J. Am. Chem. Soc. 1993, 115, 2604–2612

Poly(alkyl/aryloxothiazenes): Inorganic Polymers with a Sulfur(VI)–Nitrogen Backbone. Synthesis, Characterization, and Theoretical Calculations

Aroop K. Roy,* Gary T. Burns, George C. Lie,† and Stelian Grigoras

Contribution from Central Research and Development, Mail Stop C043C1,
Dow Corning Corporation, Midland, Michigan 48686-0994

Received September 17, 1992

Abstract: *N*-Silylsulfonimidates [$Me_3SiN{=}S(O)(R^1)OR^2$, **3**] with appropriate R^2 groups have been found to undergo thermally induced condensation to produce the sulfur(VI)–nitrogen backbone polymers poly(alkyl- or aryloxothiazenes), $[N{=}S(O)R^1]_n$ **4** and **5**. Polymers **4** and **5** represent the first alkyloxothiazene polymers and the first characterized aryloxothiazene polymers. Modeled after the well-known condensation of *N*-silylphosphoranimines to poly(phosphazenes), the polycondensation of **3** to **4** appears to be a fairly general reaction. The design and novel synthesis of **3** are described in a companion article. The thermal condensation of **3** is catalyzed by Lewis acids and bases such as $BF_3{\cdot}Et_2O$, $AlCl_3$, fluoride ion, and phenoxide ion. Additionally, **3** can be quantitatively desilylated with methanol (without side reactions) to the "free" sulfonimidates [$HN{=}S(O)(R^1)OR^2$, **7**]. The free sulfonimidates, in turn, condense rapidly and quantitatively (at rates approximately two orders of magnitude faster and at temperatures 20 to 40 °C lower, than **3**) to poly(oxothiazenes). The polymers have been characterized by gel permeation chromatography, NMR spectroscopy, thermoanalytical methods, and by elemental microanalysis. Theoretical calculations indicate a cis–trans helical conformation for poly(methyloxothiazene) **4a** to be the most stable conformation. A major difference with phosphazene structure geometry is indicated by a near-tetrahedral N–S–N bond angle of 103°.

Introduction

During the second half of this century, the science and technology of synthetic polymers and materials has advanced by leaps and bounds. Most of these macromolecular systems are based on repeating skeletal units consisting primarily of carbon atoms. In contrast, only a few, well-developed synthetic polymer systems are known where the skeletal units are derived exclusively or essentially from inorganic elements. Of these, perhaps the most extensively studied are the poly(siloxanes)[1] and the poly(phosphazenes).[2] However, the field of poly(silanes) has been steadily developing, and, in recent years, several new phosphazene-based and other polymers have been reported where the backbone incorporates either exclusively noncarbon elements (including metals) or a hybrid of essentially inorganic elements together with carbon atoms.[3] These mark a conscious effort on the part of the chemical community to develop polymeric systems with special properties that are unlikely to be obtained from carbon-based polymers alone. Of the known inorganic polymer systems, most are based on either phosphorus or silicon atoms as part of the skeletal repeat unit. While poly(sulfurnitride) has been known since the early years of this century,[4] sulfur-nitrogen based polymer systems have received little attention even though the small molecule chemistry of S–N compounds has been studied quite extensively. In this paper, we report the results of our effort directed at the synthesis of alkyl and aryl substituted polymers based on the repeating unit [$N{=}S(O)R$].[5]

During the early 1960s, several groups reported the synthesis of poly(oxothiazenes),[6] a class of polymers based on a backbone of alternating sulfur(VI) and nitrogen atoms with one variable and one "fixed" (oxygen) substituent on each sulfur atom. While poly(fluoro oxothiazene) and poly(amino oxothiazene)[7] were prepared by the condensation of $S(O)F_4$ with NH_3,[8] poly(phenyloxothiazene)[9] was said to form from the condensation of phenyl benzenesulfonimidate, (PhO)S(O)(NH)Ph, and from the condensation of *N*,*N*-dimethylarenesulfonimidamides.[10] However, little experimental information was reported on the condensation of the sulfonimidamides, and no characterization data were provided, in either case, for the inferred S-aryl polymers identifying the condensation products as polymeric. Within the past 30 years, the only other linear oxothiazenes reported were low molecular weight oligomers of trifluoromethyloxothiazene with possibly up to ten repeating S–N units in the chains. These were obtained from the decomposition of trifluoromethanesulfi-

---

† Permanent address: IBM Corporation, 2125 Ridgewood Dr., Midland, MI 48642.

[1] (a) Noll, W. *Chemistry and Technology of Silicones*; Academic: New York, 1984. (b) Kendrick, T. C.; White, J. W.; Parbhoo, B. *Comprehensive Polymer Science*; Eastmond, G. C.; Ledwith, A.; Russo, S.; Sigwalt, P., Eds.; Pergamon: New York, 1989; Vol. 4, Part II, p 459.

[2] For recent reviews, see: (a) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. (b) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

[3] (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) See ref 2a. (c) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (d) Roesky, H. W.; Lücke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (e) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (f) Allcock, H. R.; Coley, S. M.; Manners, I.; Nuyken, O.; Renner, G. *Macromolecules* **1991**, *24*, 2024. (g) Dodge, J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268. (h) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044.

[4] Labes, M.; Love, P.; Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1.

[5] (a) Roy, A. K. U.S. Patent 5,068,379, 1991. (b) Roy, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 1530.

[6] Prior to this work, the few known polymers of this type were referred to as "poly(oxosulfur nitrides)" and cyclic species were named "sulfanuric" compounds. However, we feel that the "oxothiazene" nomenclature is preferable because of close analogy with the well-established phosphazene structure and nomenclature. This should allow easier recognition of cyclic and linear species in a uniform manner as the oxothiazene chemistry develops. It should be mentioned that Banister and Bell suggested the use of the "cyclotrithi(VI)azene" nomenclature (with *a* and *e* prefixes to denote axial and equitorial substituents) for cyclic trimeric species in the following: Banister, A. J.; Bell, B. *J. Chem. Soc. A* **1970**, 1659.

