,35]

Elemental sulfur was combined with aqueous solutions of AAC, MAC, and DADMAC at 160 °C for 6 h. Despite the hydrophobicity of sulfur, each of the cationic monomers became miscible with sulfur over time enabling successful polymerization (Figure 1C). All three resulted in the formation of products with very low viscosities, indicating low molecular weights. When characterized by ^{1}H NMR all showed incomplete polymerization. To ensure that the presence of water was not affecting the synthesis, a hole was drilled into the cap to allow the water to boil off during the reaction. This resulted in thicker, tacky polymers throughout the entire reaction vessel. The complete reaction was confirmed using ^{1}H NMR by the disappearance of alkene peaks between 5 and 6 ppm and the formation of new HC−C and HC−S bonds with peaks at 1−2 and 3.5−4.5 ppm, respectively (Figures S1−S3). A clear decrease in allyl peaks and increase in sp^3 C−H and C−C stretching was observed by IR spectroscopy (Figure S4). Because inverse vulcanization is often conducted at 185 °C, polymerizations at this higher temperature were also conducted resulting in materials that were much harder and all experienced ∼10% decrease in water solubility. Thus, 160 °C was chosen as the final reaction temperature.

Thin layer chromatography in conjunction with differential scanning calorimetry (DSC) was performed to determine if all of the sulfur present had reacted. Both results showed that in lower sulfur content polymers (20−60% sulfur) there was typically no unreacted sulfur (Figures S5 and S6). This is likely because there was ample monomer to stabilize the sulfur contained in these polymers. However, in materials made with

https://doi.org/10.1021/acsapm.1c01536
ACS Appl. Polym. Mater. 2022, 4, 1110−1116

70% S, elemental sulfur was more commonly detected. This was frequently reported in the literature and can be attributed to either very long polysulfide loops present in the structure of the polymer or more likely unreacted sulfur.[36−38] DSC was also used to determine the glass transition temperature (T_g) of these materials. Poly(S-DADMAC) exhibited a T_g of −18, −9, and −2 °C at 30, 50, and 70% sulfur, respectively (Figure S6).

Gel permeation chromatography (GPC) was performed to determine the molecular weight of the polymers. Normally, IVPs are not very soluble in most organic solvents, making GPC difficult but these soluble polymers allow for a more complete picture of the materials. Polymers were synthesized containing 20−70% S to determine the impact of the S/monomer ratio. Analysis revealed that the sulfur content had little influence on the molecular weight (Figure S9 and Table S1). Generally, these polysulfides had low molecular weights ranging from 1000 to 1500 g mol^{-1}, making them more like oligomers. These values were on the lower end of previously published values for inverse vulcanization, which typically ranges from 800 to 8000 g mol^{-1}.[10,14,39] However, the charged nature of these monomers and presence of sulfur loops may limit the accuracy of the results. For poly(S-DADMAC) and poly(S-MAC), the GPC traces were monomodal as expected. However, poly(S-AAC) tended to have a bimodal trace, indicating that portions of the poly(S-AAC) reacted to create a higher molecular weight than the rest of the polymer. All of the polymers reported here have an extremely low polydispersity index (PDI) of less than 1.14, especially compared to previously reported IVPs that typically have PDIs between 2.5 and 3, which is representative of polymers of non-uniform chain length. It is possible that the exceptionally low PDIs reported here are due to the lower molecular weights rather than demonstrating a more controlled polymerization.

Solubility. One major limitation of many IVPs is their insolubility in most solvents. The lack of polymer solubility makes it difficult to fully characterize the material. Some efforts have successfully improved polysulfide solubility in organic solvents.[32,33,40−42] Nevertheless, complete water solubility remains elusive without a multistep modification.[18,33] Poly(S-AAC), poly(S-MAC), and poly(S-DADMAC) all exhibit improved water solubility when compared to typical IVPs, such as poly(S-DVB) (Figure 2). Originally, nearly all monomers used consisted of nonpolar hydrocarbons, with a few exceptions.[15] These monomers contributed no added polarity to the overall polymer structure, so the lack of solubility in most polar solvents is to be expected. Since then, many polar monomers have been utilized, which improve solubility in organic solvents, yet there is no evidence of dissolution in water.[23,43] By incorporating a charged monomer into the polymer structure, a drastic increase in water solubility was achieved. Additionally, poly(S-AAC), poly(S-MAC), and poly(S-DADMAC) exhibit enhanced solubility in most other organic solvents as well (Figure S7). This is beneficial because it can make liquid-based characterizations such as ^{1}H NMR and GPC easier.

