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Synthesis, Characterization, and Theoretical Analysis of Soluble Poly(oxothiazenes): The Ambient Temperature Lewis Acid Catalyzed *in Situ* Polymerization of *N*-Silylsulfonimidoyl Chlorides

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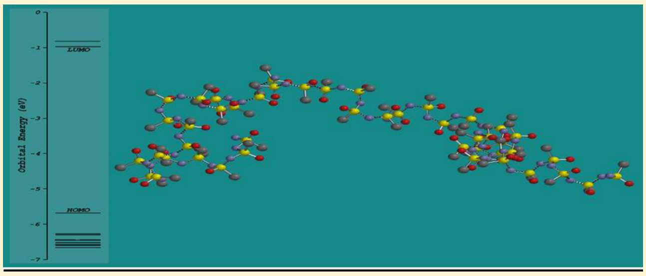
Supporting Information

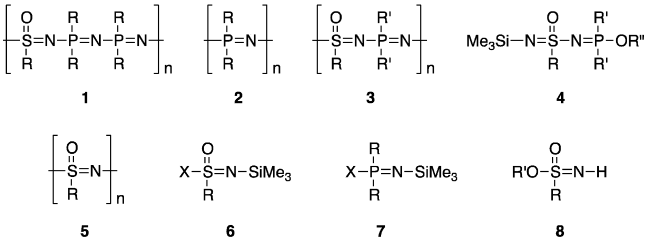


ABSTRACT: The ambient temperature condensation, to yield low molecular weight poly(methyloxothiazene) (M_w = 1 × 10^4; PDI = 1.4), can be achieved by the reaction of $MeS(O_2)NHSiMe_3$ and $SOCl_2$—this latter reaction being performed in an attempt to isolate ClSMe(O)$NSiMe_3$ (**6a**). The *in situ* addition of a Lewis acid initiator (e.g., PCl_5) to freshly prepared samples of *N*-silylsulfonimidoyl chlorides (ClSR(O)$NSiMe_3$, **6a−d**, R = Me, Et, Ph, *p*-C_6H_4Me) yielded high molecular weight, narrowly dispersed polymers, **5a−d** (M_w = 6.7 × 10^4−3.3 × 10^6; PDI = 1.2−1.6) of general formula $[RS(O){=}N]_n$. These materials have been characterized by GPC, NMR (^1H, ^{13}C) spectroscopy, and DSC. UV−vis spectroscopy of CH_2Cl_2 solutions of **5a−d** reveal a high-energy $\pi-\pi^*$ transition (λ_{max} = 300−350 nm) that tails into the visible. Additionally, theoretical modeling of oligomeric (methyloxothiazenes) at either a semiempirical, Hartree−Fock, or DFT level of theory suggests that these polymers adopt an irregular helical architecture.

■ INTRODUCTION

Sulfur-containing main group polymers comprise a diverse number of heterochain polymers, including but not exclusively limited to polythiophenes,[1a,b] sulfur-containing polyarylenes,[2a,b] poly(sulfur nitride)s,[3a,b] polythiophosphazenes,[4] polythionylphosphazenes,[5a,b] and poly(oxothiazene)s.[6a−d] These polymers possess a variety of unusual and interesting properties that are useful for applications in photonics[1a] and conductive electronic materials[7] and as matrices for barometric oxygen sensors.[8] A subset of these sulfur-containing polymers includes the high oxidation state $[RS^{VI}(O){=}N]_n$ unit: whole or in part of the main group polymer backbone. The most extensively studied $[RS^{VI}(O){=}N]_n$ polymers within this class are the polythionylphosphazenes **1** (R = Cl: Chart 1), first reported by Liang and Manners in 1991.[5a] These polymers are accessed from the thermal ring-opening polymerization (ROP) of cyclic thionylphosphazenes and consist of a repeat unit of one S(VI)═N link for every two $R_2P{=}N$ units. As with the halogenated polyphosphazenes (**2**, R = Cl: Chart 1), the chlorine atoms of these polymers are substitutionally liable and can replaced with aryloxy or amino substituents; this typically yields materials with modest molecular weights but relatively narrow PDI's (3.3 × 10^4−1.5 × 10^5 Da, PDI: 1.4−3.1). The T_g values for polythionylphosphazenes were generally observed to be lower than their polyphosphazene analogues; these materials therefore have macromolecular properties that range from gums to glasses. Turner *et al.* reported on the successful preparation of linear, low molecular weight alternating copolymers **3** (M_n = 8000 g/mol) (e.g., R, R′ = Me) of phosphazene ($R'_2P{=}N$) and oxothiazene (RS(O)═N) units. These compounds are made thermally by the self-condensation reaction of *N*-silylthionylphosphazene monomers **4** (e.g., OR″ = OCH_2CF_3, R, R′ = Me: Chart 1).[9] Poly(alkyl/aryloxothiazenes) (**5**: Chart 1) are polymers with an alternating sulfur(VI)−nitrogen backbone and represent an underdeveloped class of polymers with structures that are presumably analogous to the industrially important polyphosphazenes (**2**). As with **2**, the physical and chemical properties of **5** are determined largely by the nature of the side group (i.e., −R) that is covalently bound to the sulfur atoms of the main chain. However, only a very limited number of well-characterized poly(oxothiazenes) have been described

Chart 1



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in the literature.[6a−f] In the 1960s, poly(fluorooxothiazenes) and poly(aminooxothiazenes) had been reported as the products formed by the condensation of $O{=}SF_4$ with ammonia.[10,11] Similarly, poly(phenyloxothiazene) has been reported from the condensation of either phenyl benzenesulfonimidate or *N,N*-dimethylarenesulfonimidamides.[12,13] Unfortunately, little characterization data were provided to support the suggested polymer architectures in either of these cases.

