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New Polymers Possessing a Disulfide Bond in a Unique Environment

Tyler A. Graf,[†] Jun Yoo,[†] Adam B. Brummett,[†] Ran Lin,[‡] Markus Wohlgenannt,[‡] Daniel Quinn,[†] and Ned B. Bowden^{†,*}

[†]Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States [‡]Department of Physics, University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: The synthesis and some of the physical properties of the first poly(disulfidediamines) are reported. The disulfidediamine functional group (R₂NSSNR₂) possesses a disulfide bond in a unique environment that leads to a low bond dissociation energy (calculated BDE of $43.1 \text{ kcal mol}^{-1}$). These polymers were synthesized in high yields and with conversions up to >98% by reactions between secondary diamines and a new disulfide monomer. The disulfide monomer was synthesized in two steps without the need for column chromatography. The polymerizations were robust



and completed at room temperature, under ambient atmospheric conditions, and in solvents that were used as purchased. These polymers were stable, but they rapidly decomposed under acidic, aqueous conditions or by heating to 175 °C as shown by thermal gravimetric analysis. The first fully conjugated poly(disulfidediamine) was synthesized, and its electrical conductivity was characterized in the solid state.

INTRODUCTION

Sulfur has been a critically important atom in polymer chemistry since the beginning of the polymer industry. In the mid 1800s, the discovery of the vulcanization of rubber by Charles Goodyear led to many of the first practical uses of synthetic rubber. Here, sulfur was used to cross-link the polymer, and the physical properties of the material were mostly set by the cross-linked matrix. In more recent work, polymers have been developed that take advantage of the chemical and physical properties that the presence of sulfur adds to the final material. For example, poly(p-phenylene sulfide) is sold industrially as Ryton, Fortron, or Sulfar due to its resistance to acids and bases and its stability at high temperatures.¹⁻⁶ Self-healing polymers have been synthesized with either disulfides or trithiocarbonates as the active functional groups that led to healing after the polymer has been scratched or fractured.^{7–13} Monosulfide and disulfide polymers have been studied for their applications in medicine.^{14,15} For instance, polymers with monosulfides have been investigated for their ability to affect the redox cycle inside and outside of cells after an injury had taken place.¹⁴ Polymers with disulfide bonds have been synthesized as new biodegradable polymers for applications in gene and drug delivery as well as for biodegradable agents in magnetic resonance contrast imaging with Gd(III).^{7,16–21} Polymers with disulfide bonds are biodegradable because of the presence of disulfide reducing agents, such as glutathione, that degrade polydisulfides into small molecules or oligomers that are readily excreted from the body.²²

We were interested in studying the synthesis and properties of polymers containing the disulfidediamine functional group (R_2NSSNR_2) along the backbone. This functional group is very understudied in organic chemistry, and no polymers that contain this functional group are known.²³⁻³⁰ The most common use of disulfidediamines is as a thermally active crosslinking agent in the rubber industry due to the facile homolytic cleavage of its S-S bond at temperatures below 200 °C.³¹⁻³³ This cross-linking step yields functional groups that are different from disulfidediamines. This functional group has also found limited applications in the study of insecticides, fungicides, and as corrosion inhibitors in oil.^{34,35} One interesting aspect of the disulfidediamine functional group is that it possesses an S-S bond in a unique environment that leads to a low bond dissociation energy. In a recent report, the stability of the RS-SR bond toward homolytic cleavage (resulting in 2 equivalents of RS-) was studied for a variety of different molecules.^{32,36} Interestingly, H₂NS-SNH₂ had the lowest ΔH° (43.1 kcal mol⁻¹) for homolytic cleavage for all of the molecules that contained only two sulfur atoms. In contrast, CH₃SSCH₃ ($\Delta H^{\circ} = 63.9 \text{ kcal mol}^{-1}$) and even NCS-SCN $(\Delta H^{\circ} = 46.6 \text{ kcal mol}^{-1})$ had significantly higher values for ΔH° and higher stabilities. Despite the low bond dissociation energy for the disulfide bond in disulfidediamines, molecules possessing this functional group are stable and readily handled using normal techniques.