[7] Named in the original literature as poly(fluorooxosulfur nitride) and poly(aminooxosulfur nitride), respectively.

[8] (a) Seel, F.; Simon, G. *Angew. Chem.* **1960**, *72*, 709. (b) Parshall, G. W.; Cramer, R.; Foster, R. E. *Inorg. Chem.* **1962**, *1*, 677. (c) Cramer, R. D. U.S. Patent 3,017,240.

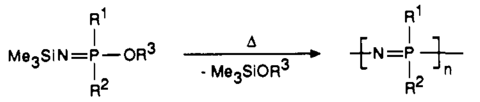
[9] Referred to in the original report (English version) as "probably polymer of arylisosulfonate".

[10] (a) Levchenko, E. S.; Kozlov, E. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1962**, *32*, 2585. (b) Levchenko, E. S.; Kozlov, E. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1963**, *33*, 565.

0002-7863/93/1515-2604$04.00/0

nylazide.[11] Although brief references were made in two other reports to the formation of polymeric species in the reaction of some benzenesulfonimidoyl chlorides and hydrochlorides with amines, these polymeric species were not characterized.[12]

Unlike hexachlorocyclotriphosphazene, $(N{=}PCl_2)_3$, which undergoes thermally activated ring-opening polymerization,[13] α-sulfanuric chloride (or, by our suggested nomenclature, trichlorocyclotrioxothiazene), $[N{=}S(O)Cl]_3$, has been reported to exothermically decompose at 250–285 °C.[14] Further, α-$[N{=}S(O)F]_3$, though stable to 350 °C, does not apparently polymerize under the conditions reported.[15] While the ring-opening polymerization of cyclooxothiazenes could possibly serve as a viable route to polyoxothiazenes under appropriate conditions, for the purpose of synthesizing poly(alkyl/aryloxothiazenes), $[N{=}S(O)R]_n$, we chose to investigate a condensation pathway modeled after the synthesis of poly(alkyl/arylphosphazenes), $[N{=}PR_2]_n$, from the condensation of *N*-silylphosphoranimines (eq 1).[16] From the close structural analogy between the P–N and S–N systems, synthesis of poly(oxothiazenes) from the condensation of *N*-silylsulfonimidates **3** appeared feasible.



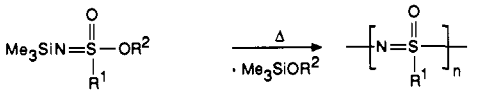
$$Me_3SiN{=}P(R^1)(R^2){-}OR^3 \xrightarrow[-\,Me_3SiOR^3]{\Delta} [N{=}P(R^1)(R^2)]_n \quad (1)$$

1 2

$OR^3 = OCH_2CF_3$, OPh R^1, R^2 = alkyl, aryl

Results and Discussion

Thermal Polycondensation of *N*-Trimethylsilylsulfonimidates 3. The synthesis of *N*-trimethylsilylalkane- and -arenesulfonimidates **3** was accomplished by a novel, yet simple, method from readily available sulfur(VI) starting materials as described in the preceding paper in this issue. The *N*-silylsulfonimidates used for polycondensation studies were purified by two to four vacuum distillations prior to condensation.



$$Me_3SiN{=}S(O)(R^1){-}OR^2 \xrightarrow[-\,Me_3SiOR^2]{\Delta} [N{=}S(O)(R^1)]_n \quad (2)$$

3

$OR^2 = OCH_2CF_3$, OPh

3a: R^1 = Me, $OR^2 = OCH_2CF_3$;

3b: R^1 = Me, OR^2 = OPh;

3c: R^1 = Et, OR^2 = OPh;

3d: R^1 = Ph, $OR^2 = OCH_2CF_3$;

3e: R^1 = Ph, OR^2 = OPh;

3f: R^1 = 4-F-C_6H_4, OR^2 = OPh;

4a: R^1 = Me

4b: R^1 = Et

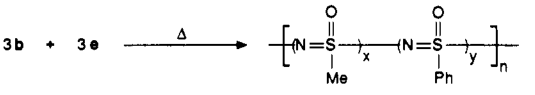
4c: R^1 = Ph

4d: R^1 = 4-F-C_6H_4

(a) Uncatalyzed Condensations. When heated in evacuated, sealed Pyrex ampules or stainless steel Parr reactors at 120–170 °C for 2–8 days, the *N*-silylsulfonimidates condensed to produce a two-phase system containing the solid oxothiazene polymer, silyl ether, and any uncondensed precursor (eq 2). For the purpose of acquiring preliminary understanding of the polymerization process, the condensation of only **3a** (R^1 = Me, $OR^2 = OCH_2CF_3$) and **3b** (R^1 = Me, OR^2 = OPh) was examined in detail with regard to polymerization time and temperature. The liquid contents after condensation were analyzed by ^{1}H NMR after removal from the ampule either by trap-to-trap distillation on a vacuum line (for **3a**) or simply by pipet withdrawal (for all phenyl sulfonimidates).

For **3a**, only 17% condensation occurred at 120 °C after 144 h. At 160 °C, 80–98% condensation was observed over 96–144 h. However, on some occasions with **3a**, little polymer was obtained, and the odor of lower valent sulfur compounds was evident, even though $Me_3SiOCH_2CF_3$ was the main condensation byproduct. The cause for this anomalous behavior has not been determined. However, because of this, and similar observations with **3d** (R^1 = Ph, $OR^2 = OCH_2CF_3$), all later sulfonimidate condensations were carried out with only phenyl sulfonimidates for preparative and characterization purposes. All phenyl sulfonimidates that could be isolated and purified by distillation (**3b**: R^1 = Me, **3c**: R^1 = Et, **3e**: R^1 = Ph, **3f**: R^1 = 4-F-C_6H_4; OR^2 = OPh in all cases) always cleanly produced polymer and Me_3SiOPh on condensation. Polymer characterization and properties are discussed in later sections.

