

Polymerization of Primary Amines with Sulfur Monochloride to Yield Red Polymers with a Conjugated SN Backbone

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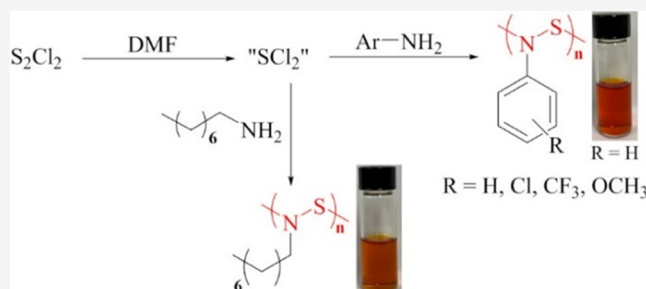


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ABSTRACT: A series of polymers that possessed a backbone solely composed of alternating nitrogen and sulfur single bonds were synthesized for the first time. The structures of these polymers were based on polythiazyl (SN)_x, which only possesses nitrogen and sulfur and is electrically conducting at room temperature in the absence of doping and superconducting at low temperatures. The polymers reported in this manuscript were synthesized using the reaction between sulfur dichloride (S₂Cl₂) and either anilines or octylamine. The isolated yields ranged from 48% to 74%, and the molecular weights were found using light scattering and refractive index detectors to be 6,200–35,000 g mol^{−1}. The UV–vis spectra of the polymers were obtained, and the polymers possessed peak maxima around 450 nm and appeared red. The poly[(N,N-amino)sulfide] (polyNAS) synthesized from octylamine also was red, which demonstrated that the color was due to conjugation along the NS backbone. These polymers are the first polymers containing a backbone of alternating N and S, and are easily processed due to the groups attached to the nitrogens.



1. INTRODUCTION

Polythiazyl (SN)_x was first synthesized in 1906 and contains alternating sulfur and nitrogen atoms along its backbone (Figure 1).^{1–4} It has many interesting properties such as being one of only two examples of a synthetic polymer that is metallic at room temperature under atmospheric pressure and in the absence of doping.^{5–9} This polymer is also superconducting with a critical temperature of 0.3 K.^{10–12} Unfortunately, its straightforward composition does not lead to simple methods to alter its structure or properties, most research has described doping with different chemicals.^{13–16} This polymer has been heavily investigated since its discovery, and different methods to synthesize it and its derivatives have been developed as well as numerous potential applications that take advantage of its electrical conductivity through the alternating sulfur–nitrogen bonds.^{17–25} Unfortunately, its applications are limited due to its unstable nature that leads to degradation in water or under atmospheric conditions to give a gray powder.^{2,3,12,17,26,27} Although a large diversity of small organic compounds containing sulfur–nitrogen bonds have been studied for their biological activities^{4,28–48} and synthesis of transition-metal complexes,^{49–52} surprisingly few polymers possess nitrogen–sulfur bonds along the backbone.^{30,53,54} We recently reported the synthesis of poly-sulfenamides, polydiaminosulfides, and polydiaminodisulfides, but these polymers possess sp³ hybridized carbon atoms along their backbones that interrupt conjugation.^{4,29,30,55–57} We also

recently reported the first well-defined poly[N,N-(phenyl-amino) disulfides] that only possess nitrogen and sulfur along the backbone (Figure 1). These polymers were similar to polythiazyl, but they possess two sulfur atoms for every nitrogen atom.⁵⁸

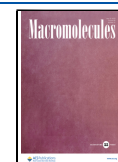
In prior work, we reported the synthesis of poly[N,N-(phenylamino)disulfides] by the reaction of anilines with sulfur monochloride (S₂Cl₂). The backbone of these polymers was the NSS functional group with anilines bonded to the nitrogen. These polymers had colors that ranged from pale yellow to red to green. The color was strongly affected by whether electron-withdrawing or -donating groups were bonded to the aromatic rings and the adsorption was at longer wavelengths as the identity and number of electron-donating groups increased. If the aromatic ring was replaced with a cyclohexyl ring, the polymer was colorless. This prior work showed that the conjugation of the NSS backbone was strongly influenced by the aromatic ring.

In this article, we report the first synthesis of polymers that contain an alternating arrangement of nitrogen and sulfur that

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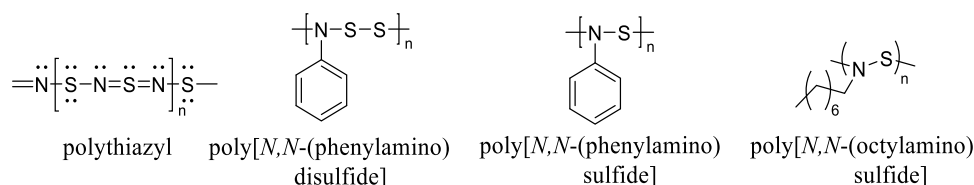


Figure 1. Polymers possessing nitrogen–sulfur backbones.

mimic the backbone of polythiazyl, as shown in Figure 1. These polymers are labeled as poly[(*N,N*-amino)sulfides] or polyNAS, and they possess a backbone that consists entirely of N and S and with side groups that are easily altered. These polymers were inspired by polythiazyl and the opportunity to synthesize polymers related to polythiazyl that could be easily processed unlike polythiazyl. These polymers were all brightly colored with only a small dependence of their color on the nature of the groups attached to the nitrogen atoms. These polymers were conjugated along the NS backbone, and this conjugation was investigated by synthesizing numerous polyNAS using anilines and octylamine. The colors of the synthesized polymers were studied, and their stabilities in the presence of thiols are reported.