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Our interest in synthesizing poly(disulfidediamines) was based on their unique structure and the presence of a disulfide bond. Disulfide bonds are common in biology and were recently used in the synthesis of new biodegradable polymers and for self-healing polymers as previously described. We hypothesized that poly(disulfidediamines) would degrade by two different, complementary routes in the body that would make them attractive targets in medicine. Poly-(disulfidediamines) may degrade similar to polydisulfides by the action of glutathione on the interior and exterior of cells.^{7,16-20} Also, poly(disulfidediamines) may be readily cleaved under acidic conditions that is an important degradation pathway for polymers used in drug and gene delivery.³⁷⁻⁴⁷ Pharmaceutical drugs are often loaded into nanoparticles composed of polyesters that are stable in the bloodstream at pH of 7.4 but rapidly degrade after endocytosis into cells. These nanoparticles are trafficked to the endosome and lysosome within cells where the pH drops to approximately 5.0 which leads to a rapid, acid-catalyzed degradation of polyesters and release of a pharmaceutical drug. Although data in the literature on the acid-catalyzed degradation of disulfidediamines was lacking, we anticipated that they would rapidly degrade under acidic conditions based on analogy to sulfenamides (R₂NSR) and diaminosulfides (R₂NSNR₂). Both of these functional groups degrade within minutes under acidic conditions in water with first order rate constants of approximately $2 \times 10^{-2} \text{ s}^{-1.48,49}$ These rate constants are several orders of magnitude faster than the degradation of ester bonds under similar conditions.⁵⁰

In related work, we recently reported the synthesis of poly(sulfenamides) and poly(diaminosulfides) that are structurally related to poly(disulfidediamines).^{48,49} These three functional groups possess distinctly different reactivities, structures, and reaction products (Figure 1). One way to understand the



Figure 1. Polymers based on esters, anhydrides, and diacyl peroxides belong to one class of polymers, but these polymers have different reactivities and reaction products. Similarly, polymers based on sulfenamides, diaminosulfides, and disulfidediamines belong to the same class of polymers but also have important differences in their reactivities and reaction products.

differences between these functional groups is to compare them to esters, anhydrides, and acyl peroxides. It is well-known that esters, anhydrides, and acyl peroxides belong to the same class of molecules and are all based on oxygens and carbonyls, but they are well recognized as possessing different reactivities and yield different reaction products. Sulfenamides, diaminosulfides, and disulfidediamines are also members of the same class of molecules and are based on sulfur and nitrogen, but they have very different reactivities and reaction products. Despite the similarities in sulfenamides, diaminosulfides, disulfidediamines, it is the differences that are important and lead to different reactivities and products.

In this article, the first synthesis of poly(disulfidediamines) is reported as well as initial work to demonstrate that the disulfidediamine functional group is stable to various conditions. These polymers were briefly studied for their stability at elevated temperatures as well as their electrical conductivity.

RESULTS AND DISCUSSION

Synthesis and Stability of Disulfide Monomers. The synthesis of poly(disulfide diamine)s was proposed to occur by the reaction of secondary diamines with a disulfide monomer as shown in Figure 2. Although sulfur monochloride (S_2Cl_2) was

$$n \stackrel{|}{HN-R-NH} + n X-S-S-X \longrightarrow (\stackrel{|}{N-R-N-S-S} + 2n HX$$

Figure 2. General reaction scheme for the proposed synthesis of poly(disulfidediamines).

commercially available and known to react with amines to yield disulfidediamines, it was not chosen for the polymerization reaction due to its reactivity with other functional groups such as alcohols and olefins and because HCl would be produced.^{51–53}

Disulfide transfer agents based on succinimide and phthalimide were well-known in the literature (Figure 3) and



Figure 3. (a and b) Synthesis of molecules A and B, based on literature procedures. (c) Synthesis of a new disulfide monomer developed based on inexpensive, commercially available starting materials.

were investigated for the synthesis of poly-(disulfidediamines).^{54–56} The synthesis of molecule A yielded side products that were challenging to remove from the final product and limited the scale at which this reaction could be completed. Additionally, it was poorly soluble in organic solvents and had an upper limit for solubility of 50 mg mL⁻¹ in methylene chloride. Although molecule B was synthesized in good yield and high purity, it possessed lower solubility than molecule A in many organic solvents. It was believed that the low solubility of these molecules would hinder their usefulness in step polymerizations.