When heated together, **3b** and **3e** cleanly co-condensed to yield the methyl-co-phenyloxothiazene polymer **5** (eq 3). The solubility behavior and T_g (as discussed later) of **5** identified it as a true copolymer and not a physical blend of the two respective homopolymers.



$$\mathbf{3b} + \mathbf{3e} \xrightarrow{\Delta} [(N{=}S(O)(Me))_x(N{=}S(O)(Ph))_y]_n \quad (3)$$

5

x = y

It is particularly noteworthy that in all condensation reactions of **3**, there was no evidence of the formation of cyclic oxothiazene species. Even the sulfonimidoyl chlorides,[17] which have limited stability but are crucial intermediates for the synthesis of **3**, were found to decompose by condensation to yield what appear to be only polymeric oxothiazenes. Further, the early work on poly(fluoro oxothiazene), poly(amino oxothiazene), and the condensation of phenyl benzenesulfonimidate and benzenesulfonimideamides did not report the formation of cyclic species.[8,10] While cyclic trimeric halooxothiazenes[18] are known, and a few cyclic aryl- and mixed alkyl-halo oxothiazenes have also been reported,[19] the conspicuous absence of cyclic species in all reported condensation polymerizations suggests the presence of one or more elements of instability in the structure of cyclooxothiazenes. It is known that α-$[N{=}S(O)Cl]_3$ is quite susceptible to ring-opening or alteration of ring structure with nucleophiles like simple amines and alcohols,[19] and this could partially explain the absence of cyclics in polymerizations where nucleophilic species are present.

While 2,2,2-trifluoroethyl- and phenyl sulfonimidates thermally condensed with the elimination of the corresponding silyl ether, an interesting observation was made with the thermolysis of the ethyl sulfonimidate **3g** (R^1 = Me, OR^2 = OEt). When heated in an ampule (as above) at 140 °C for 144 h and then at 160 °C for 72 h, **3g** failed to condense to polymer. Instead, complete rearrangement to *N*-ethyl-*N*-trimethylsilylmethanesulfonamide **6** occurred (eq 4). Similar rearrangements of methyl- and ethyl arenesulfonimidates have been reported by Levchenko.[20] However, unlike Levchenko's compounds, **3g** showed no sign of rearrangement at room temperature over a period of 9–10 months or during distillation. Compound **6** was identified by comparison

---

(11) Bechtold, T.; Eingelbrecht, A. *J. Fluorine Chem.* **1982**, *19*, 379.

(12) (a) Jonsson, E. U.; Bacon, C. C.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5306. (b) Johnson, C. R.; Jonsson, E. U.; Bacon, C. C. *J. Org. Chem.* **1979**, *44*, 2055.

(13) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic Press: New York, 1972.

(14) Mckenney, R. L.; Fetter, N. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3569.

(15) Seel, F.; Simon, G. *Z. Naturforsch.* **1964**, *B 19b*, 354.

(16) (a) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875. (c) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci.-Chem.* **1981**, *A16*, 425. (d) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

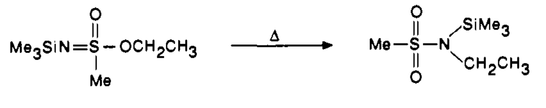
(17) See preceding paper in this issue for the synthesis of sulfonimidoyl chlorides.

(18) Referred to in the literature as "sulfanuric halides". We, like Banister (ref 6), feel this nomenclature should be replaced because of its drawbacks and suggest the "oxothiazene" alternative.

(19) For a short review of these, see: Heal, H. G. *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: New York, 1980; Chapter 5.

(20) Levchenko, E. S.; Markovskii, L. N.; Kirsanov, A. V. *Zh. Org. Khim.* **1967**, *3*, 1481.

of its ^1H and ^{13}C NMR spectra with those of **3g**. A clear upfield shift of the CH_2 signal was observed because of the change of its attachment from oxygen to nitrogen. Further, the CH_2 protons lost their diastereotopic nature in going from **3g** to **6**. The thermal rearrangement behavior of **3g** suggests that only electronegative leaving groups (i.e., those where the C–O bond is not readily amenable to cleavage) on sulfur allow the 1,2-elimination of silyl ether necessary for the synthesis of poly(oxothiazenes) from *N*-silylsulfonimidates.



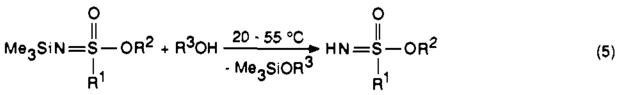
$$Me_3SiN{=}\overset{O}{\overset{\|}{S}}(Me){-}OCH_2CH_3 \xrightarrow{\Delta} Me{-}S(=O)_2{-}N(SiMe_3)(CH_2CH_3) \qquad (4)$$

3g **6**

(b) Catalyzed Condensations. While catalysis of the condensation of *N*-silylphosphoranimines **1** to poly(alkyl/arylphosphazenes) **2** has not been reported,[21] catalysis of the ring-opening polymerization of cyclic halophosphazenes has been studied quite extensively. Because of the long polymerization times required to achieve significant condensation with *N*-silylsulfonimidates **3**, we examined a variety of both Lewis acids and bases as potential catalysts. Some of the compounds representative of each class were as follows: $BF_3{\cdot}Et_2O$, $AlCl_3$, Sn(octoate)$_2$, $FeCl_3$, WCl_6, KF/18-crown-6, LiOPh, and tris(dimethylamino)sulfur (trimethylsilyl)difluoride (TAS-F).