2. EXPERIMENTAL SECTION

2.1. Materials. The amines were purchased from Sigma-Aldrich and purified by sublimation or distillation prior to use. Triethylamine (TEA) was purchased from Fischer Scientific and used without further purification. Sulfur monochloride (S_2Cl_2) was purchased from Sigma-Aldrich and distilled over crystalline elemental sulfur within a week of use and stored in the refrigerator under nitrogen gas. Nitrogen gas was purchased from Prax Air. Dimethylformamide (DMF) was purchased from Sigma-Aldrich, dried over anhydrous $MgSO_4$, and then stored over molecular sieves (4 Å).

2.2. General Procedure for the Synthesis of polyNAS. All polyNAS were synthesized by the same general procedure. S_2Cl_2 (1.02 g, 7.58 mmol) dissolved in 12 mL of dry dimethylformamide (DMF) was added to a flame-dried, N_2 -purged Schlenk flask. The contents were stirred at RT for 45 min. The system was then cooled at $-61^\circ C$ for 30 min in a chloroform-dry ice bath. The flask was equipped with a pressure-equalizing addition funnel which was charged with the appropriate phenylamine monomer (6.0 mmol), cross-linker (*p*-phenylenediamine, 0.6 mmol), and TEA (1.68 g, 16.67 mmol) dissolved in 8 mL of dry DMF. The amine solution was added dropwise to the S_2Cl_2 solution at $-61^\circ C$ for 10–12 min. The reaction was stirred at $-61^\circ C$ for two additional hours. The reaction was maintained under positive nitrogen pressure during the reaction. After 2 h of stirring at $-61^\circ C$, the reaction was filtered while it was still cold to remove the triethylammonium chloride that precipitated during the reaction. The filtrate was then precipitated in ~ 120 mL of ice-cold methanol (MeOH). The precipitate was collected via filtration and then dissolved in ~ 10 mL of dichloromethane (DCM). The polymer solution in DCM was then washed with ice-cold distilled water (~ 120 mL in triplicate) and brine (~ 60 mL). The DCM layer was then dried over anhydrous $MgSO_4$. DCM was evaporated from the polymer solution to obtain the polymer. 1H NMR spectroscopy of poly(NAS) was performed with a Bruker ADVANCE 400 MHz in chloroform-*d*.

Polymer A: Poly[*N,N*-(4-chloro-3-(trifluoromethyl) phenylamine)-sulfide] Isolated red powder (0.64 g, 56%). 1H NMR (400 MHz, $CDCl_3$) δ 6.9–7.9 (broad, m)

Polymer B: Poly[*N,N*-(3,5 dichloro phenylamine)sulfide] Isolated red powder (0.64 g, 56%). 1H NMR (400 MHz, $CDCl_3$) δ 6.6–7.7 (broad, m)

Polymer C: Poly[*N,N*-(4-chloro phenylamine)sulfide] Isolated red powder (0.59 g, 62%). 1H NMR (400 MHz, $CDCl_3$) δ 6.8–7.5 (broad, m).

Polymer D: Poly[*N,N*-(phenylamine)sulfide] Isolated red powder (0.67 g, 74%). 1H NMR (400 MHz, $CDCl_3$) δ 6.8–7.6 (broad, m).

Polymer E: Poly[*N,N*-(4-methyl phenylamine)sulfide] Isolated red powder (0.53 g, 54%). 1H NMR (400 MHz, $CDCl_3$) δ 6.8–7.5 (broad, m, 5H), δ 2.1–2.4 (broad, m, 3H).

Polymer F: Poly[*N,N*-(2,4,6-trimethyl phenylamine)sulfide] Isolated red powder (0.57 g, 52%). 1H NMR (400 MHz, $CDCl_3$) δ 6.5–6.9 (broad, m, 2H), δ 2.0–2.6 (broad, m, 9H).

Polymer G: Poly[*N,N*-(3,4-dimethoxy phenylamine)sulfide] Isolated red powder (0.68 g, 57%). 1H NMR (400 MHz, $CDCl_3$) δ 6.1–7.3 (broad, m, 5H), δ 3.5–4.0 (broad, m, 6H).

Polymer H: Poly[*N,N*-(3,4,5-trimethoxy phenylamine)sulfide] Isolated red powder (0.70 g, 51%). 1H NMR (400 MHz, $CDCl_3$) δ 5.9–7.2 (broad, m, 2H), δ 3.4–4.2 (broad, m, 9H).

2.3. Polymerization to Yield Poly[*N,N*-octylamino)sulfide]. S_2Cl_2 (1.02 g, 7.58 mmol) was added to a flame-dried 100 mL Schlenk flask with a stir bar and dissolved in dry DMF (11.5 mL) stirred at RT for 45 minutes. The flask was equipped with a pressure-equalizing addition funnel and charged with octylamine (0.93 g, 7.2 mmol) and TEA (1.68 g, 16.67 mmol) dissolved in dry DMF (11.5 mL). The system was purged with N_2 gas prior to reaction and cooled to $-61^\circ C$ in chloroform/dry ice bath for 30 min. The amine solution was added dropwise to the cooled S_2Cl_2 solution for approximately 10–15 min. The reaction was allowed to stir for two additional hours at $-61^\circ C$ before removing from the bath and vacuum filtering. DCM (20 mL) was added to dissolve the filtrate, and then it was washed with distilled water (120 mL in triplicate) to remove TEA and DMF. The DCM layer was collected and concentrated to a volume of ~ 5 mL in a rotovap and then added dropwise to a solution of cold ice-cold MeOH (60 mL) to precipitate the polymer. The polymer was then separated by vacuum filtration. A second precipitation was required to obtain the pure polymer. 1H NMR characterization was performed with a Bruker ADVANCE 400 MHz spectrometer at room temperature in chloroform-*d*.

Polymer I: Poly[*N,N*-(octylamine)sulfide]. Isolated red powder (0.68g, 48%). 1H NMR (400 MHz, $CDCl_3$) δ 1–1.9 (broad, m, 12H), δ 0.8–0.9 (broad, 3H).