Some 20 years ago, Roy reported the development of a polycondensation route to polyoxothiazenes (**5**) from single source *N*-silylsulfonimidate (**6**, X = OCH_2CF_3, R = alkyl/aryl: Chart 1) precursors[6a,b] in a process involving the elimination of trimethylsilyl ethers. This route was modeled after the polycondensation pathway that can be employed in the synthesis of polyphosphazenes (**2**) from *N*-silylphosphoranimines (**7**, X = OCH_2CF_3, R = alkyl/aryl: Chart 1).[14] Alternatively, a higher yielding route to **5** can also be accessed via the elimination of alcohols from analogous polycondensations of free sulfonimidates (**8**).[6d] This latter seminal work provided the first unambiguous examples of high molecular weight poly(alkyl/aryloxothiazenes).[6a−f] The polycondensation of **6** (X = OCH_2CF_3, R = alkyl/aryl) or **8** (OR′ = OCH_2CF_3, Chart 1) does indeed lead to the successful preparation of a variety of high molecular weight examples of **5** (and hence enables characterization). There are, however, several limitations to this pathway. These limitations include the necessity for long reactions times (>96 h) at high reaction temperatures (up to 160 °C) even in the presence of Lewis acids catalysts.[6d] Such synthetic protocols invariably lead to a lack of molecular weight control (sometimes resulting in bimodal M_w distributions) and to high PDI values (up to 21).[6b] These same drawbacks were observed in the original polycondensations of **7**[14] or **8**.[6c] There are no known ring-opening polymerization (ROP) routes to poly(oxothiazenes) in contrast to the polyphosphazenes and polythionylphosphazenes, which can also be synthesized via the ROP of hexachlorotriphosphazene (i.e., $(N{=}PCl_2)_3$) or cyclic thionylphosphazenes (i.e., $N{=}S(O)X(N{=}PCl_2)_2$; X = Cl, F), by either thermal[15,5a] or Lewis acid catalyzed routes.[16,17] Indeed, α-sulfanic chloride, $[N{=}S(O)Cl]_3$, is known to simply exothermically decompose (250−285 °C)[18] while the fluorinated analogue remains stable at temperatures as high as 350 °C, and hence neither decomposes nor undergoes ROP.[19]

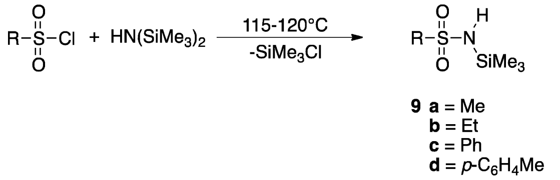
In 1995, Allcock and Manners reported the ambient temperature living polycondensation of *N*-trimethylsilyltrichlorophosphoranimine (**7**, X, R = Cl) via the elimination of Me_3SiCl in the presence of a Lewis acid catalyst (e.g., PCl_5).[20] Interestingly, Roy had earlier noted that during the attempted synthesis of the analogous *N*-trimethylsilylsulfonimidoyl chloride (**6a**, X = Cl, R = Me) by the treatment of *N*-silylchlorosulfonamide (**9a**) with PCl_5 or Ph_3PCl_2, a facile decomposition of **6a** at room temperature (RT) occurred with concomitant release of the same Me_3SiCl.[6c] This process results in the formation of a linear, oligomeric methyloxothiazene (**5a**). Since these earlier investigations, little new work in this area of main group polymer chemistry has emerged. Therefore, we have chosen to investigate the *in situ* Lewis acid catalyzed polycondensation of *N*-silylsulfonimidoyl chlorides as a potential novel reaction pathway which could address the limitations previously reported for the synthesis of these complex heteroatomic macromolecules.

RESULTS AND DISCUSSION

Preparation of *N*-Silylsulfonamides. As part of our efforts to identify improved routes to poly(oxothiazenes), a preliminary exploration of alternate synthetic approaches to the preparation of *N*-silylsulfonimidoyl chlorides was undertaken.[21] Manners has reported a high yield synthesis of **7** (X, R = Cl) using SO_2Cl_2 as both chlorinating and oxidizing agent; this results in SO_2(g) release during the chlorination process.[22] Using this approach as inspiration, we have chosen to explore an analogous route using $SOCl_2$ as a chlorinating source and oxygen atom scavenger (removing one oxygen atom from the sulfur atoms in *N*-silylsulfonamides), which could also result in the release of SO_2(g) and thus eliminate the need for external P(V) reagents during the chlorination process.