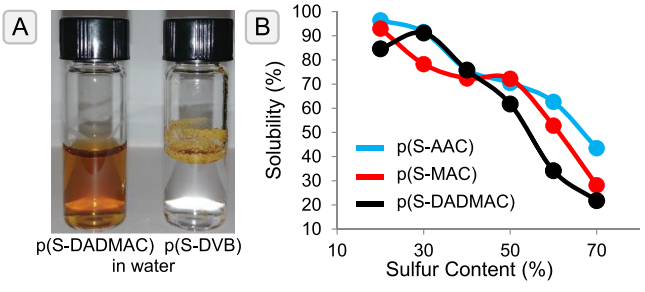

Figure 2. (A) Image of poly(S-DADMAC) and poly(S-DVB) in water. (B) Quantified solubility of poly(S-AAC) (blue), poly(S-MAC) (red), and poly(S-DADMAC) (black).

AAC and MAC are both monofunctional, so it was expected that they would have higher solubility due to their linear or branched structures rather than cross-linked. It was surprising then that the difunctional DADMAC monomer produces a polymer with similar solubility to poly(S-AAC) and poly(S-MAC) at low sulfur contents. This suggests that despite the difunctional nature, the DADMAC monomer is producing a branched structure that contains polysulfide loops as has been suggested in the literature or forms a 5-membered ring (Figure 1B).[13,14,35,44] However, its solubility began to drop off more sharply above 50% sulfur content (Figure 2B). This was anticipated due to the increased sulfur overwhelming the decreased charge of the polymer. Poly(S-AAC) and poly(S-MAC) also experience this drop off to a lesser extent, likely because the branched structure was being maintained even with the increase in sulfur content. Even the highest sulfur content polymers made with the charged monomers demonstrate increased solubility when compared to poly(S-DVB), which is insoluble in water regardless of the sulfur content. Slightly improved solubility was observed when the polymers are made on a larger reaction scale (>5 g) with poly(S-DADMAC) obtaining a maximum solubility of 93% with 30% S and maintaining 28% solubility at 70% S.

Metal Binding. Most materials synthesized by inverse vulcanization suffer from limited surface area available for metal binding. Others have approached this by fabricating materials using methods that vastly increase the surface area.[12,18,19,26,31] Additional studies have shown that increasing the hydrophilicity of the organic cross-linkers improves polysulfide mercury sorbents for ionic mercury such as $HgCl_2$.[17] By creating water-soluble polysulfides, the entire material can interact with aqueous metal ions more effectively overcoming any surface area limitations. Due to the low molecular weight of these materials, we hypothesized that these polysulfides would be able to function as flocculants. Upon binding of heavy metal ions to sulfur atoms in the polymer, multiple polymer strands come together, increasing the effective molecular weight and forcing it to precipitate. Poly(S-DADMAC) was used for metal binding analysis due to the low cost and more widespread use of the monomer. 50% sulfur was chosen to provide a balance between the sulfur content and solubility.