2.4. SEC-MALLS Determination of Molecular Weight (MW) of Poly-Phenylaminosulfides. Size exclusion chromatography (SEC) was performed on a Waters Styragel Column (7.8 mm $\times$ 300 mm, 500 Da–30 KDa) using a Waters 515 HPLC pump (0.5 mL/min) equipped with an auto-injection port (50 μ L inj. vol.). The molecular weights were measured using a Wyatt Dawn Heleos II (664 nm) multiangle light laser scattering (MALLS) detector in line with a Wyatt T-rEX refractometer. Samples were weighed using Radwag Microbalance MYA 21.3Y, dissolved in HPLC-THF, and filtered prior to injection with Tisch Scientific 0.2 μ m PTFE syringe filters. Weight-average molecular weights (M_w) were calculated from estimated dn/dc values given by assuming 100% mass recovery.

2.5. Ultraviolet–Visible Characterization of PolyNAS. Ultraviolet–visible spectra of all polymers were collected on an Agilent Cary 5000 UV–Vis/NIR spectrophotometer system and software using a double-front method compared against pure HPLC-THF (200–800 nm). All samples were dissolved in HPLC-THF and measured in Hellma Analytics High Precision Cells made from optical glass (10 mm path length). All samples were prepared at a starting concentration between 30 mM and 50 mM in 1 mL of HPLC-grade THF and serially diluted by half for each subsequent sample. All data were processed using Microsoft Excel for UV–vis plots and Fityk peak fitting software (gaussian, Lev-Mar method).

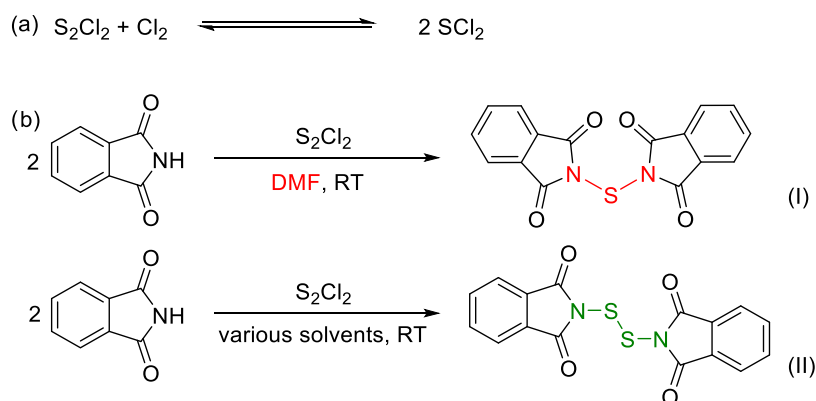


Figure 2. (a) Synthesis of sulfur dichloride from sulfur monochloride and chlorine gas. (b) Synthesis of monosulfide (I) and disulfide (II) transfer reagents using similar reaction conditions but different solvents.

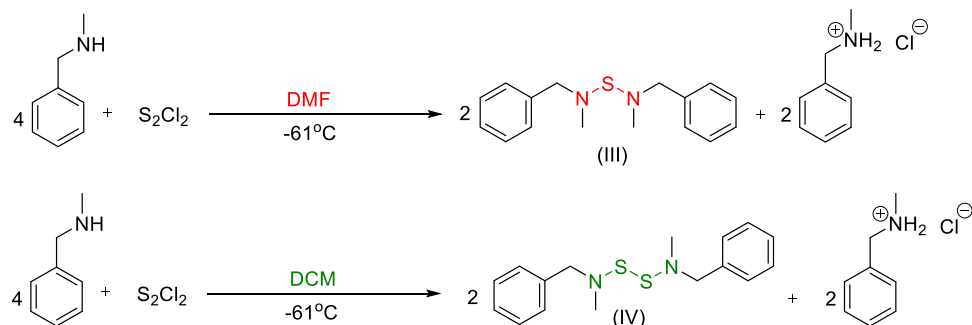


Figure 3. Synthesis of bis(*N*-methylbenzylamino)sulfide (III) and (bis(*N*-benzyl-*N*-methyl)disulfide) (IV).

2.6. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 under N_2 atmosphere. An aluminum pan was used, and a ramp rate of $5^\circ C\ min^{-1}$ equilibrated at $500^\circ C$ was used.

2.7. Elemental Analysis. Polymer samples were sent to Atlantic Microlab, GA, for elemental analysis using a CHNS probe.

2.8. Chemical Sensitivity Test. For the chemical sensitivity test of polyNAS with 2-mercaptoethanol (2-ME), ethanoic acid, and 1-propanamine, solutions of polymers B, D, F, and I were prepared at 3 mg/mL concentration in dry THF. Photographs were taken of the polymer solutions before and after addition of the chemicals in excess (1 SN functional group for every 50 molar equivalents of the chemicals).

3. RESULTS AND DISCUSSION

3.1. Synthesis of Sulfur Dichloride (SCl_2) from DMF and S_2Cl_2 . In the commonly used synthesis of SCl_2 , S_2Cl_2 is reacted with highly reactive and corrosive chlorine gas.⁵⁹ The SCl_2 is rapidly formed, but it remains in rapid equilibrium with S_2Cl_2 (Figure 2a). To maintain a high concentration of SCl_2 , it is stored in the presence of a small amount of Cl_2 , which complicates working with SCl_2 . Because SCl_2 is not readily commercially available and the reaction with chlorine gas presents hazards, a different method to synthesize it was investigated.