A modified synthesis of a disulfur monomer was developed as shown in Figure 3c. The first step was the hydrogenation of tetrahydrophthalimide using Pd/C. This reaction yielded a clean product after simple filtration of the Pd/C and did not require any further purification. The product was reacted with S_2Cl_2 in the presence of triethylamine to yield a solid that was readily purified by crystallization. Because neither step in the synthesis required column chromatography, they could be scaled up to >20 g without any limitation.



Figure 4. Reaction between molecule A and two molar equivalents of molecule E. They were investigated according to this reaction scheme.

The stability of molecule A was studied in C_6D_6 , $CDCl_3$, $DMSO-d_6$, and CD_3OD under normal atmospheric conditions to investigate any limitations in the use of this class of molecules. The stability of molecule A rather than molecule D was studied because of the simplicity of its ¹H NMR spectrum made investigating its decomposition clear. No decomposition of molecule A was observed after 61 days in either C_6D_6 or $CDCl_3$. Approximately 10% of molecule A decomposed after 50 days in DMSO- d_{6} , and 18% of it decomposed in CD_3OD in 5 h.

Synthesis and Stability of Disulfidediamines. The reaction of a disulfide monomer with two molar equivalents of benzylmethylamine was investigated to learn the kinetics of this reaction (Figure 4). This reaction was completed in both $CDCl_3$ and C_6D_6 under dilute conditions to slow the reaction so that it could be studied by ¹H NMR spectroscopy.

The reaction kinetics were modeled based on the reactions in Figure 4. The differential equations were solved numerically by a fourth-order Runge–Kutta integration as described in the Supporting Information, and a fit to the experimental data was shown in Figure 5.⁵⁷ The values for the rate constants measured



Figure 5. Kinetics of the transamination reaction between molecule A and 2 molar equiv of molecule E in C_6D_6 .

in C₆D₆ ($k_1 = 7.8 \times 10^{-4} M^{-1} s^{-1}$, $k_2 = 1.9 \times 10^{-4} M^{-1} s^{-1}$, $k_3 = 3.8 \times 10^{-6} M^{-1} s^{-1}$) were slightly slower than the rate constants measured in CDCl₃ ($k_1 = 1.3 \times 10^{-3} M^{-1} s^{-1}$, $k_2 = 2.5 \times 10^{-4} M^{-1} s^{-1}$, $k_3 = 4.4 \times 10^{-6} M^{-1} s^{-1}$). Inclusion of the side reaction, with rate constant k_3 , was justified because, when this process was not included, the fits of the time courses were coincident at long reaction times for benzylmethylamine (molecule E) and the monosubstituted product (molecule F). Inclusion of the side reaction accounts for the observation that the concentrations of these two species diverged at long reaction times. It is important to note that the value for k_3 is 50–295 times smaller than the values for k_2 and k_1 , so the side reaction is very minor during polymerization.

Because the disulfidediamine functional group is not wellknown, the stability of a small molecule with this functional group was investigated in a variety of solvents. The stability of disulfidedi(ethylmethylamine) in different organic solvents was investigated by its addition to NMR tubes with C_6D_6 , $CDCl_3$, DMSO- d_6 , and CD_3OD followed by sealing the NMR tubes. No evidence of degradation of disulfidedi(ethylmethylamine) was observed in any of these solvents for 61 days.

The stability of this molecule was also investigated in 4/1 (v/v) CD₃OD/D₂O under acidic, neutral, and basic conditions to learn its stability in more challenging solvents.⁵⁸ The decomposition of disulfidedi(ethylmethylamine) with 9 molar equiv of acetic acid was rapid with a rate constant of 1.08 × 10^{-3} s⁻¹, and approximately 95% of it degraded within 42 min. The decomposition of disulfidedi(ethylmethylamine) was nearly 10 000 times slower under both neutral and basic conditions. Under neutral conditions the rate constant for decomposition was 2.56×10^{-7} s⁻¹ and only 68% of it degraded after 40 days. Under basic conditions (with 9 molar equiv of KOH), the rate constant was 5.02×10^{-7} s⁻¹, and 75% of it degraded in 20 days.