Qualitative studies were conducted by combining a variety of metal salt solutions with the polymer solution. Upon the addition of heavy metal ions, a precipitate was formed (Figure S8). The combined polymer−metal solution had a pH = 3. This pH does not change over time as the polymer precipitates from solution. The most noteworthy precipitation appeared for Au^{3+}, Ag^{+}, Pb^{2+}, and Cd^{2+}. All of these ions have demonstrated an affinity for sulfur-containing materials.[30,45] Sodium and calcium were used as controls and did not produce any precipitate helping confirm that the polymer was not simply precipitating due to solution saturation. These samples were subjected to quantitative analysis by atomic absorption spectroscopy. Poly(S-DADMAC) demonstrated the highest affinity for gold and silver with binding capacities of 602 and

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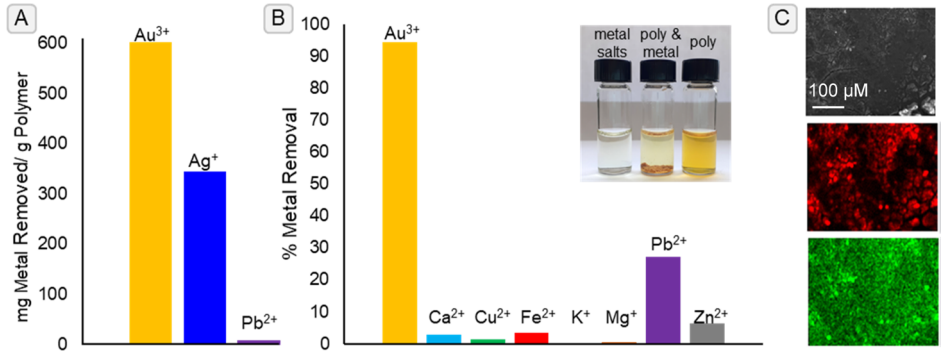

Figure 3. Analysis of metal removal by poly(S-DADMAC). (A) Maximum adsorption capacities for Au^{3+}, Ag^{+}, and Pb^{2+} in mg metal per gram poly(S-DADMAC). (B) Percent metals removed from a complex metal ion solution and the image of precipitate formation. (C) Scanning electron microscopy and EDS analysis of the precipitate from (B). EDS maps indicate the presence of sulfur (red) and gold (green).

344 mg/g polymer, respectively (Figure 3A). Only 3.57 mg metal/g polymer was removed for cadmium and less than 0.3 mg K^{+}/g polymer was removed. The removal of Na^{+} could not be quantified due to interference from the polymer solution. Gold(III) adsorbents have been reported with maximum binding capacities from ∼40 to 3260 mg/g adsorbent with most systems obtaining less than 900 mg/adsorbent.[23,26,45,46] However, unlike the polysulfides formed here, many of the successful adsorbents require multistep or complex syntheses and require the use of organic solvents.

To examine the selectivity, poly(S-DADMAC) was added to a solution containing 200 ppm of a variety of common, precious, and heavy metal ions. Even in this complex solution, 94% of the gold ions were removed (Figure 3B). There was nearly 30% removal of lead ions as well, but less than 5% removal of common ions such as calcium, copper, and iron that are commonly found in water. Because gold is a soft acid and sulfur is a soft base that has demonstrated high affinity for other soft acids such as Hg^{2+} and Pd^{2+},[10,17] it is likely that this is the driving force for the selective removal of gold. Others have used density functional theory to study the interactions between hydrogen sulfide and precious metals and found the strongest bonds were formed between sulfur and Au.[47] However, due to removal by precipitation and filtration, additional factors may also be a factor. Energy dispersive X-ray spectroscopy (EDS) was used to analyze the precipitate from the complex metal solution (Figure 3C). EDS mapping shows co-localization between sulfur from the polymer and the gold from the solution confirming the removal of gold by poly(S-DADMAC).

In an attempt to determine the molecular weight of the precipitates, GPC was performed on the sediment formed by the addition of heavy metal ions. Upon addition of the GPC solvent, the sodium-containing sediment immediately went into solution, indicating that this was likely an undissolved polymer. No change in the molecular weight was observed. However, the gold-, silver-, and lead-containing precipitates were completely insoluble. During sample preparation for analysis, the insoluble particulates were filtered out of the testable solution, so no quantitative data was obtained. However, the drastic decrease in solubility indicates that there was likely an increase in the molecular weight and/or cross-linking of the polymer that was removed from solution.