In a report published in 1966, scientists showed that the reaction of S_2Cl_2 with phthalimide in various solvents yielded the expected disulfide transfer reagent (II), but the same reaction in DMF yielded the monosulfide transfer reagent (I) (Figure 2b).⁶⁰ The authors repeated this reaction in solvents such as *N,N*-dimethylacetamide and acetone as well as in more basic solvents such as pyridine, but only DMF was shown to yield the monosulfur transfer reagent. A clue to how it was

formed was that one equivalent of S_2Cl_2 yielded one equivalent of the monosulfide transfer reagent despite the presence of two sulfur atoms. In addition, the disulfide transfer reagent (II) was stable in the presence of excess phthalimide, which indicated that the reaction in DMF proceeded through a monosulfide intermediate. We hypothesized that SCl_2 was produced *in situ* via reaction with DMF, but the yield and approximate rate of this reaction were unknown.

To investigate if phthalimide was needed to synthesize the N-S-N functional group, the reaction of *N*-methylbenzylamine with S_2Cl_2 in DMF was completed at room temperature, $0^\circ C$, and $-61^\circ C$. The reaction was highly exothermic and reactions at room temperature and $0^\circ C$ yielded a complex mixture of products. The reaction at $-61^\circ C$ proceeded smoothly, and the 1H NMR spectrum showed that it yielded the NSN bridge product (III) in >97% yield (Figure 3). This product was isolated and characterized using 1H NMR spectroscopy and high-resolution mass spectroscopy to confirm its structure (Figure S9). In addition, the NSSN bridged product (IV) was obtained by a reaction between with *N*-methylbenzylamine and S_2Cl_2 in DCM and characterized by 1H NMR spectroscopy and high-resolution mass spectroscopy. The CH_3 and CH_2 peaks in the 1H NMR spectrum for IV were shifted upfield from compound III by 0.3 and 0.4 ppm (Figures S9 and S10).^{61,62} These reactions demonstrated that the reaction of S_2Cl_2 in DMF yielded a monosulfide transfer reagent (likely SCl_2) that could react with amines in high yields. All attempts to isolate SCl_2 by distillation were unsuccessful.

3.2. Synthesis of polyNAS. To synthesize polyNAS, aniline derivatives were polymerized following the reaction conditions that were successful to yield product III with the

N–S–N functional group. The step-growth polymerization between aniline and S_2Cl_2 required careful control of the ratio of the two monomers, but the yield of conversion of S_2Cl_2 to SCl_2 was unknown. This polymerization was investigated with different molar ratios to determine the optimal ratio of the two monomers. The polymerization with a 1:1 molar ratio of aniline and S_2Cl_2 yielded a low-molecular-weight polymer that did not precipitate into ice-cold methanol. When the molar ratio was changed to 0.95:1 of aniline: S_2Cl_2 , the polymer precipitated into methanol and had a molecular weight of 6,500 g mol⁻¹. Lowering this ratio to 0.92:1 or 0.90:1 yielded polymers with decreasing molecular weights so the ratio of 0.95:1 was chosen for the polymerizations. The polymers in Figure 5 were synthesized using this ratio to yield polymers with molecular weights from 2,300 to 6,500 g mol⁻¹ (Table 1).

Table 1. Optimization of Reaction Conditions for Polymerization^a

amine: S_2Cl_2	yield (%)	MW (g/mol)
1:1	no precipitation	-
0.97:1	53	8300
0.95:1	74	15,800
0.92:1	54	7200
0.90:1	no precipitation	-

^a10% cross-linker was used in all of these reactions.

To increase the molecular weight of the polymers, 10% by mole of *p*-phenylenediamine was added as a cross-linker and to add branches to the polymers (Figure 4). The molecular weight of the polymer obtained with a molar ratio of 0.95:1 increased to 15,800 g mol⁻¹ with 10% of the cross-linker. A series of polymerizations were completed at different mole ratios of aniline: S_2Cl_2 with 10% mole ratio of *p*-phenylenediamine, and the highest molecular weight was obtained with a ratio of 0.95:1 (Table 1), so this ratio was used in all subsequent polymerizations to yield all of the polymers shown in Figure 5. Although the polymers were synthesized under N_2 , all subsequent characterization and handling was completed under normal atmospheric conditions.

3.3. Characterization of the Polymers. The polymers were thoroughly characterized by ¹H NMR spectroscopy, SEC-MALLS, and elemental analysis. The ¹H NMR spectra showed the broadening of the peaks as expected (Figures S11–S18). The absolute molecular weights and dispersities of the polymers were measured by SEC-MALLS (Table 2). The molecular weights for the polymers synthesized without the diamine were all lower than polymers synthesized using the diamine. The diamine increased the molecular weights by adding branches to the polymers and mildly cross-linking polymer chains. Although the dispersities were lower than expected, one possible reason may have been that low-

molecular-weight fractions of the polymers did not precipitate during isolation. Importantly, the molecular weights for the polymers synthesized with the diamine were consistently around 10,000 g mol⁻¹ except for D and G, which possessed higher molecular weights.

To confirm the structure of the polymers and the presence of sulfur, elemental analyses of five representative polyNAS (B, C, D, E, and F) were performed using a CHNS probe. The CHNS composition was measured two times for each polymer, and the average values are shown in Table 3. The calculated and observed sulfur-to-nitrogen ratios were compared for each of the polymers. For polymer D, the calculated S/N ratio was 2.28 and the observed S/N ratio was 2.29 (>99% match), indicating the presence of the hypothesized S–N backbone in the synthesized polymer. Polymer E showed the largest difference between calculated S/N ratio (2.28) and observed S/N ratio (2.41), but the match was still > 94%. These results demonstrate that the polymers contained sulfur at levels that were close to the expected values. These results were important because the characterization of the polymers by ¹H NMR spectroscopy did not report the presence of sulfur, but it was inferred from the composition of the materials.

3.4. UV–Vis Spectra of the Polymers. The polyNAS were colorful polymers due to conjugation along their backbone. To illustrate the conjugation, two resonance structures of polythiazyl and two resonance structures of a polyNAS are shown in Figure 6ab to illustrate the pi conjugate in these polymers. The pi conjugation in polyNAS mirrors that of polythiazyl and demonstrates that polyNAS is conjugated even when it is synthesized from an aliphatic amine. The polymer solutions of similar concentrations appeared to have different shades of red on physical observation (Figure S20). The UV–vis spectra of the polymers at a range of concentrations were obtained to analyze the visible absorptions responsible for their colors (Figures S1–S8).