Even at 0.05 mol % concentration (based on **3**), both acidic and basic species accelerated condensation at 120 °C, though the rate enhancement observed was only moderate at best. Again, mainly **3b** was used for the catalysis study. One of the best combinations of high polymer molecular weight, relatively low polydispersity, and acceptable condensation rate was obtained with the use of $BF_3{\cdot}Et_2O$. In general, acidic catalysts yielded slightly higher molecular weight polymer. Catalysts containing chloride led to the highest polydispersities, while KF/18-crown-6 provided the lowest polydispersity polymer. Preparative and molecular weight data for both uncatalyzed and catalyzed condensations are summarized in Table I.

Desilylation of *N*-Silylsulfonimidates 3 to Free Sulfonimidates 7. In the companion article, derivatization of *N*-silylsulfonimidates utilizing the reactivity of the Si–N bond was described. In order to explore this reactivity further and also to investigate the possibility of developing a general condensation synthesis of poly(alkyl/aryloxothiazenes) from free sulfonimidates, the reaction of *N*-silylsulfonimidates **3** with various alcohols was studied (eq 5). The alcohols used were methanol, 2,2,2-trifluoroethanol, and phenol in the presence or absence of catalytic amounts of potassium fluoride.



$$Me_3SiN{=}\overset{O}{\overset{\|}{S}}(R^1){-}OR^2 + R^3OH \xrightarrow[-\,Me_3SiOR^3]{20-55\ ^\circ C} HN{=}\overset{O}{\overset{\|}{S}}(R^1){-}OR^2 \qquad (5)$$

3

R' = Me, $CH_2CH_2CH_2Cl$,
CH=CH-Ph, Ph

7a: R^1 = Me, OR^2 = OCH_2CF_3
7b: R^1 = Me, OR^2 = OPh
7c: R^1 = $CH_2CH_2CH_2Cl$, OR^2 = OCH_2CF_3
7d: R^1 = CH=CH-Ph, OR^2 = OCH_2CF_3
7e: R^1 = Ph, OR^2 = OPh
7f: R^1 = Me, OR^2 = OCH_2CH_3

When used in excess, all the alcohols brought about complete desilylation of **3** to **7**. However, the reaction in eq 5 was studied primarily with methanol. With a phenoxy group on sulfur, a 100% or 200% molar excess of methanol was required for complete conversion to **7** depending on whether R^1 was methyl or phenyl, respectively. The reaction was carried out at 20–25 °C. With OR^2 = 2,2,2-trifluoroethoxy, heating the reaction mixture at 40–50 °C with at least a 500% molar excess of methanol was necessary. When the alkoxy function on sulfur was OCH_2CH_3, it was necessary to use a catalytic amount (0.5 mol %) of KF in conjunction with a 500% molar excess of methanol, at 50–52 °C, for complete conversion of **3** to **7**.

With phenyl sulfonimidates, no ester exchange was observed with any of the alcohols used for desilylation. With some 2,2,2-trifluoroethyl sulfonimidates, only a few mole percent of what appeared to be methyl sulfonimidates were observed by ^1H NMR after desilylation with methanol, but these did not interfere with the NMR characterization or subsequent condensation of the free 2,2,2-trifluoroethyl sulfonimidates. However, at a lower temperature (30–35 °C), but with a 1000 mol % excess methanol, no methyl sulfonimidate was observed in the desilylation of the 2,2,2-trifluoroethyl *N*-silylsulfonimidates. As will be seen later, successful desilylation of **3** with alcohols without competition from transesterification is particularly significant for polymer synthesis from the resulting free sulfonimidates, since simple alkyl sulfonimidates do not appear to undergo thermal polycondensation. It was also found that two *N*-silyl sulfonimidates with different R^1 substituents, could be simultaneously desilylated in admixture to the respective free sulfonimidates, with no side reaction occurring during or after desilylation. While desilylation of *N*-silylsulfoximides with methanol has been reported,[22] the above reaction represents the first synthesis of free sulfonimidates from the alcoholysis of *N*-silylsulfonimidates.

The free 2,2,2-trifluoroethyl sulfonimidates obtained in this study were clear, viscous liquids, while the free phenyl sulfonimidates were crystalline solids. All the free sulfonimidates partially condensed overnight at room temperature, but remained stable for at least five to seven days at −20 to −25 °C. Because of their lack of extended stability at room temperature, they were characterized by ^1H and ^{13}C NMR spectroscopy. While the chemical shifts for the respective signals in **3** and the corresponding free sulfonimidates **7** were similar, Me_3Si signals were not observed for **7**, and the free 2,2,2-trifluoroethyl sulfonimidates did not exhibit diastereotopic OCH_2CF_3 protons.

Polycondensation of Free Sulfonimidates 7a–e. All the free phenyl- as well as 2,2,2-trifluoroethyl sulfonimidates prepared in this study condensed rapidly and reproducibly to poly(oxothiazenes) at temperatures between 85 and 120 °C, at atmospheric or reduced pressures, either neat or in solution (eq 6). In all cases, the condensation was nearly quantitative and was essentially complete in 1–3 h. In contrast, Levchenko reported the near-quantitative condensation of **7e** to occur at 200 or 250 °C.[10a] We have found that these higher temperatures are unnecessary for the condensation and are in fact close to the decomposition temperatures for these polymers. The ability to synthesize polyoxothiazenes via condensation at relatively low temperatures should be important for both sulfonimidates and polymers bearing temperature-sensitive substituents. As in the case of *N*-silylsulfonimidates **3b** and **3e**, the corresponding free sulfonimidates **7b** and **7e** cocondensed on heating to poly(methyl-co-phenyloxothiazene) (eq 7). This emphasizes the ability to readily alter polymer composition through incorporation of suitable substituents from various "monomers" using a simple co-condensation process. Preparative and molecular weight data for polymers obtained from free sulfonimidates are summarized in Table II.