Exchanging the chloride counterion present in poly(S-DADMAC) for nitrate, led to a substantial decrease in solubility. However, the exchange created a visible color change in response to the addition of a variety of metal ions (Figure 4). There is a distinct red shift in the absorption

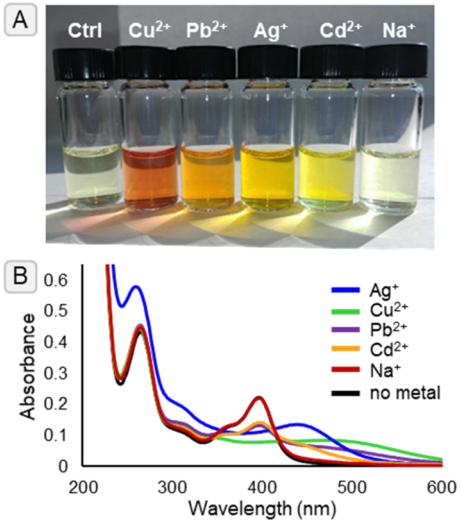

Figure 4. (A) Image of poly(S-DADMAN) with the addition of a variety of metals. (B) Corresponding UV−vis spectrum of the polymer−metal ion solutions.

spectrum for cadmium and copper(II). Although there is no peak shift for silver and lead, there is an increase in the baseline from approximately 415 to 510 and 560 nm, respectively, which corresponds to a visible color change. Transition metal ions with sulfide ligands are known to have ligand-to-metal charge-transfer bands in the visible region. This is likely the cause of the dramatic colors observed here.[48,49] The increased baseline absorption is often caused by the particulates in solution. In this case, that could be caused by the binding of sulfur within the polysulfide to the heavy metals. Each of these changes occurs in the visible range making poly(S-DADMAN) a potential sensor for specific metal ions.

Due to widespread concern of lead contamination in drinking water, having an inexpensive and simple method for detecting lead would be especially beneficial. A range of lead contents from 0 to 160 ppm were added to poly(S-DADM) with a chloride counterion (Figure 5A) and a nitrate counterion (Figure 5B,C). When the polymer with the chloride counterion is used, an obvious color change is observed beginning at 20 ppm. Lower and likely more relevant levels of lead show no obvious color change. However, when

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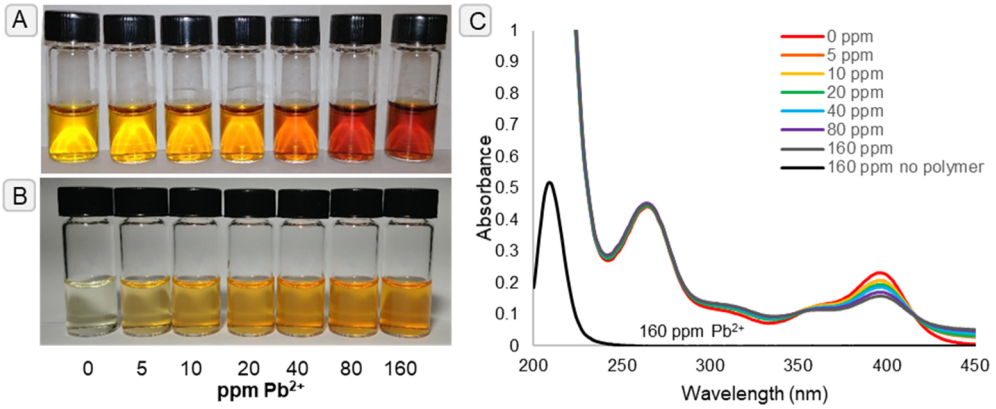

Figure 5. Images of poly(S-DADM) with a (A) chloride counterion and (B) nitrate counterion with the addition of 0−160 ppm Pb^{2+}. (C) UV−vis spectrum corresponding to the polymer−metal ion solutions in (B).

the counterion was changed to nitrate, a more apparent color change occurs at lower lead concentrations and becomes more difficult to discern above 20 ppm. Together, these two polymer solutions could offer a way to detect the presence of lead without the use of complex instrumentation.