Strong absorption peaks were seen in the UV region for all of the polymers which overlapped with the peaks in the visible spectrum. Hence, a peak fitting software was used to determine the absorption maxima in the visible spectrum. In Figure 6, representative spectra of each polymer and the peaks in the visible region are shown, and the peak maxima for each polymer is shown in Table 4. There was only a mild dependence on the peak maxima based on the electron-donating/electron-withdrawing groups on the aromatic rings. The maxima shifted from a low of 437 nm for the polymer with the most electron-withdrawing groups to 462 nm for the polymer with the most electron-donating groups. A low-molecular-weight oligomer was synthesized using aniline and *N*-methylphenylamine with a molecular weight of 1,230 g/mol (Figure S37). This polymer had a peak at 418 nm, which was expected based on the shortened backbone resulting in a higher HOMO/LUMO gap (Figure S3b).

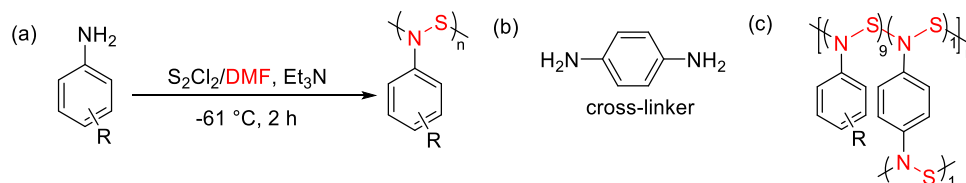


Figure 4. (a) Synthesis of polyNAS from the reaction between aryl amines and S_2Cl_2 in DMF. (b) Cross-linker used in the polymerization. (c) Repeat unit of the crosslinked polymer.

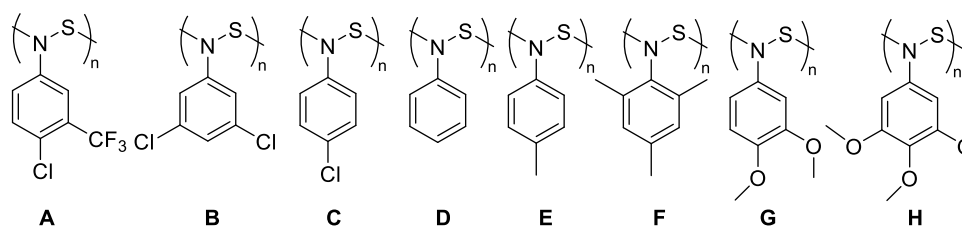


Figure 5. Polymers that were synthesized from the reaction between aryl amines and S_2Cl_2 in DMF.

Table 2. Weight-Average Molecular Weights (MW) and the Dispersities ($\bar{D}$) of the polyNAS Obtained Using SEC-MALLS

Poly- NAS	polymers synthesized with diamine		polymers synthesized without diamine	
	MW (g/mol)	dispersity ($\bar{D}$)	MW (g/mol)	dispersity ($\bar{D}$)
A	9900	1.15	4500	1.50
B	9700	1.36	4000	2.16
C	11,100	1.11	4600	1.17
D	15,800	1.29	6500	1.72
E	10,400	1.46	3500	1.13
F	10,200	1.21	3300	1.32
G	35,000	1.36	5400	1.56
H	10,500	1.20	2300	1.53

The small dependence of peak maxima on the electron-donating or -withdrawing groups on the aromatic rings led to a hypothesis that the polymers may be colorful in the absence of an aromatic ring. This hypothesis was investigated by polymerizing 1-octylamine to yield poly[*N,N*-(octylamine)-sulfide] (polymer I) without any cross-linker (Figure 7). A red-colored polymer with a molecular weight of 6,200 gmol^{-1} and absorption maxima at 441 nm (Figure S19) in the UV-vis spectrum was isolated (48% yield). This result demonstrates that the color of the polymers was due to the electronic transitions in the N–S backbone and had little dependence on the identity of the groups used in their synthesis.

3.5. TGA of Selected Polymers. The polymers were synthesized under N_2 but handled under atmospheric conditions. ^1H NMR spectra of the polymers showed no decomposition even after 8 months of storage at room temperature under atmospheric conditions. The thermal decomposition properties of polymers B and D were studied using TGA (Figure 8). It was found that the onset of decomposition started at 141 °C for B and 126 °C for D. The residual mass was 21% for B and 10% for D. The higher residual mass for B was likely due to the presence of the Cl atoms.

3.6. Density Functional Theory (DFT) of PolyNAS. We performed DFT calculations to investigate the electronic structure of the polyNAS. To obtain geometries for our calculations, a crystal structure for polythiazyl (SN) ∞ was used as a starting point.⁶³ Methyl groups were added to the backbone at the nitrogen atoms to model the octyl groups in polymer I and the minimum-energy geometry (Figures 9 and S34–S36) was found using periodic DFT from the Vienna Ab initio Software Package (VASP 6.3).⁶⁴ The following calculation parameters were used: a PBE0 functional,⁶⁵ a 2x2x4 k-point mesh, and 1.3 times the default cutoffs from the potential files. As the crystal structure was not known, further calculations were performed on an oligomer with 12 repeat units with end groups of –NH using a molecular density functional theory package (Q-Chem 5.3),⁶⁶ with common calculation parameters of a B3LYP⁶⁷ functional with a D3 correction and 6–31G(d,p) basis set. To corroborate the findings from periodic DFT, the difference between single point and relaxed geometries was considered, as well as the difference between the methyl and phenyl groups (to model polymers I and D, respectively). Comparison was made with calculations on polythiazyl as a control as this has been well studied. Preliminary calculations showed that the same trends existed for polymer D as for the methyl model, so we focused our attention on the methyl model as these calculations had fewer atoms and ran faster.