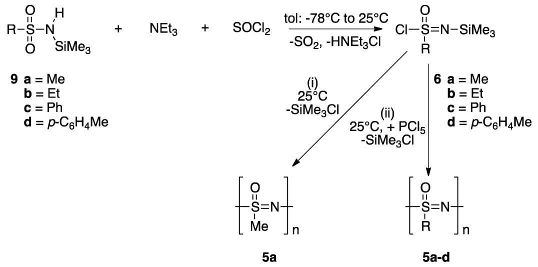
Following procedures described by Roy,[6c] a series of *N*-silylsulfonamides ($RSO_2{-}N(H)SiMe_3$, **9a−d**) were prepared (yields 73−91%) via the reaction of sulfonyl chlorides (R = Me (**a**), Et (**b**), Ph (**c**), *p*-C_6H_4Me (**d**)) with hexamethyldisilazane (Scheme 1). Although the previously reported *N*-silylsulfonamides have been described as materials best purified by vacuum distillation, it was found that recrystallization of *N*-silylmethylsulfonamide (**9a**) from a CH_2Cl_2/hexanes mixture (−30 °C) resulted in the formation of high quality, colorless, crystals.[23] A single crystal X-ray study of **9a** reveals an average S−N bond (1.601(2) Å) of intermediate length to that of a typical S−N (1.74 Å) single and double S=N bond (1.54 Å) length.[24] Full details of the structural aspects of **9a** can be found in our previous communication.[23]

Scheme 1



Preparation and *in Situ* Polymerization of *N*-Silylsulfonimidoyl Chlorides 6a−d. In an attempt to prepare **6a** using protocols devoid of phosphorus reagents, **9a** was treated with $SOCl_2$ in the presence of 3 equiv of NEt_3 (−78 °C) with the intention of chlorinating the sulfur center of the sulfonamide while simultaneously eliminating SO_2(g). NMR (^1H) analysis of the reaction mixture showed two singlet resonance signals (δ_H = 0.53 and 3.31 ppm: integration 3:1, respectively) consistent with the formation of **6a**. Further analysis showed that the integration ratio of the two resonance signals began to alter immediately after the solvent was removed or when the sample was stored in solution at RT for more than 2 h, indicative of the decomposition of the initially formed material. After the sample of **6a** was allowed to fully decompose, removal of the solvent *in vacuo* resulted in the isolation of a dark brown, viscous and tacky material. A subsequent precipitation of this crude material, by addition of a CH_2Cl_2 extracted mixture into Et_2O, results in the isolation of a solid displaying a singlet resonance signal (δ_H = 3.18 ppm) consistent with the formation of polymeric **5a**. Analysis of **5a** thus obtained (GPC: THF solution) supported the formation of a linear, low molecular weight material ($M_w = 1 \times 10^4$, PDI = 1.4). These data suggest that the decomposition of **6a** likely takes place via a polycondensation pathway (see Scheme 2, pathway i).

Scheme 2



Although storage of the solution at reduced temperatures (−35 °C) slowed the rate of this decomposition, all attempts to isolate the *N*-silylsulfonimidoyl chlorides (**6a**−**d**) from solution were unsuccessful. Therefore, the investigation of the polymerization of **6a**−**d** initiated *in situ via* the subsequent addition of a Lewis acid initiator to the above reaction mixture was undertaken. Consequently, a catalytic amount of PCl_5 (0.5 mol %) was added to freshly prepared **6a** (toluene: 25 °C) and the resulting solution stirred at RT until the solution had turned dark brown in color. NMR (^1H) analysis of this mixture revealed that within 2−3 h **6a** cleanly converts to polymer **5a** (δ_H = 3.18 ppm) accompanied by the formation of the condensation byproduct, Me_3SiCl. A light brown material was isolated after removal of the volatiles *in vacuo* and subsequent precipitation of the solids by the addition of a CH_2Cl_2 solution of the crude products into Et_2O, followed by aqueous extraction of salts. The thus isolated **5a** was found to be THF soluble, of high molecular weight, and narrowly dispersed (M_w = 3.3 × 10^5; PDI: 1.2; see Table 1). These data are in contrast to the reported properties of polymeric **5a** prepared by higher temperature condensation processes,[6d] notably their low solubility except in very polar solvents (e.g., DMF).

Table 1. Comparison of Molecular Weight and T_g's of Poly(oxothiazenes) Formed from Different Condensation Routes

polymer	M_w	PDI	T_g, °C	monomer
5a[6d]	4.8 × 10^5	9.0	55−65	**6** (X = OR, R = Me)
5a[6d]	5.0 × 10^4	4.2	55−65	**8a** (R = Me)
5a[a]	1.0 × 10^4	1.2		**6a**
5a[a]	3.3 × 10^5	1.2	41	**6a**
5b[6d]	2.1 × 10^5	7.4	29	**6** (X = OR, R = Et)
5b[a]	6.7 × 10^4	1.6	33	**6b**
5c[6d]	3.0 × 10^5	1.3	86	**8c** (R = Ph)
	2.4 × 10^4	1.3		
5c[a]	1.0 × 10^5	1.3	32	**6c**
5d[a]	8.5 × 10^4	1.4	55	**6d**

[a] This work.