Synthesis of Poly(disulfidediamines). In the polymerization reaction shown in Figure 6 secondary amines can react



Figure 6. How poly(disulfidediamines) were synthesized using molecule D as the disulfide monomer.

with molecule D to add to a polymer chain, or they can undergo a transamination reaction with a disulfidediamine functional group along the backbone of the polymer. The transamination reaction between a diamine monomer and a disulfidediamine functional group along the polymer backbone will lead to a broadening of the polydispersity of the polymer and affect its final stability if an amine is an end group of the polymer. The kinetics of the transamination reaction shown in Figure 7 were studied in C_6D_{67} CDCl₃₇ DMSO- d_{67} and CD₃OD.



Figure 7. Rate constants for the three transamination reactions given in Table 1.

The rate constants for the reaction were found to be approximately 10^4 times slower than the rate constants for the polymerization reactions in C_6D_6 and $CDCl_3$ (Table 1).

Table 1. Rate Constants for the Reactions Shown in Figur	Та	able	1.	Rate	Constants	for	the	Reactions	Shown	in	Figure	7
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functional group	solvent	rate constant $(M^{-1} s^{-1})$	ref
disulfidediamine	C_6D_6	$<3.75 \times 10^{-9}$	this article
diaminosulfide	C_6D_6	5.47×10^{-6}	49
sulfenamide	C_6D_6	3.80×10^{-6}	48
disulfidediamine	CDCl ₃	2.84×10^{-8}	this article
diaminosulfide	CDCl ₃	2.79×10^{-5}	49
sulfenamide	CDCl ₃	4.60×10^{-6}	48
disulfidediamine	DMSO- d_6	9.04×10^{-8}	this article
diaminosulfide	DMSO- d_6	4.89×10^{-5}	49
sulfenamide	DMSO- d_6	3.46×10^{-6}	48
disulfidediamine	CD_3OD	6.61×10^{-6}	this article
sulfenamide	CD ₃ OD	5.06×10^{-4}	48

Thus, the desired polymerization reaction is heavily favored. In fact, in comparison to similar transamination reactions for diaminosulfides and sulfenamides, the transamination reactions of disulfidediamines are approximately 10^2 times slower in all solvents measured.

A series of polymerizations were completed with molecule D as the disulfide monomer and secondary diamines as the other monomer (Table 2). These polymerizations were completed in CH_2Cl_2 at room temperature for 24 h. The solvent was used as purchased without further purification, and the reactions were completed under ambient atmospheric conditions. The polymers were characterized by ¹H and ¹³C NMR spectroscopy and size exclusion chromatography (SEC) using a laser light scattering apparatus (Figure 8). These polymers are the first

Table 2. Polymerizations Completed As Shown in Figure 6

examples of poly(disulfidediamines) ever reported in the literature.



Figure 8. SEC chromatograph of the polymer from entry 1 of Table 2.

The reactions to yield polymers went to high conversions of 97–98% based on calculations from the values for $M_{\rm p}$. Despite the high conversions, the observed molecular weights for the polymers were modest due to the low molecular weights for the monomers. For instance, the disulfide monomer only contributed 64 g mol^{-1} when added to the growing polymer chain. Furthermore, the values for PDIs were lower than expected for step polymerizations for several possible reasons. The polymers may have been fractionated in the isolation steps resulting in a loss of some low molecular weight polymer. In Table 2 the isolated yields of the polymers are reported to demonstrate that a majority, but not all, of the polymer was isolated. Another possible reason for the lower than expected values for PDI was due to the challenge of accurately measuring the PDI for low molecular weight polymers. For instance, low molecular weight polymers have higher rates of diffusion than high molecular weight polymers which makes separating based on molecular weight and maintaining the separation challenging. Also, although the columns used in the separation were rated to separate polymers with these molecular weights, the