We found common structural motifs in the simulations (Table 5). In each case, the average S–N bond length was 1.70–1.72 Å, which was slightly longer than the S–N bond in polythiazyl. This result was expected since polythiazyl has sulfur–nitrogen double bonds in its important resonance structures. The nitrogen centers were found to be trigonal planar with slight out-of-plane distortion (average SNS = 114–124°) indicating sp^2 hybridization and lone pair conjugation. This result was important because the polyNAS with methyl amine would be expected to have SNS bond angles close to 109° with N as sp^3 hybridized if it was not in conjugation with the sulfur atoms in the backbone, but the SNS was close to 120°, which indicated that the resonance structures in Figure 6b are important. The average NSN bond angle at the sulfur

Table 3. Elemental Analyses of the Composition of Polymers B, C, D, E, and F as an Average ($n = 2$)^a

elements	Polymer									
	B		C		D		E		F	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
C	38.13	36.21	45.38	42.42	56.54	55.11	59.18	58.01	63.26	60.05
H	1.84	1.96	2.67	2.73	4.04	4.37	4.99	5.03	6.44	6.68
N	8.00	9.50	9.62	10.08	11.99	12.31	10.90	10.82	9.21	10.04
S	18.30	20.23	22.02	23.51	27.44	28.21	24.94	26.14	21.09	23.23
S/N	2.28	2.12	2.28	2.33	2.28	2.29	2.28	2.41	2.28	2.31

^aNumbers are percent composition by mass.

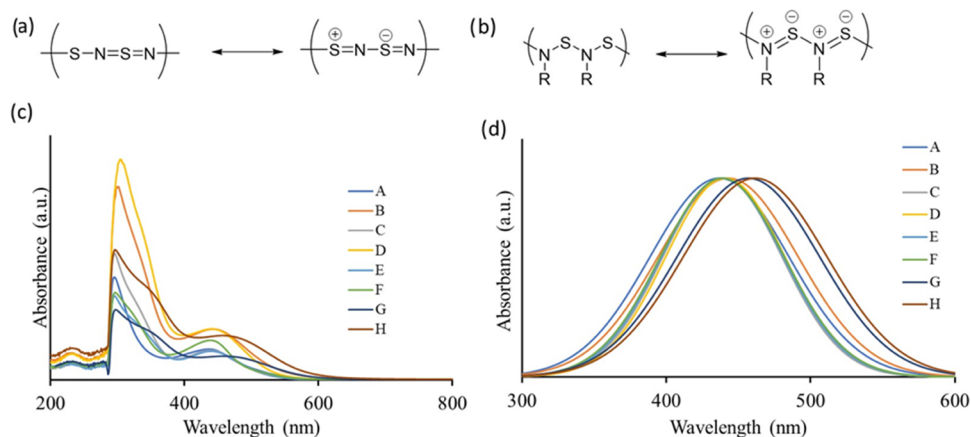


Figure 6. (a) Two resonance structures of polythiazyl are shown to illustrate that the backbone is conjugated. (b) Two resonance structures of the polyNAS are shown to illustrate that the backbone is conjugated. (c) UV-vis spectra of polymers A–H. (d) Normalized peaks from the peak fitting for polymers A–H.

Table 4. Visible Absorption Maxima of PolyNAS (A–H)

Poly-NS	wavelength maxima (nm)
A	437
B	444
C	442
D	447
E	443
F	445
G	457
H	462

center was 104–107°, which closely resembles our calculations for polythiazyl; however, there were differences in the backbone seen in the periodic DFT calculations. Relative to polythiazyl, which is planar at the sulfur center, the backbone of poly[(N,N-methylamine)sulfide] is nonplanar at the sulfur center resulting in the nitrogen centers being pushed down relative to the plane. The result is a similar zig-zig-zag-zag pattern to polythiazyl with all of the sulfur atoms in one plane but with none of their bonds in the plane (Figures S34–S36). The atomic Mulliken charges in atomic units were found to be 0.4 and 0.6 at the S centers and −0.6 to −0.7 at the N centers and show strong similarity between polythiazyl and poly[N,N-(methylamine)sulfide]. Additional molecular DFT calculations showed similar structural characteristics except that the backbone did not form a straight chain, and examples of this are presented in the Supporting Information.

We simulated the UV/Vis spectra of the molecular oligomer model for poly[N,N-(methylamine)sulfide] using excitation energies from time-dependent density functional theory (TDDFT) in Q-Chem. These were performed in a 6–31G(d,p) basis set using B3LYP, PBE,⁶⁸ PBE07,⁶⁹ and LC- ω PBE;⁷⁰ we found the first 20 excited states. All calculations had a wide range of UV absorbances consistent with experimental data (Figure 6cd); they also had additional distinct peaks at higher wavelengths coming from excitations

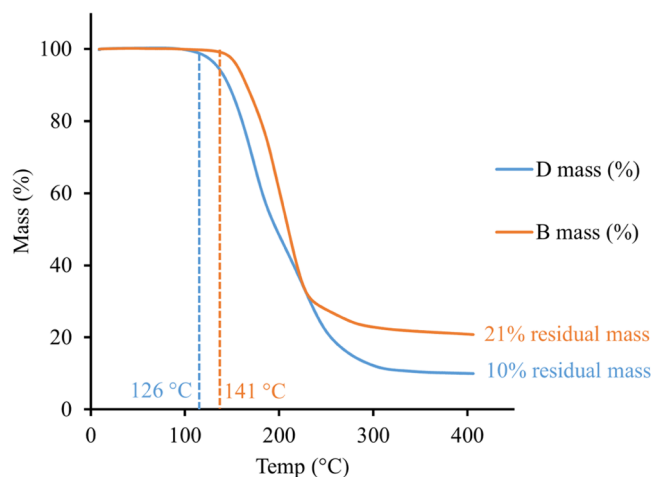


Figure 8. TGA of polymers B and D. The onset temperatures and residual mass after thermal degradations are labeled.

between multiple frontier molecular orbitals localized to the S–N backbone. However, these peaks had a strong functional dependence and varied between 265 and 471 nm (Table S1). Inspection of the HOMO and LUMO showed that they were delocalized across the backbone but not the whole backbone (instead 3–6 repeat units out of 12). The strong functional dependence and delocalization pattern is strongly indicative of a charge transfer excitation, which means that the UV/Vis spectrum is more challenging to model correctly with TDDFT. As such, the level of agreement achieved in our calculations is considered typical.