The above protocols were repeated for additional alkyl- and aryl-substituted *N*-silylsulfonimidoyl chlorides (R = Et (**b**), Ph (**c**), *p*-C_6H_4Me (**d**)) in order to investigate whether this pathway could also be used as a more general route to poly(oxothiazenes). These monomers were observed to decompose if they are set aside at ambient temperature. In each case, fresh samples of **6b**, **6c**, and **6d** were prepared (−78 °C) *via* the treatment of the corresponding sulfonamide (**9b**−**d**) with $SOCl_2$ followed by the addition of 0.5 mol % of PCl_5. ^1H NMR spectroscopy was employed in all cases to monitor these reactions. In each case, high molecular weight materials with relatively narrow polydispersities could be isolated (see Table 1).

DSC analysis of the resulting materials revealed differences in the properties of the polymers formed at ambient temperature when compared to those synthesized previously at elevated temperatures. In the case of **5a**, the observed T_g (41 °C) is significantly lower than the corresponding material formed at >140 °C (T_g = 55−65 °C).[6d] It is possible that this difference reflects a variance in the tacticity of the polymers formed by the two different methods, which would result in different packing effects in the two materials. Alternatively, the differences in T_g may be related to the differences in the molecular weight distributions that arise from the different synthetic approaches. Poly(ethyloxothiazene) **5b** exhibits a T_g of 33 °C, which is consistent with the expected trend from chain packing effects. Interestingly, substitution of the methyl group with aromatic side chains results in a similar decrease (**5c**: T_g = 33 °C), which is in stark contrast to the complementary material made from sulfonimidates.[6d] In this latter situation, a 20−30 °C increase in T_g values is observed between the corresponding polymers.[1] Curiously, the T_g of 55 °C observed for poly(*p*-tolyloxothiazene) **5d** is greater than that observed for **5c**, suggesting that, along with the chain packing effects, other factors (such as potential differences in tacticity) may be playing significant roles in determining the T_g of the final materials. No endothermic transitions have been observed during DSC analysis of the materials, suggesting the absence of cyclic oligomeric species contained within these polymers that have been isolated from the ambient temperature process.

Electronic Properties of Poly(oxothiazenes). In all cases, brown powder or gums of the poly(oxothiazenes), **5a**−**d**, were recovered. UV−vis spectroscopic analysis of **5a**−**d** (Figure 1 and Table 2) reveals two distinct λ_{max} absorptions. A higher energy transition is found in the UV region (215−260 nm) and a second lower energy transition (321−360 nm) that tails into the visible region in all cases. A notable red shift (≈30

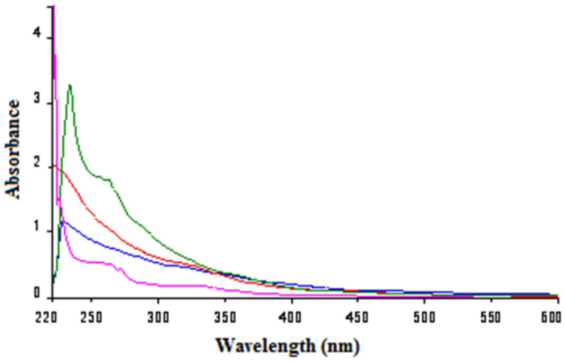


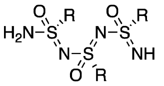
Figure 1. UV−vis spectroscopic analysis of poly(oxothiazenes): (red) **5a**, (blue) **5b**, (pink) **5c**, (green) **5d**.

Table 2. Comparison of the Electronic Transitions in Poly(oxothiazenes) 5a−d

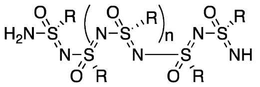
polymer	λ_{max1}, nm (ε, L mol^{-1} cm^{-1})	λ_{max2}, nm (ε, L mol^{-1} cm^{-1})
5a	215 (2067)	321 (512)
5b	229 (1174)	324 (444)
5c	259 (539)	325 (179)
5d	262 (1834)	360 (300)

nm) of the lower energy transition is observed for poly(oxothiazenes) with the *p*-tolyl substituent (**5d**) compared to their alkyl analogues (**5a**, **5b**). The possibility of an inorganic chromophore originating from the S(VI)−N backbone arising from either delocalized π-bonding or through highly polarized bonds (analogous to polarized P−N bonds observed in cyclic phosphazenes)[25] is intriguing. This would suggest that the "island model", with distinct alternating double bonds in the polymer backbone put forth by Manners *et al.*[26] for polythionylphosphazenes (**1**), is not operating here. Supportive evidence for greater multiple bond character or polarization of bonds along the polymer backbone in poly(oxothiazenes) is indicated from the theoretical treatment of larger linear oxothiazene oligomers (see next section) where S−N bond lengths are found to be intermediate between known S−N single and S═N double bond values.