Entry	Polymer	Reaction Time $(h)^a$	Isolated Yield (%)	${{ m M}_{ m w}}{{ m (g/mol)}^b}$	\mathbf{DP}^{c}	Conversion ^c (%)	PDI
1	+NN-S-S+	24	70	11,400	60	98	1.4
2	-(N_N-S-S)-	48	73	5,000	37	97	1.3
3	-(N_N-S-S)	48	75	4,100	31	97	1.2
4 ^{<i>d</i>}	-(n_n-s-s) -	24	71	-	-	-	-
5	(N_N-S-S)-	24	65	3,900	37	97	1.2
6	-(n_n-s-s)-	24	67	5,300	55	98	1.2
7	-(N_N-s-s)-	24	70	8,700	60	98	1.8

^{*a*}All reactions performed at ambient atmospheric conditions in CH₂Cl₂. ^{*b*}The measured values for M_w based on the absolute molecular weights calculated from the SEC micrographs and using refractive index and laser light scattering detectors. ^{*c*}The values for the degree of polymerization (DP) and the conversions were calculated from M_n . ^{*d*}The solubility of entry 4 was too low to allow for full characterization.

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choice of columns was not optimized for polymers with these molecular weights. It is important to note that although the PDIs were lower than expected, the molecular weights were found using refractive index and laser light scattering detectors that allowed a determination of the absolute molecular weights. Thus, the molecular weights and conversions found from the isolated polymers are accurate and demonstrate that the polymerizations were successful.

Although small molecule reactions by us and others have shown that the reactions between secondary amines and molecules A, B, or D result in disulfidediamines, the presence of sulfur in the polymers was not directly probed by ¹H or ¹³C NMR spectroscopy. To provide further evidence for the presence of disulfidediamine functional groups, the polymer shown in entry 1 of Table 2 was studied by elemental analysis. The theoretical mass percentages (C, 57.3%; N, 10.3%; S, 23.5%; H, 8.8%) for the repeat unit closely matched the values that were measured (C, 55.3%; N, 9.7%; S, 23.1%; H, 8.5%). The analyzed elements accounted for 97% of the initial mass of the sample.

Thermal Gravimetric Analysis (TGA). The polymer shown in entry 1 of Table 2 was studied by TGA (Figure 9).



Figure 9. TGA of the polymer from entry 1 in Table 2.

The sample was heated at a rate of 1 °C per min under N₂. The polymer was stable at elevated temperatures but underwent a sudden loss of weight at 175 °C. This sudden loss of mass was expected based on the use of small molecules possessing disulfidediamines as vulcanizing agents in the rubber industry.^{31–33}

Electrically Conducting Poly(disulfidediamines). The first inorganic, electrically conducting polymer was polythiazyl, and it was first synthesized in 1953 (Figure 10).⁵⁹⁻⁶⁴ In fact,

$$+ N' S = N S = N S = N S + N' S + S$$

Figure 10. Structure of polythiazyl.

polythiazyl is the only known undoped polymer that is superconducting at low temperatures.^{59,65} Polythiazyl is composed entirely of sulfur and nitrogen arranged in an alternating pattern which does not allow its electrical properties to be readily changed by varying its molecular structure. In contrast, the physical and chemical properties of electrically conducting polymers based on organic functional groups (i.e., polythiophene and polyaniline) can be varied by the addition of functional groups along the polymeric backbone.

The interesting electrical properties of polythiazyl led us to investigate whether poly(disulfidediamines) were also electrically conducting. The synthesis of the polymer shown in Figure 11 was first attempted using molecule D as the disulfide monomer but no reaction was observed. Instead, the polymer



Figure 11. Synthesis of a conjugated poly(disulfidediamine).

was synthesized using S_2Cl_2 as the disulfide monomer and triethylamine as a base to remove the HCl that was produced. The resulting polymer was characterized by ¹H and ¹³C NMR spectroscopy and SEC using laser light scattering. The value for M_w was 4300 g mol⁻¹ (PDI = 1.31) which led to a calculated degree of polymerization of 42. This polymer was very interesting because the conjugation was through the inorganic disulfidediamine functional group, but the aromatic ring bonded to the nitrogen would allow the conjugation to be altered by varying the presence of functional groups. Thus, this polymer combined conductivity through inorganic functional groups with the ability to alter the conductivity by the presence of organic functional groups.