3.7. Sensors Based on Reactions of the NS Backbone.

The polymers were all red, but they had differences in the aromatic or alkyl groups attached to the amines that could affect their stabilities to various chemicals. To explore the chemical sensing properties of these polymers, solutions of polymer D (3 mg/mL) in THF were exposed to excess 50

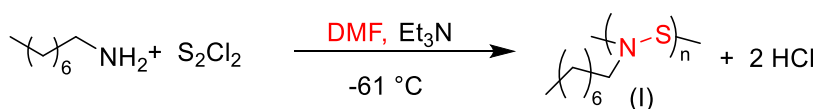


Figure 7. Synthesis of Poly[(N, N-octylamino)sulfide].

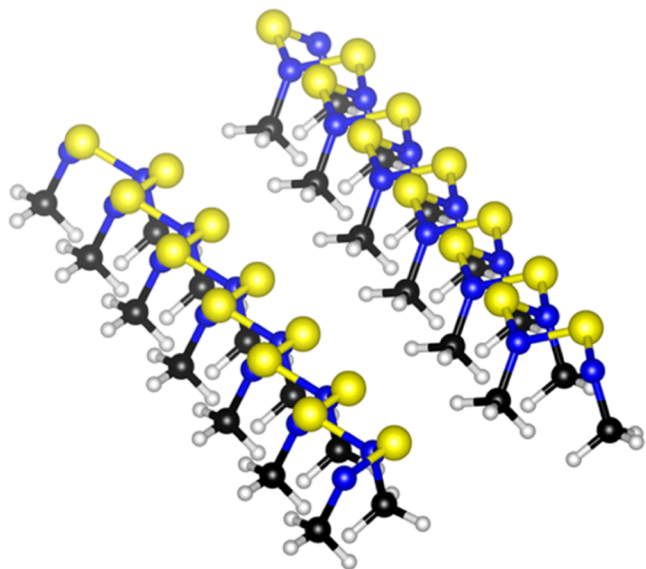


Figure 9. Optimized structure of poly[(*N,N*-methylamine)sulfide] from periodic DFT.

equivalents of 1-propylamine (a), ethanoic acid (b), and 2-mercaptoethanol (c) separately at room temperature. The polymer solution did not change its color when exposed to ethanoic acid but changed slowly with 1-propanamine and rapidly changed with 2-mercaptoethanol (Figure 10).

To test the responsiveness of different polyNAS to 2-mercaptoethanol, polymers B, D, F, and I were exposed to 2-mercaptoethanol (Figure 11). The polymers were dissolved in THF at the same concentrations (3 mg/mL) and then 50 equiv of 2-mercaptoethanol were added to each vial. Images of the vials were taken before the addition and after 5, 15, and 45 min. The change in color for polymer D was observed within a minute, and all of the solutions were nearly clear by 45 min of addition of 2-mercaptoethanol except I.

The kinetics of reaction between polymers B, D, F, I, and 2-mercaptoethanol in THF were investigated by UV–vis spectroscopy at room temperature (Figure 12). The polymers were dissolved in THF, and an excess amount of 2-mercaptoethanol (N–S bonds in polymer: 2-ME = 1:50) was added. UV–vis spectra were collected periodically. The molar absorptivity (ϵ) was calculated for each polymer using the absorbance maxima of the polymer solution of known concentration, which subsequently was used to calculate the concentrations of the solutions at different time intervals to calculate the rates of the reactions. The concentration vs time plots for polymers B, D, F, and I and excess of 2-

mercaptoethanol showed that the reactions followed pseudo-first-order reaction kinetics (Figures S22–S25).

The reaction rates and half-lives of the reactions were also calculated from the kinetics plots, and it was found that polymer D had the shortest half-life in the presence of excess 2-ME (Table 6). The half-lives of reactions between 2-ME and polyNAS synthesized from aniline or aniline derivatives were similar and varied by approximately 5x, but the reaction between polymer I and 2-ME was significantly slower. The degradation of this polymer was over 110x slower than the other polymers. These results demonstrate that the degradation of the polymers is affected by the groups attached to the amines. In future work, we will explore the use of these polymers as sensors.

To investigate the products of these reactions, polymer C was reacted with an excess of 2-mercaptoethanol. Based on prior work, it was hypothesized that 2-mercaptoethanol degraded the polymer by the formation of the corresponding trisulfide and the release of the aniline-based monomer (Figure S39). The trisulfide would further react with excess 2-mercaptoethanol to yield hydrogen sulfide and disulfide. The reaction of polymer C and an excess of 2-mercaptoethanol was completed in a vial housed within a larger vial with a white lead acetate strip (Figure S40). The lead acetate strip turned black due to the release of hydrogen sulfide as expected from the reaction shown in Figure S39. The ^1H NMR spectrum of the products of the reaction showed the expected product of 4-chloroaniline, trisulfide, disulfide, and unreacted 2-mercaptoethanol (Figure S41). The reaction of these polymers with thiols provides a method to release hydrogen sulfide, which is actively studied as an important gasotransmitter.