Theoretical Treatment of Model Compounds and Small Oligomers. A previous theoretical treatment of an oxothiazene trimer fragment, **10a**, to determine conformation and other structurally useful information, was carried out by Roy *et al.* over 15 years ago. These Hartree−Fock (HF) calculations were performed at the 3-21G* level of theory. As was shown for both the poly(dihalophosphazenes) (NPX_2, where X = F, Cl, Br) and sulfur(IV) polymers of formula $(SN)_x$, this analysis suggested that the preferred stable structural confirmation is that of a *trans*−*cis* conformer adopting a helical rather than a planar structure. This latter effect serves to minimize the interactions between adjacent methyl groups in the case of **10a** (below). The alternating idealized S−N "single" and "double" bond lengths for the central $[CH_3S(O)N]_n$ unit were calculated to be 1.60 and 1.56 Å, respectively. An unusually small bond angle for the N−S−N fragment (103°) was calculated for the trimer, a value much smaller than that for an equivalent bond angle for the N−P−N fragment (120°).[27]



10 a-c a = Me, b = Et, c = Ph



11 (n = 5), **12** (n = 7), **13** (n = 10) **a-c**

We have revisited the same simple model system $[CH_3S(O)N]_n$ and a number of other sulfur(VI) model compounds using improved computational tools with the hopes of addressing any uncertainties from the previous calculations and to further probe any intriguing electronic and structural properties of these materials. Two structurally characterized monomeric model compounds were used to access the validity of the computational methods as reasonable predictors of their respective structure and properties. The model compounds are *N*-(trimethylsilyl)methanesulfonamide[23] and naturally occurring methionine sulfoximine.[28] Details on these materials can be found in the Supporting Information. To summarize, the two model compounds gave acceptable structural data parameters at the B3LYP/6-31G* level of DFT from structures that were initially optimized *via* semiempirical (PM6) calculations. The former level of computational sophistication was thereafter employed in a theoretical treatment of the methyl oxothiazene containing 7, 25, and 50 repeating monomer units. The calculated bond lengths, bond distances, and bond angles for selected oligomer structures are found in Table 3 in addition to the Supporting Information. Our objectives in carrying out these calculations included two primary goals. First, a large polymer (>20 monomer units) structure would give one some insight as to the structural nature of the polymeric chain. Indeed, Figures S14, S15, and S17 display the calculated structures of a 25- and 50-unit Me-derived poly(oxothiazene). The helical nature of the materials, as suggested previously, is not contradicted by these data. A second objective was to estimate the degree of possible electronic connectivity along the polymer backbone by calculating the energies and locations of the various HOMO/LUMOs and their respective band gap energies and hence evaluate the possibility of any significant orbital delocalization along the polymer chains. Unfortunately, such calculations are often hampered by "end-group" effects in which the HOMO and LUMO tend to be found at opposite ends of the polymer or short-chain oligomeric chain (Figure S11). This aspect has been noted in earlier calculations of inorganic polymers.[6d,23,29−34] Despite these limitations, the calculated 7-monomer unit methyl-based oligomer suggests some electronic delocalization along the backbone, although the end-group effects are still noteworthy within the compounds examined from a theoretical perspective here (see Supporting Information, pp S-3 to S-15). This effect is also clearly denoted in a potential radical cation, in which the SOMO is delocalized over several atoms (Figure S13). Time-dependent-DFT (TD-DFT) calculations run on model linear oligomers predict that the higher energy transitions observed in the UV−vis spectra of **5a**

Table 3. Calculated Bond lengths, Bond Distances, and Bond Angles for Model Oxothiazenes

compound	S═N[a] (Å)	S−N[a] (Å)	C1···C1[a] (Å)	SNS[a] (deg)	NSN[a] (deg)
10a[b]	1.56	1.60		123.5	103
10a[c]	1.578	1.66	5.200 (NH_2), 4.909 (NH)	120.17 (NH_2), 118.73 (NH)	109.73
11a Me (*n* = 5)	1.592	1.662	5.200 (NH_2), 4.909 (NH)	117.18 (NH_2), 125.96 (NH)	113.23
12a Me (*n* = 7)	1.604	1.640	4.592 (NH_2), 4.782 (NH)	127.35 (NH_2), 118.81 (NH)	97.56 (NH_2), 104.97 (NH)
13a Me (*n* = 10)	1.624 (NH_2), 1.637 (NH)	1.610 (NH_2), 1.613 (NH)	4.797	118.83	114.67
10b Et (*n* = 3)	1.581	1.676	4.780 (NH_2), 4.999 (NH)	122.85 (NH_2), 123.56 (NH)	114.80
11b Et (*n* = 5)	1.591	1.657	4.952 (NH_2), 5.024 (NH)	124.83 (NH_2), 122.48 (NH)	104.91
11c Ph (*n* = 5)	1.577	1.650	4.896 (NH_2), 5.246 (NH)	123.93 (NH_2), 130.16 (NH)	105.90

[a] Central bond or central bond angle (NH or NH_2 indicates the values for the first bond length and bond angle for the given category observed on the corresponding side of the oligomer relative to the central atom or bond as appropriate). [b] Roy. [c] This work.

likely corresponds to the excitation of electrons from the HOMO to the LUMO+3.