As in the case of *N*-silylsulfonimidate **3g**, the free sulfonimidate **7f** did not condense to polymer on heating between 85 and 120 °C. Instead, partial rearrangement to *N*-ethylmethanesulfonamide (together with other unidentified products) was indicated by ^1H NMR. Again, this emphasizes the need to use appropriately substituted sulfonimidates in order to ensure that the strong drive

---

[21] Recently, catalysis of the condensation of $(CF_3CH_2O)_3P{=}NSiMe_3$ and other similar phosphoranimines by fluoride ion as well as by other anionic initiators was reported in the following: (a) Matyjaszewski, K.; Green, J. B.; Montague, R. A. *Polymer Preprints* **1992**, *33*(2), 174 and references cited therein. (b) Matyjaszewski, K.; Lindenberg, M. S.; Spearman, J. L.; White, M. L. *Polymer Preprints* **1992**, *33*(2), 176.

[22] Hwang, K.-J. *J. Org. Chem.* **1986**, *51*, 99.

Table I. Preparative and Molecular Weight Data for Polymers **4** and **5** from *N*-Silylsulfonimidates

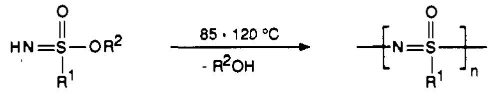
sulfonimidate	polymer	catalyst[b]	time, h	% condensation	mol wt[a]	
					M_w	M_n
3a	**4a**		96[c]	80	52 000	6 000
3b	**4a**		144[d]	39	481 000	35 000
3b	**4a**	$AlCl_3$	144	82	193 000	9 000
3b	**4a**	$BF_3{\cdot}Et_2O$	144	62	479 000	53 000
3b	**4a**	Sn(octoate)$_2$	144	69	428 000	30 000
3b	**4a**	WCl_6	144	97	197 000	7000
3b	**4a**	KF/crown-6	144	83	175 000	23 000
3b	**4a**	TAS-F[e]	144	58	375 000	33 000
3b	**4a**	LiOPh	144	46	286 000	18 000
3c	**4b**	$BF_3{\cdot}Et_2O$	160[c]	94	208 000	28 000
3d	**4c**		100[c]	89	10 000	4000
3e	**4c**		144[d]	32	195 000	138 000
					14 000	12 000
3e	**4c**	KF/crown-6	144	48	66 000	17 000
3f	**4d**		243	52	539 000	389 000
					43 000	35 000
3b + **3e**	**5**		142[c]	>90	256 000	37 000

[a] GPC molecular weights in DMF against polystyrene standards. The aryl homopolymers showed bimodal molecular weight distribution. [b] Catalyst concentration: 0.05 mol % based on sulfonimidate. [c] Polymerization temperature for these were 160, 140, 170, and 140 °C, respectively. [d] Polymerization temperature for catalyzed reactions, including these controls, was 120 °C. [e] Tris(dimethylamino)sulfur (trimethylsilyl)difluoride.

Table II. Preparative and Molecular Weight Data for Polymers **4** and **5** from "Free" Sulfonimidates

sulfonimidate	polymer	temp, °C	time, h	pressure, mmHg	mol wt[a]	
					M_w	M_n
7a	**4a**	105–110	2.0	10	45 000	10 000
7b	**4a**	105	1.5	760	50 000	12 000
7b[b]	**4a**	90–95	1.25	760	87 000	27 000
7e	**4c**[c]	100–105	2.0	1.5/0.2	299 000	230 000
					24 000	18 000
7e	**4c**[c]	200–205	1.0	1.0	332 000	255 000
					32 000	27 000
7e	**4c**[c]	250	0.5	1.2	299 000	214 000
					25 000	21 000
7c	**4e**	115/100	0.3/1.7	6.0	44 000	6000
7d	**4f**	120/110	1.0/1.0	9.0/0.2	60 000	6000
7b + **7e**	**5**	115/105	1.0/1.0	4.5/1.0	55 000	15 000

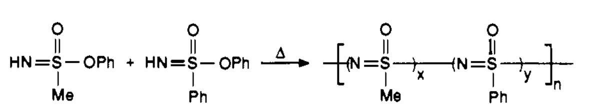
[a] GPC molecular weights in DMF against polystyrene standards. [b] In DMF as 1 M solution. [c] Bimodal molecular weight distribution in all cases.



(6)

7a-e

4a: R¹ = Me
4c: R¹ = Ph
4e: R¹ = CH₂CH₂CH₂Cl
4f: R¹ = CH=CH-Ph



(7)

7b **7e** **5**

x = y

toward formation of the stable $-SO_2-$ entity during heating is totally suppressed.

Characterization and Properties of Poly(alkyl/aryloxothiazenes)

(a) ^{1}H and ^{13}C NMR Spectra. In preliminary studies, mainly poly(methyloxothiazene) has been examined by ^{1}H and ^{13}C NMR spectroscopy in DMSO-d_6. A somewhat broad S–Me signal is observed for the methyl protons at 3.45–3.50 ppm, about 0.2 ppm downfield from the corresponding signal in the precursor sulfonimidates **3a** and **3b**. While a broad triad structure is discernible for the S–Me carbon (centered at 46.4 ppm) in the ^{13}C NMR spectrum, other outer peaks are also apparent suggesting perhaps the presence of both stereoregular and atactic polymer. This is in contrast with the structure of poly(methylphenylphosphazene) which has been found to be completely atactic by NMR analysis.[23]

The ^{1}H NMR spectrum of polymer **4e** showed quite broad signals for the $ClCH_2CH_2CH_2$–S protons. It was very useful, however, to note the alternate upfield and downfield shift of the CH_2–S signal in the sequence of transformations sulfonyl chloride → sulfonamide → sulfonimidoyl chloride → sulfonimidate → polymer. Downfield shifts brought about overlap of this signal with that for the $ClCH_2$ moiety, such that ultimately the polymer exhibited only two resonances.