4. CONCLUSIONS

A series of polyNAS were synthesized by the reaction of amines with S_2Cl_2 in DMF. The addition of S_2Cl_2 in DMF yielded a monosulfur reagent, likely to be SCl_2 , that reacted rapidly with aryl and aliphatic amines to yield polyNAS. Surprisingly, these polymers were all red despite the use of anilines and octylamine in their synthesis. In prior work with polymers synthesized using anilines bearing the repeat unit of NSS in their backbones, their colors strongly depended on the groups bonded to the nitrogen, and when an aliphatic amine was polymerized, the polymer was white. In this work, the polymers had a backbone repeat unit of NS that was conjugated and the color was nearly independent of the group on the nitrogen. Surprisingly, polymerization of octylamine yielded a red polymer. This work demonstrates a method to synthesize soluble, easily processed polymers based on polythiazyl that may have applications as sensors.

Table 5. Structural Characteristics of the PolyNAS Structures Modeled^a

system	Avg. S–N bond length (Å)	Avg S–N–S bond angle (°)	Avg N–S–N bond angle (°)	Avg Mulliken charges (a.u.)
poly[<i>N,N</i> -(methylamine) sulfide]	1.70–1.72	114–124	104–107	S 0.4 N –0.6
poly[<i>N,N</i> -(phenylamine) sulfide] (polymer D)	1.72	120	105	S 0.4 N –0.7
polythiazyl	1.60–1.63	122–123	105–106	S 0.6 N –0.6

^aRanges are presented when data were drawn from more than one calculation. The poly[*N,N*-(methylamine) sulfide] and polythiazyl data came from periodic and molecular calculations. The poly[*N,N*-(phenylamine) sulfide] data come from one molecular calculation.

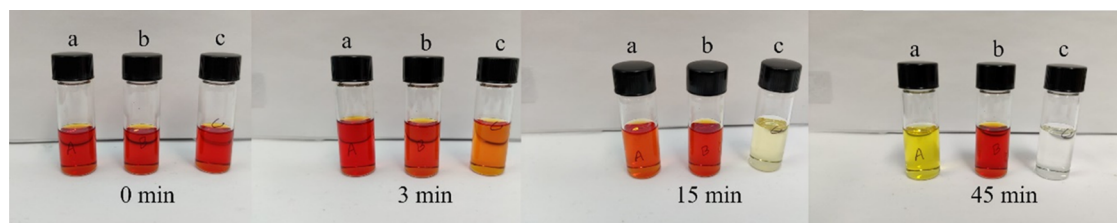


Figure 10. Photographs of reaction between solution of polymer D in THF with excess of 1-propanamine (a), ethanoic acid (b), and 2-mercaptoethanol (c) at room temperature.

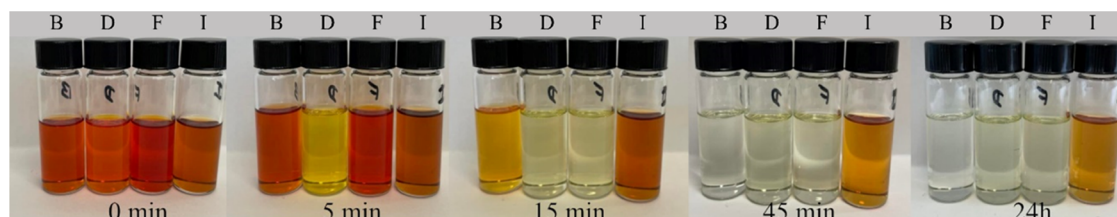


Figure 11. Photographs of reaction between polymers B, D, F, and, I, respectively, from left to right with 2-mercaptoethanol.

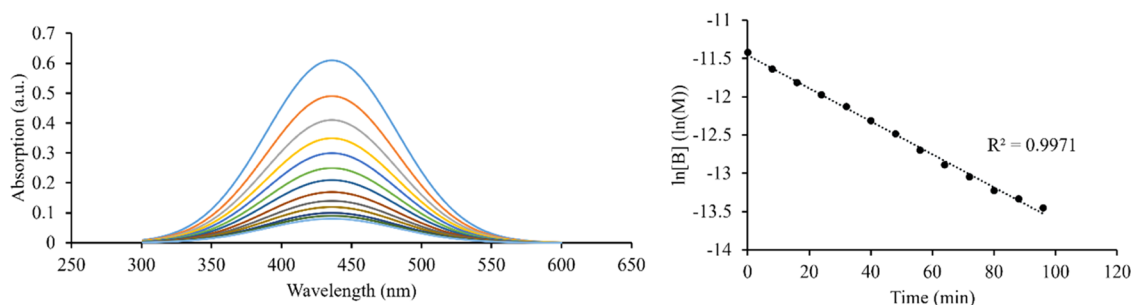


Figure 12. (a) Gradual decrease in absorbance max in the UV-vis absorption spectra of the reaction solution of polymer B and 2-ME. The tallest curve represents the polymer solution before any 2-ME was added. The subsequent UV-vis spectra collected at every 8 min after the addition of 2-ME. (b) Fit of the plot between the natural log of concentration of polymer B vs time.

Table 6. Rate Constants and Half-Lives for the Reactions between polyNAS and 2-ME

polymer	reaction rate	$t_{1/2}$ (min)
B	$2.16 \times 10^{-2} \text{ min}^{-1}$	31.5
D	$1.06 \times 10^{-1} \text{ min}^{-1}$	6.5
F	$4.95 \times 10^{-2} \text{ min}^{-1}$	14
I	$1.78 \times 10^{-1} \text{ day}^{-1}$	3600

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c02507>.

UV-vis spectra of the polymers, ^1H NMR spectra of the polymers, optical photo of red polymers, kinetics of degradation of polymers in 2-mercaptoethanol, RI and MALLS of the polymers, structures of polyNAS by computation, synthesis of oligomeric polyNAS, and degradation of polymers using 2-mercaptoethanol (PDF)

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Notes

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