In addition, there is little variation within the calculated bond lengths for the S═N and S−N bonds represented in the central units of the linear oligomers (<0.1 Å for compounds **10−13**, see Table 3) and the values (1.577−1.66 Å) are all intermediate between those of typical S═N double bonds and S−N single bonds as noted earlier.[24] These same trends are also demonstrated for the larger 25- and 50-monomer unit polymers (Supporting Information, pp S-16 to S-22). However, TD-DFT calculations for **12a** (and shorter oligomer species; see Supporting Information pp S-23 to S-26) reveal average atomic charges on sulfur (+1.20) and nitrogen (−0.717) atoms that suggest one electron has been formally transferred from S to N, consistent with the presence of highly polarized σ bonds that have been contracted by electrostatic interactions rather than through delocalization. Further discussions of the calculated monomers, oligomers, and various side-chain polymers will be the subject of a later publication.

■ CONCLUSION

A new condensation route to high molecular weight poly(oxothiazenes) from the Lewis catalyzed *in situ* polymerization of *N*-silylsulfonimidoyl chlorides has been described. The properties of the poly(oxothiazenes) prepared by this method differ markedly from materials prepared from the high-temperature condensation reactions involving *N*-silylsulfonimidates or silyl-free analogues. In particular, these polymers prepared by the *in situ* route are more narrowly dispersed, have good solubility in both polar and apolar solvents, and express unique thermal behavior. Molecular modeling of oligomers of **5a−d** suggests that the polymers adopt a defective helical structure, and a theoretical treatment (DFT 6-31G*) of short chain **5a** species (up to $[\mathrm{MeS(O)}{=}\mathrm{N}]_{50}$) suggests that a zwitterionic model may best describe the S−N bonding along the main chain.

■ EXPERIMENTAL SECTION

Materials and General Procedures. All reagents and solvents were obtained from commercial sources and used without further purification unless noted. Hexanes, toluene, THF, and Et_2O were dried using an MBraun solvent purification system. ^{1}H NMR (400 MHz), ^{13}C NMR (100.6 MHz), and ^{29}Si NMR (79.5 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances, while ^{29}Si NMR was referenced to external TMS. All experiments were performed under inert atmosphere conditions (N_2) using an MBraun glovebox or Schlenk techniques. Synthesis of *N*-silylsulfonamides was adapted from the procedures reported by Roy.[6c]

Molecular modeling calculations were performed using the Spartan 10.0 suite of programs.[36] Initial geometric minimizations were carried out using the (semiempirical) PM6 level of theory. These optimized geometries were then used as a starting point for DFT calculations at the B3LYP/6-31G* level of theory.[37,38] Zero point energy (ZPE) calculations were performed on all materials with the exception of the 25- and 50-unit methyl side chain polymers due to computational restrictions. The defective helical nature shown in this example was arrived at from the optimization of an essentially linear starting point and allowing convergence *via* a nonsymmetrical restricted basis. These data suggest that the helical array shown is a potential low *E* conformation of such macromolecules. TD-DFT was performed on optimized structures after zero point energy calculations had been confirmed. Calculations where performed with the B3LYP method in the 3-21G* basis set.[35]

Synthesis of *N*-Silylmethylsulfonamide, 8a. Methanesulfonyl chloride (7.00 mL, 103 mmol) was added under an inert N_2 atmosphere to a three-neck round-bottom flask equipped with a magnetic stirring bar, gas inlet, reflux condenser, and rubber septa. Hexamethyldisilazane (20.0 mL, 103 mmol) was added dropwise, at RT over a 10 min time period, with stirring. The flask was then placed into an oil bath, and the reaction mixture heated to between 90 and 100 °C. The temperature of the oil bath was then increased to between 115 and 120 °C (2 h), and the mixture thus refluxed at this temperature. This mixture was then allowed to cool to RT, and all the volatiles were then removed *in vacuo*. The resulting crude white colored powder was recrystallized from a CH_2Cl_2/hexane (1:1) mixture producing white crystals (yield =15.6 g, 91%). X-ray crystallographic analysis of the crystals was consistent with the proposed structure of the product.[23] NMR data were also consistent with data previously reported by Roy.[6c]

***N*-Silylmethylsulfonamide, 8a.** ^{1}H NMR ($CDCl_3$) δ (ppm): 0.32, (s, 9H, Me_3Si), 3.02 (s, 3H, Me-S), 4.27 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.047 (Me_3Si), 44.36 (Me−S). ^{29}Si NMR ($CDCl_3$) δ (ppm): 10.40 (s, Me_3Si).