This polymer was fabricated into a layered device to measure its current–voltage curve in the solid state (Figure 12). The



Figure 12. Current-voltage curve for the polymer synthesized as shown in Figure 11.

cross-sectional area was $16.9 \times 10^{-3} \text{ mm}^2$ and the thickness of the poly(disulfidediamine) was 40 nm. The data in figure 12 show that the polymer possessed diode characteristics and was weakly electrically conducting. The conductivity between 9 and 10 V was estimated to be 4.73×10^{-8} S cm⁻¹. Although this value was very low and similar to that of distilled water, it was comparable to values for other undoped polymers. For instance, undoped polythiophene, polyaniline, and polyacetylene have conductivities of approximately $10^{-5}-10^{-9}$ S cm^{-1.66-70} In contrast, insulating polymers such as paraffin wax have conductivities of approximately 10^{-20} S cm⁻¹. Polythiophene, polyaniline, and polyacetylene must be doped to reach more desired conductivities of $1-10^3$ S cm⁻¹. The effect of dopants was briefly studied by exposing the device to iodine vapor for 5 min and then immediately measuring the conductivity (see Figure 12). The iodine doping enhanced the electrical conductivity and the measured value was 2.85×10^{-7} S cm⁻¹. In future work, we will study how the presence of additives alters the conductivities of poly(disulfidediamines).

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CONCLUSIONS

Poly(disulfidediamines) were unknown prior to this work despite a long-term interest in polymers possessing sulfide and disulfide bonds. To synthesize these polymers, a new disulfide monomer was synthesized in two steps in high yield without the need for chromatography. Despite a low bond dissociation energy for the disulfidediamine functional group, these polymers were very stable in protic and aprotic solvents. Studies with small molecules showed that the disulfidediamine functional group was stable in various solvents but rapidly decomposed in methanol/water in the presence of a carboxylic acid. These polymers have high stabilities that are desired for many applications, they are easy to handle, and they possess no noticeable odor.

Working with new functional groups offers new opportunities, and two opportunities opened up by the synthesis of poly(disulfidediamines) were explored. In one application we showed that these polymers were thermally stable but underwent a rapid and nearly complete degradation when heated to 175 °C. We believe, but have not shown, that this degradation was due to the homolytic cleavage of the S-S bond in these polymers to yield highly reactive sulfur based radicals. In a second opportunity, a conducting polymer was synthesized and characterized. This polymer has conjugation through organic and inorganic functional groups and can be considered a "hybrid" polymer. These polymers combine some of the attractive electrical properties of polymers based on SN bonds with the ability to tailor electrical properties by varying the presence of organic functional groups. In future work, opportunities offered by working with electrically conducting poly(disulfidediamines) will be pursued.

EXPERIMENTAL SECTION

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 and 75 MHz respectively. SEC was performed using chloroform as the mobile phase (1.0 mL min⁻¹) at 35 °C. A Waters 515 HPLC pump and a Waters column (Styragel HR4E) were used. A DAWN EOS 18 angle laser light scattering detector from Wyatt Corp. to measure light scattering and a Wyatt Optilab DSP to measure changes in refractive index were used to measure absolute molecular weights of polymers. Current–voltage (*I–V*) measurements were performed on a Keithly 2400 source measurement unit. The polymeric film thickness was measured with a Veeco optical profilometer. Thermal gravimetric analysis was performed on a TA Instruments TGA Q5000.

Materials. Phthalimide, *cis*-1,2,3,6-tetrahydrophthalimide, benzylmethylamine, ethylmethylamine, palladium on carbon, acetic acid, potassium hydroxide, and triethylamine were purchased from Aldrich or Acros and used as received. Hydrogen was purchased from PraxAir. Succinimide, 4,4'-trimethylenedipiperidine, piperazine, and *trans*-2,5dimethylpiperazine were purchased from Aldrich and purified by recrystallization. *N*,*N*'-Dimethylhexanediamine and *N*,*N*'-dimethyloctanediamine were purchased from Aldrich and purified by vacuum distillation. Sulfur monochloride and *N*,*N*'-di-*sec*-butyl-*p*-phenylenediamine were purchased from Aldrich, purified by vacuum distillation, and stored under N₂. HPLC grade chloroform purchased from Acros Organics was used as the GPC solvent after filtration through a glass frit. All other solvents were reagent grade and purchased from Acros Organics.