(b) Solubility and Surface Tension. Polymers **4a–f** exhibit interesting solubility behavior. Poly(methyloxothiazene) **4a** is soluble in DMF, DMSO, nitromethane, and to some extent in hot water (above about 50–60 °C) but insoluble in most common polar and nonpolar organic solvents as well as in cold water. Based on this, a solubility parameter (δ) in the range 12–13 seems likely for **4a**. All the other polymers (except **4d**), including copolymer **5**, are soluble in CH_2Cl_2 and $CHCl_3$. Quite surprisingly, neither of the *S*-aryl polymers **4c** and **4d** nor the copolymer **5** is soluble in THF. This solubility behavior of polyoxothiazenes most likely is a reflection of the highly polar nature of the polymer chains.

The polar nature of polyoxothiazene chains was clearly borne out by contact angle measurements on **4a** using water and methylene iodide. The total solid surface tension of 44.8–50.5 mN/m as calculated by the Owens–Wendt method[24] is among some of the highest seen with synthetic polymers. An average contact angle with water of 57–64° bears out the hydrophilicity of the polymer and suggests the possibility of synthesizing water-soluble oxothiazene polymers with appropriate substituents on sulfur. The very polar S=O group at every other link along the polymer chain undoubtedly makes a significant contribution toward polymer polarity.

While the acid–base properties of the polymers in this study have not been examined in any detail, the solubility behavior of **4a** in various acids suggests much weaker basicity of backbone nitrogen atoms in poly(oxothiazenes) compared with poly(alkyl/arylphosphazenes). For example, **4a** is insoluble in acetic acid and dilute or even concentrated hydrochloric acid. It dissolves in concentrated sulfuric acid and can be recovered unchanged if

---

(23) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.

(24) Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.

immediately precipitated into water. However, several hours in this strong acid appears to degrade the polymer. Clearly, the strongly electronegative oxygen substituent on sulfur reduces the basicity of skeletal nitrogen atoms. The polymer **4a** remains unaffected in 1 N KOH at least over several days at room temperature.

(c) Molecular Weight Determination. Gel permeation chromatography (GPC) provides a relatively fast method for determining relative molecular weights of polymers. Hence, we chose this method to obtain initial, rough estimates of molecular weights of poly(oxothiazenes) obtained from both *N*-silylsulfonimidate and free sulfonimidate condensations. In order to obtain true pictures of molecular weight, molecular weight distribution, degree of polymerization, etc. for this new polymer system, future studies will undoubtedly have to include methods for absolute molecular weight determination. It is noteworthy in this connection that while the general insolubility of poly(oxothiazenes) in several common solvents might be advantageous for some potential applications, it certainly constitutes a problem for solution property studies. Neither THF nor toluene, both of which are common GPC solvents, was appropriate for polymers **4** and **5**. Hence, all GPC data were obtained in DMF solution at 90 °C against polystyrene standards. Because DMF is a poor solvent for polystyrene but a good solvent for poly(oxothiazenes), molecular weights obtained by GPC for the latter polymers should only be interpreted in terms of their comparative value (within the series) toward understanding the effects of various substituents and leaving groups in the new polycondensation process.

For condensations with **3**, the highest molecular weights were seen with the S–Me polymer, followed by the S–Et, S–(4-F-C_6H_4), and S–Ph polymers, respectively. This would be consistent with increasing steric effects on the polymerization process in going from Me to Et to Ph substituents. On occasions when polymers were obtained from the trifluoroethyl sulfonimidates, their molecular weights were approximately an order of magnitude lower than those from phenyl sulfonimidates. In all cases except with the aryl polymers, relatively broad peaks, often with shoulders on the higher molecular weight end, were observed in the chromatograms though no significant tailing was observed. The aryl polymers, on the other hand, showed distinctly bimodal molecular weight distribution with low polydispersities. The significant increase in polydispersities with chloride based catalysts could be an indication of degradative effects of these catalysts on the polymer since some of the other catalysts seemed to actually lower polydispersities though only slightly.

Quite interestingly, poly(methyloxothiazene), obtained from either of the free sulfonimidates **7a** and **7b**, showed molecular weights roughly an order of magnitude lower than that obtained from **3b**. While copolymer **5** derived from the respective free phenyl sulfonimidates also exhibited lower molecular weight, poly(phenyloxothiazene) obtained from **7e** had molecular weights in approximately the same range seen for samples obtained from **3e**. Understanding the cause or causes underlying this difference will require further detailed studies of these two polycondensation processes.

One of the practical advantages of free sulfonimidate condensation is the ability to carry out the condensation in a round-bottomed flask. The solution polymerization of **3b** in DMF yielded polymer with approximately twice the molecular weight of that obtained from the neat polymerization. This would be expected on the basis of the solubility of the polymer in DMF, which would allow for molecular weight buildup by keeping the growing polymer chains in solution. Although some degradative effects on molecular weight have been observed with DMF during long, automated sampling procedures on the GPC at 90 °C, solution polymerization with judicious choice of conditions appears to hold promise for increasing molecular weight using free sulfonimidates.

Table III. DSC and TGA Data for Polymers **4** and **5**[a,b]

polymer	R^1	T_g, °C	T_{10}, °C helium	T_{10}, °C air
4a	CH_3	55–65	290[c,d]	284
4b	CH_2CH_3	29	278	272
4c	C_6H_5	85	294	285
4d	4-F-C_6H_4	86	300[e]	
4e	$CH_2CH_2CH_2Cl$	−1	208[f]	
4f	$CH{=}CH{-}C_6H_4$	47	223[f]	
5	CH_3, C_6H_5	72	279	270

[a] Polymers derived from *N*-silylsulfonimidates unless otherwise noted. [b] Heating rate: 10 °C/min. [c] 280–285 °C with polymers from free sulfonimidate. [d] Often lower by 10–30 °C for samples from catalyzed polymerization. [e] Approximate value. [f] Polymer from free sulfonimidate.