Synthesis of *N*-Silylethylsulfonamide, 8b. Ethanesulfonyl chloride (0.53 mL, 5.5 mmol) was added under an inert N_2 atmosphere to a three-neck round-bottom flask equipped with a magnetic stirring bar, gas inlet, reflux condenser, and rubber septa. Hexamethyldisilazane (1.15 mL, 5.52 mmol) was added dropwise, at RT over a 10 min time period, with stirring. The flask was then placed into an oil bath, and the reaction mixture was heated to between 90 and 100 °C. The temperature of the oil bath was then increased to between 115 and 120 °C (2 h), and the mixture was refluxed at this temperature. This orange-colored mixture turned dark brown during reflux before being allowed to cool to RT, and all the volatiles were then removed *in vacuo*. The crude product was further purified using a reduced pressure distillation at 96 °C/0.06 mmHg to give a brown oil (yield = 0.82 g, 82%). NMR data were consistent with data previously reported by Roy.[6c]

***N*-Silylethylsulfonamide, 8b.** ^{1}H NMR ($CDCl_3$) δ (ppm): 0.25, (s, 9H, Me_3Si), 1.33 (t, 3H, $\underline{\mathrm{CH_3}}$−$CH_2$−S), 3.00 (q, 2H, CH_3−$\underline{\mathrm{CH_2}}$−S), 4.88 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.035 (Me_3Si), 8.63 ($\underline{\mathrm{C}}H_3$−$CH_2$−S), 50.20 ($CH_3$−$\underline{\mathrm{C}}H_2$−S). ^{29}Si NMR ($CDCl_3$) δ (ppm): 9.83 (Me_3Si).

Synthesis of *N*-Silylphenylsulfonamide, 8c. Benzenesulfonyl chloride (0.56 mL, 4.4 mmol) was added under an inert N_2 atmosphere to a three-neck round-bottom flask equipped with a magnetic stirring bar, gas inlet, reflux condenser, and rubber septa. Hexamethyldisilazane (1.0 mL, 4.8 mmol) was added dropwise at RT, over a 10 min time period, with stirring. The flask was then placed into an oil bath, and the reaction mixture was heated to between 90 and 100 °C. The temperature of the oil bath was then increased to between 115 and 120 °C (2 h), and the mixture was thus refluxed at this temperature. This mixture was then allowed to cool to RT, and all the volatiles were then removed *in vacuo*. The crude product was further purified using a reduced pressure distillation at 100 °C/0.06 mmHg to give a colorless liquid (yield = 0.90 g, 89%). NMR data were consistent with data previously reported by Roy.[6c]

***N*-Silylphenylsulfonamide, 8c.** ^{1}H NMR ($CDCl_3$) δ (ppm): 0.26 (s, 9H, Me_3Si), 4.69 (br, 1H, NH), 7.64 (t, 2H, *m*-Ph, J_{op} = 4.0 Hz), 7.71 (t, 1H, *p*-Ph, J_{mp} = 7.6 Hz) 8.09 (d, 2H, *o*-Ph, J_{mp} = 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.13 (Me_3Si), 127.08 (*o*-Ph), 129.83 (*m*-Ph), 135.39 (*p*-Ph), 144.48 (*i*-Ph).

Synthesis of *N*-Silyltolylsulfonamide, 8d. Tolylsulfonyl chloride (0.76 g, 4.0 mmol) was added under an inert N_2 atmosphere to a three-neck round-bottom flask equipped with a magnetic stirring bar, gas inlet, reflux condenser, and rubber septa. Hexamethyldisilazane (0.85 mL, 4.0 mmol) was added dropwise at RT, over a 10 min period, with stirring. The flask was then placed into an oil bath, and the reaction mixture was heated to between 90 and 100 °C. The temperature of the oil bath was increased to between 115 and 120 °C (2 h), and the mixture was thus refluxed at this temperature. This mixture was then allowed to cool to RT, and all the volatiles were then removed *in vacuo*. The crude product was further purified using a reduced pressure distillation at 100 °C/0.06 mmHg to give a colorless liquid (yield = 0.71 g, 73%).

***N*-Silyltolylsulfonamide, 8d.** ^{1}H NMR ($CDCl_3$) δ(ppm): 0.14 (s, 9H, Me_3Si), 2.42 (s, 3H, $C\underline{H}_3$–Ph), 2.54 (s, NH), 7.44 (d, 2H; $C\underline{H}$=C–CH_3, J_{om} = 8 Hz), 7.98 (d, 2H; $C\underline{H}$=C–S, J_{om} = 8 Hz). ^{13}C NMR ($CDCl_3$) δ(ppm): 2.49 ($\underline{C}H_3$–Si), 21.80 ($\underline{C}H_3$–Ph), 127.05 (*o*-Ph), 130.22 (*m*-Ph), 141.73 (*i*-Ph-S), 146.58 (*i*-Ph–CH_3).

Attempted Synthesis of *N*-Silylmethylsulfonimidoyl Chloride, 6a. A solution of **8a** (0.194 g, 1.04 mmol) in toluene (ca. 25 mL) was prepared in a round-bottom flask equipped with a magnetic stirring bar, gas inlet, and rubber septum in an inert atmosphere. Et_3N (0.436 mL, 3.13 mmol) was added dropwise to the reaction mixture, resulting in the formation of a yellow suspension. The reaction mixture was cooled in a dry ice/acetone bath to −78 °C, and $SOCl_2$ (0.152 mL, 2.09 mmol) was added dropwise to the solution; the resulting mixture was stirred at this temperature for 2 h.