Synthesis of Molecule A. Succinimide (3.0 g, 30.3 mmol) was added to a round-bottom flask containing triethylamine (4.5 mL, 32.3 mmol) and THF (75 mL). This mixture was cooled to 0 $^{\circ}$ C with an ice bath. Sulfur monochloride (1.2 mL, 15.2 mmol) was added dropwise over one min. The solution was immediately filtered by vacuum and washed with additional THF (50 mL). The solvent was removed under vacuum to yield a light yellow solid. This solid was

dissolved in a minimal amount of CH₂Cl₂ to which an excess of hexanes was added. The colored impurities precipitate from the solution and the liquid was removed and concentrated under vacuum to yield a white crystalline solid (6.2 g, 46%). ¹H NMR: δ 2.86 (s). ¹³C NMR: δ 175.7, 29.0. HRMS: calcd for C₈H₈N₂O₄S₂, 259.9926; found, 259.9931.

Synthesis of Molecule B. This molecule was synthesized by modification of a literature procedure.^{54–56} Phthalimide (2.9 g, 19.7 mmol) was dissolved in THF (40 mL) and triethylamine (4 mL). The mixture was cooled in a salt ice bath, and then sulfur monochloride (0.8 mL, 10 mmol) was added dropwise to the cooled mixture. The solution was stirred for 1 h, and then quenched with 70 mL of H₂O. The resulting precipitate was filtered and washed with diethyl ether. Crystallization from 2:1 (v:v) CHCl₃:CH₃OH yielded white crystals (3.5 g, 98%). ¹H NMR: δ 7.94–7.98 (m, 2H), 7.81–7.85 (m, 2H), 1.58 (s, 1H). ¹³C NMR: δ 167.2, 136.5, 132.5, 125.1.

Synthesis of Molecule C. *cis*-1,2,3,6-Tetrahydrophthalimide (25 g, 165 mmol) was dissolved in CH₂Cl₂ (150 mL) and added to a metal Parr reactor. Palladium (10% by wt on carbon, 500 mg) was added to this solution. The reactor was pressurized with H₂ (1000 psi) and stirred at 25 °C for 24 h. The palladium on carbon was removed by filtration, and the solvent was removed under vacuum to yield a white solid (22 g, 88%). ¹H NMR: δ 7.79–8.02 (s, 1H), 2.87–2.95 (m, 2H), 1.75–1.89 (m, 4H), 1.45–1.49 (m, 4H). ¹³C NMR: δ 181.0, 41.1, 23.8, 21.9.

Synthesis of Molecule D. Molecule C (31.5 g, 209 mmol) was dissolved in 500 mL CH₂Cl₂ and triethylamine (43.5 mL, 312 mmol). The mixture was cooled to -78 °C. Sulfur monochloride (8.5 mL, 104 mmol) was added slowly over 20 min using a pressure equalizing addition funnel. The solution was stirred for 10 min at -78 °C then washed with two 500 mL portions of sat. NaCl followed by two 500 mL portions of 0.2 M NaOH. The solution was dried with MgSO₄ and the solvent removed under vacuum. The resulting solid was crystallized from 8:3 (v:v) hexanes:EtOAc yielding a white solid (27.3 g, 71%). ¹H NMR δ 2.99 (m, 4H), 2.05 (m, 8H), 1.5 (m, 8H). ¹³C NMR: δ 177.4, 40.6, 25.4, 23.9, 22.1, 21.7. HRMS: calcd for C₁₆H₂₀N₂O₄S₂, 368.0865; found, 368.0864.