(d) Thermal Analysis. Of the few poly(oxothiazenes) previously reported, none was studied with the objective of elucidating the thermal behavior of these sulfur–nitrogen backbone polymers. Hence, it was of considerable interest to examine **4** and **7** by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA). Thermal analysis data for the polymers are summarized in Table III.

The known, inherent flexibility of the backbone in poly(siloxanes) and poly(phosphazenes) strongly suggested skeletal flexibility in poly(oxothiazenes), particularly in light of the analogous structures in the phosphorus and sulfur polymers, the comparable atomic sizes of the two elements, and the very similar P–N and S–N bond lengths in cyclic phosphazenes and oxothiazenes.[25] Indeed, poly(fluorooxothiazene) was reported to be an elastomeric material, though its T_g was not determined.[8b] Therefore, it was striking to find a T_g at 55–65 °C for poly(methyloxothiazene) by DSC when the analogous poly(dimethylphosphazene) exhibits a T_g at −46 °C. However, both poly(ethyloxothiazene) and poly(3-chloropropyloxothiazene) exhibit significantly lower T_g (at 29 °C and −1 °C, respectively) than poly(methyloxothiazene). While such a trend is usually associated with chain packing effects, the magnitude of the above decreases in T_g, together with the fact that poly(phenyloxothiazene) exhibits a T_g at 85 °C, only 20 to 30 °C higher than for the methyl polymer, suggests other factors to be involved in the unexpectedly high T_g of the latter. With poly(siloxanes) and poly(phosphazenes), substitution of methyl for phenyl causes a much larger increase in T_g.

It is noteworthy that with DSC analysis of poly(oxothiazenes), no clear melting transition has been observed with any of the polymers so far. This observation is in line with the polymers being essentially atactic. The absence of endothermic transitions is also supportive of spectroscopic data that indicate cyclic species are essentially absent in the polymers obtained via the condensation synthesis.

Thermogravimetric analysis of poly(methyloxothiazene) showed significantly lower stability of the polymer than was anticipated on the basis of the relatively high thermal stability of poly(dimethylphosphazene).[23] Surprisingly, all the polymers **4a–d** showed 10% weight loss within the relatively narrow temperature window of 270–300 °C. Analysis in air atmosphere yielded 10% loss temperatures that were only 6–10 °C lower than those in helium. Depolymerization to cyclics did not seem to occur in helium or air. This, together with the odor of lower valent sulfur compounds in the exiting gases, suggests that redox reactions are at least partly responsible for the thermal degradation of the polymers.

The above TGA observations indicate the involvement of the oxygen (oxo) substituent on sulfur in a common decomposition mechanism in the thermal degradation of the polymers. The fact that poly(3-chloropropyloxothiazene) shows 10% weight loss at

---

(25) (a) See ref 13, Chapter 3. (b) Hazell, A. C.; Wiegers, G. A.; Vos, A. *Acta Crystallogr.* **1966**, *20*, 186. (c) Arrington, D. E.; Moeller, T.; Paul, I. C. *J. Chem. Soc. A* **1970**, 2627.

208 °C suggests substituent atoms bearing lone pairs of electrons may initiate nucleophilic cleavage of the polymer chains. However, further studies are necessary to shed light on the thermal degradation mechanism of poly(oxothiazenes).

Theoretical Calculations on the Oxothiazene Backbone

Over the last 30 years, various aspects of the poly(phosphazene) structure have been investigated using theoretical methods.[26] Therefore, it was of interest to examine the oxothiazene backbone from a theoretical perspective in order to obtain information on structural aspects such as polymer conformation, bond lengths and angles, chain flexibility, and the presence or absence of π-conjugation along the backbone. Such information would not only be useful for guiding the experimental chemist in the expansion of oxothiazene chemistry but might also, in conjunction with information available on phosphazene systems, facilitate the design and development of newer heteroatom-nitrogen based polymer systems with tailored structure-property relationships.

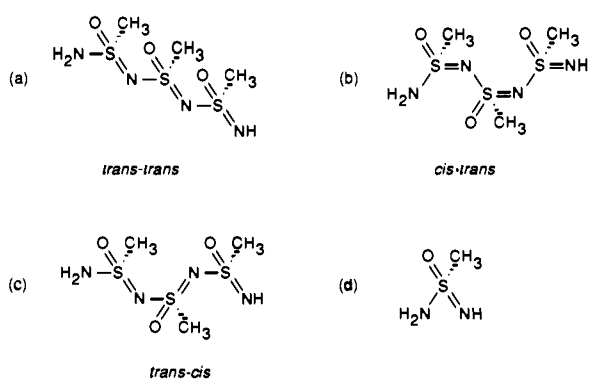
(a) Conformation of Poly(methyloxothiazene). To determine the most stable conformation of the polymer, a series of Hartree–Fock calculations was carried out on a segment of the polymer consisting of three-and-a-half structural repeat units as shown in Chart Ia–c. The selected length was based on a balance between physical soundness and the computer resources available. Thus, with the chosen segment it is believed that the bonds of the central S atom are far enough from the ends that they are not affected for the purposes of calculation by the truncation of the polymer chain and are representative of the environment in the real polymer.

The basis set used in the calculation was of the double-ζ quality, commonly denoted as 3-21G**.[27] For the system shown in Chart I, the total number of primitive Gaussian functions is 368, which were contracted to 254 functions. The side groups, $-CH_3$ and $=O$, were always restricted to form dihedral angles of 120° and 240°, respectively, with respect to the skeletal plane. Thus, only the bond angles in the backbone, together with all the bond lengths, were allowed to vary in the geometry optimization process.