A calibration curve was created by taking absorbance readings at 405 nm. Because of small differences in solubility in each batch of polymer, the baseline must be adjusted to account for this change. The calibration curve was then used to determine the lead content of poly(S-DADMAC) samples spiked with 30, 60, and 90 ppm Pb. The calculated results were within ∼5−15% of the actual lead content. Although, the potential remains to improve accuracy with more testing, this work can still provide a simple method to determine the approximate lead concentration in water.

CONCLUSIONS

By combining charged monomers and elemental sulfur, a petroleum byproduct, this work describes the first water-soluble IVPs. The solvent-free synthesis and short reaction times provide an efficient path to develop metal capture materials without further waste production. The improved water solubility allows the entire polysulfide to participate in binding rather than relying solely on surface interactions affording materials with selectivity for gold and silver ions. Simple filtration can remove the metal−polymer complex from solution, leaving behind less contaminated water. Additionally, these materials can detect heavy metals such as lead without the need for complex equipment. Using petroleum waste to create polymers for the remediation of industrial waste helps manage two waste streams with one material. The selectivity, low cost, scalability, and easily accessible synthetic methods make these materials practical for large-scale water treatment applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c01536.

^{1}H NMR and ATR-FTIR spectra, thin layer chromatography, DSC curves, images of polymer solubility in different solvents and precipitation upon the addition of heavy metals, and GPC data (PDF)

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Author Contributions

M.L.E. developed the polymer synthesis, performed polymer characterization, and wrote the manuscript. C.B.C. conducted all of the metal binding and detection analysis and performed polymer synthesis and some polymer characterization. C.L.J. was the principal investigator, developed the ideas for this project, and wrote the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation for funding this work (NSF award number 2004257). Additional thanks are owed to the NSF for providing instrument support from award number 2019074.

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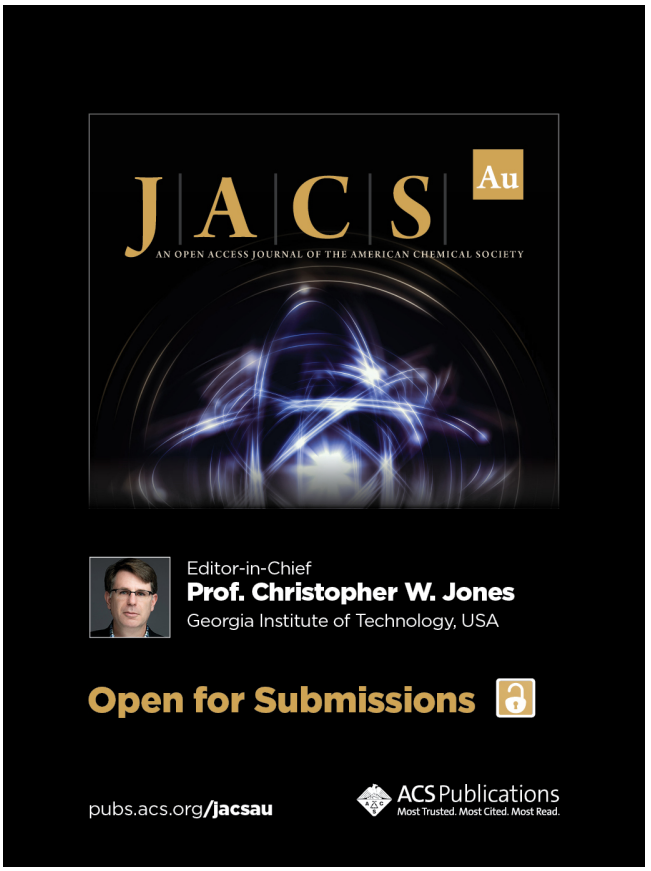

https://doi.org/10.1021/acsapm.1c01536
ACS Appl. Polym. Mater. 2022, 4, 1110−1116