6a: ^{1}H NMR (reaction mixture at 2 h): ^{1}H NMR ($CDCl_3$) δ (ppm): 0.53 (s, Me_3Si, 9H), 3.31 (s, Me–S, 3H).

The cooling bath was subsequently removed, and the reaction mixture was warmed to room temperature which resulted in the formation of a dark brown color. Analysis of the reaction mixture by ^{1}H NMR of the nonvolatile components of the reaction mixture indicated that decomposition of **6a** occurs in solution when the sample is held at ambient temperature of −35 °C for periods of longer than 2−3 h. After removal of the solvent and volatile by products *in vacuo*, a tacky dark brown solid remained. The sample was purified by precipitation from CH_2Cl_2 to Et_2O three times yielding a tacky off-white powder, **5a**. GPC analysis of this powder showed that poly(methyloxothiazene) was one of the products of the decomposition.

5a: ^{1}H NMR ($CDCl_3$) δ (ppm): 3.18 ppm (s, 3H, Me–S); $(CD_3)_2SO$) δ (ppm) 3.54 (s, 3H, Me–S).

General Procedure for the *in Situ* Synthesis of Polyoxothiazenes. A solution of **8a** (0.748 g, 4.03 mmol) in toluene (ca. 40 mL) prepared in a round-bottom flask equipped with a magnetic stirring bar, gas inlet and rubber septum in an inert atmosphere. Et_3N (1.68 mL, 12.1 mmol) was added dropwise to the reaction mixture, resulting in the formation of a yellow suspension. The reaction mixture was cooled in a dry ice/acetone bath to −78 °C, and $SOCl_2$ (0.585 mL, 8.05 mmol) was added dropwise to the solution; the resulting mixture was stirred at this temperature for 60 min. The cooling bath was subsequently removed, and the reaction mixture warmed to room temperature, which resulted in the immediate formation of a dark brown color. A solution of PCl_5 (8.2 mg, 0.039 mmol) in toluene was added to the reaction mixture and the subsequently allowed to stir for 2 h. Solvent and impurities were removed *in vacuo*, yielding a gummy, brown product. The material was purified by precipitation from CH_2Cl_2 solution into Et_2O three times, resulting in a light brown powder (polymer yield: 0.29 g, 94%).

*Poly(methyloxothiazene), **5a**.* ^{1}H NMR ($(CD_3)_2SO$) δ (ppm): 3.54 (s, 3H, Me–S). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.18 ppm (s, 3H, Me–S). ^{13}C NMR ($CDCl_3$) δ (ppm): 43.20 (Me_3S). GPC data for **5a**: $M_w = 3.3 \times 10^5$; PDI = 1.2. DSC data for **5a**: T_g = 40.9 °C.

The same procedure was followed for the preparation of polymers **5b–d**, substituting **5b–d**, respectively. Additional precipitations were required to remove final traces of $HNEt_3Cl$, which has similar solubility properties to **5b–d**.

*Poly(ethyloxothiazene), **5b**.* Yield: 0.20 g (79%) based on **5b** (0.51 g, 2.8 mmol). ^{1}H NMR ($(CD_3)_2SO$) δ (ppm): 3.45 (Br, CH_3–CH_2–S). GPC data for **5b**: $M_w = 6.7 \times 10^4$, PDI = 1.6. DSC data for **5b**: T_g = 32.8 °C.

*Poly(phenyloxothiazene), **5c**.* Yield: 0.35 g, 81% based on **5c** (0.72 g, 3.1 mmol). ^{1}H NMR ($(CD_3)_2SO$) δ (ppm): 7.33–7.62 (m, Ar, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 126.28 (*o*-Ph), 128.14 (*p*-Ph), 128.85 (*m*-Ph), 132.16 (*i*-Ph-S). GPC data for **5c**: $M_w = 1 \times 10^5$, PDI = 1.3. DSC data for **5c**: T_g = 32.2 °C.

*Poly(p-tolyloxothiazene), **5d**.* Yield: 0.29 g, (84%) based on **5d** (0.54 g, 2.2 mmol). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.71 (d, Ar, 2H, J_{om} = 9.7 Hz), 7.14 (d, Ar, 2H, J_{om} = 9.7 Hz), 2.28 (s, $C\underline{H}_3$–Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.31 ($\underline{C}H_3$–Ph), 125.90 (*o*-Ph), 128.81 (*m*-Ph), 140.29 (*i*-Ph–CH_3), 141.78 (*i*-Ph–S). GPC data for **5d**: $M_w = 8.5 \times 10^4$; PDI = 1.4. DSC data for **5d**: T_g = 54.7 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of calculated structures and MOs for *N*-(trimethylsilyl)-methanesulfonamide model compounds; calculated .mol files for the model compounds are available from the authors upon request. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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