Procedure for Table 2, Entry 1. Molecule D (3.5 g, 9.5 mmol) was combined with 4, 4'-trimethylenedipiperdine (2.0 g, 9.5 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 24 h, and then precipitated from CH₃OH to yield a white solid (1.8 g, 70%). ¹H NMR: δ 2.96–2.99 (m, 4H), 2.58–2.64 (m, 4H), 1.67–1.70 (m, 4H), 1.19–1.28 (m, 12H). ¹³C NMR: δ 57.2, 36.7, 34.5, 33.8, 24.1.

Procedure for Table 2, Entry 2. Molecule D (5 g, 13.4 mmol) was combined with *N*,*N'*-dimethylhexanediamine (1.93 g, 13.4 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 48 h, then extracted with three 50 mL portions of 4 M KOH and dried with MgSO₄. Evaporation of the solvent yielded a yellow oil (2.0 g, 72%). ¹H NMR: δ 2.62 (m, 5H), 1.45–1.65 (m, 2H), 1.23–1.44 (m, 2H). ¹³C NMR: δ 59.5, 46.9, 28.3, 26.9.

Procedure for Table 2, Entry 3. Molecule D (2.5 g, 6.86 mmol) was combined with *N*,*N'*-dimethyloctanediamine (1.18 g, 6.86 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 48 h, then extracted with three 50 mL portions of 4 M KOH and dried with MgSO₄. Evaporation of the solvent yielded a yellow oil (1.2 g, 75%). ¹H NMR: δ 2.53–2.58 (t, 2H), 2.43 (s, 3H), 1.45–1.49 (m, 2H), 1.30 (m, 4H). ¹³C NMR: δ 59.3, 46.6, 29.5, 28.2, 26.8.

Procedure for Table 2, Entry 4. Molecule D (5.36 g, 14.4 mmol) was combined with piperazine (1.24 g, 14.4 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 24 h, then precipitated into CH₃OH. The white solid was collected by filtration and dried under vacuum (1.55 g, 71%). ¹H NMR: δ 2.85–2.97 (s).

Procedure for Table 2, Entry 5. Molecule D (4.86 g, 13.2 mmol) was combined with *trans*-2,5-dimethylpiperazine (1.5 g, 13.2 mmol) in 40 mL of CH₂Cl₂. The reaction mixture was stirred for 24 h, then extracted with six 200 mL portions of 4 M KOH and dried with MgSO₄. Evaporation of the solvent yielded a white solid (1.5 g, 65%). ¹H NMR δ 2.96 (m, 4H), 2.40–2.70 (m, 2H), 1.17–1.04 (m, 6H); ¹³C NMR δ 64.1, 57.8, 18.8, 17.9.

Procedure for Table 2, Entry 6. Molecule D (10.15 g, 27.6 mmol) was combined with 2-methylpiperazine (2.7 g, 27.6 mmol) in 100 mL of CH₂Cl₂. The reaction mixture was stirred for 24 h, then extracted with nine 200 mL portions of 4 M KOH and dried with MgSO₄. Evaporation of the solvent yielded a white solid (2.9 g, 67%). ¹H NMR: δ 3.08–2.76 (m, 6H), 2.61–2.46 (m, 1H), 1.20–1.04 (m, 3H). ¹³C NMR: δ 63.9, 56.9 51.7, 46.8, 18.6, 17.9.

Procedure for Table 2, Entry 7. Molecule D (4.2 g, 11.4 mmol) was combined with 2-methylpiperazine (1.14 g, 11.4 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 24 h, then extracted with four 200 mL portions of 4 M KOH and dried with MgSO₄. Evaporation of the solvent yielded a white solid (1.3 g, 70%). ¹H NMR: δ 3.25–3.11 (m, 8H), 1.95–1.87 (m, 2H). ¹³C NMR: δ 61.0, 59.2, 30.4.

ASSOCIATED CONTENT

Supporting Information

The stability of molecule A, the transamination kinetics, the stability of the disulfidediamine functional group, the synthesis of the conjugated poly(disulfidediamine), and the diode fabrication. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

*E-mail: ned-bowden@uiowa.edu. Telephone: (319) 335-1198. Notes

The authors declare no competing financial interest.

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