With the aforementioned restrictions, there are only three different general backbone conformations to be analyzed. These are shown in Chart Ia–c where the backbone is in the plane of the paper with oxygen atoms above the plane and methyl groups below the plane. If the side groups at the first and third sulfur atoms are maintained to have the same orientation, then for each general backbone conformation there are two possible side group orientations, denoted as uuu and udu, where u stands for upward position and d for downward position of the oxygen atom. It should be noted that no accepted norm exists for designating "up" and "down" positions for a double bond and that Chart Ia–c depict only the uuu orientation for each conformation. Obviously, interchanging the oxygen and methyl groups on the middle sulfur will generate the udu orientation for each conformation in Chart Ia–c.

Our results show Chart Ic with the udu side chain to be the most stable conformation. The next stable conformation, Chart Ia with the udu side chain, lies about 4.3 kcal/mol above it; while the third most stable conformation, Chart Ic with the uuu side chain, is 7.5 kcal/mol above the most stable conformation. These results indicate that the orientations of the side groups are determined by the repulsions between the neighboring methyl groups. For Chart Ib,c the energies of both udu conformations are about 7 kcal/mol lower than those of the corresponding uuu conformations. Examination of the carbon–carbon distances (in Chart Ib,c) shows that the carbon atoms are about 5.1 Å apart in udu in comparison with 4.1 Å in uuu. In the trans–trans conformation of Chart Ia, the uuu is more than 24 kcal/mol higher than the udu, because of the short distance of 3.5 Å between the carbon atoms in the former orientation (compared with about 4.6 Å in the latter).

Chart I



trans-trans

cis-trans

trans-cis

After finding the trans–cis planar conformation to be the most stable, we also studied the effects of individual rotations around a single and a double NS bond without any further optimization of the other variables. For rotation around the central single N–S bond in Chart Ic, the minimum was found to be located at 33° off the planar conformation. Thus, a slightly helical structure, rather than completely planar is expected to be the most stable conformation for poly(methyloxothiazene). The sense of rotation is to increase the carbon–carbon distance between the side groups, thereby decreasing steric repulsion between the methyl groups. The most stable conformation calculated for $[N{=}S(O)Me]_n$ is very similar to those found experimentally for poly(dihalophosphazenes)[28-30] and poly(sulfurnitride), $(SN)_x$.[31]

Continuing rotation around the N–S single bond past the minimum, the energy increases and reaches over 20 kcal/mol above the minimum at 150°. Thus, poly(methyloxothiazene) would be expected to be much more rigid than poly(dimethylsiloxane) which has a rotational barrier of about 3 kcal/mol.[32] The N–S rotational barrier is also much higher than those calculated by Allcock et al. for $(NPF_2)_n$, $(NPCl_2)_n$, and $(NPBr_2)_n$ at 0.1, 2.8, and 8.4 kcal/mol, respectively.[33] The N–S bond rotational force constant around the minimum is 0.052 mdyne/Å (using r_e = 1.6 Å), which is about twice the value for C_2H_6. Although this may be attributed to some double bond character of the SN bond, it is more likely due to stronger substituent–substituent and substituent–backbone repulsive interactions. The latter assertion is supported by calculations using an F atom in place of the CH_3 group. With poly(fluorooxothiazene), the rotational force constant around the minimum dropped to 0.033 mdyne/Å, and the rotational energy barrier was found to be only about 7 kcal/mol, with the minimum located at 35° off the planar conformation. This should translate to a higher torsional mobility and, correspondingly, a lower glass transition temperature for this polymer.

In Chart Ic, rotation around the central double bond (in the direction of decreasing side chain repulsion) shows that the minimum is off the planar structure by about 8°. The rotational force constant of 0.19 mdyne/Å is slightly smaller than that for

---

[26] (a) See ref 13, Chapter 2. (b) Ferris, K. F.; Duke, C. B. *Int. J. Quantum Chem.* **1989**, *23*, 397. (c) Dake, L. S.; Baer, D. R.; Ferris, K. F.; Friedrich, D. M. *J. Electron Spectrosc. Related Phenom.* **1990**, *51*, 439.

[27] Hehre, W. J.; Radom, L.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.

[28] Allcock, H. R.; Konopski, R. L.; Stroh, E. G. *Chem. Commun.* **1970**, 985.

[29] Allcock, H. R.; Stroh, E. G., unpublished work, quoted in ref 13, Chapter 16.

[30] Manley, T. R.; Williams, D. A. *Polymer* **1969**, *10*, 307.

[31] Cohen, M. M.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *J. Am. Chem. Soc.* **1976**, *98*, 3844.

[32] For experimental results, see: Litvinov, V. M.; Lavruklin, B. D.; Zhdanov, A. A. *Polym. Sci. USSR* 1985. For theoretical results, see: Grigoras, S. In *Computational Modeling of Polymers*; Bicerano, J., Ed.; Marcel Dekker: New York, 1992.

[33] Allcock, H. R.; Meister, J. J.; Lehnsen, J. E., unpublished work, quoted in ref 13, Chapter 16.

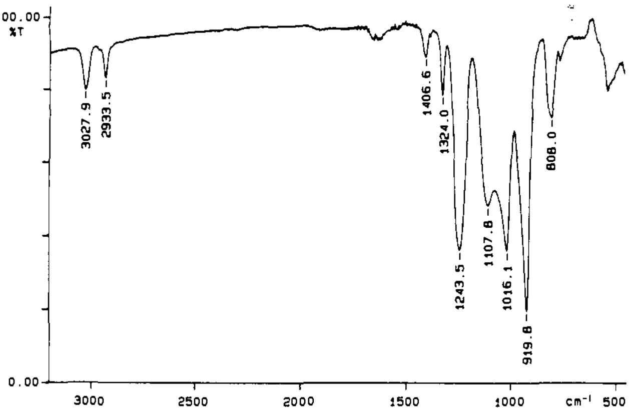


Figure 1. Experimental IR spectrum of polymer **4a**.

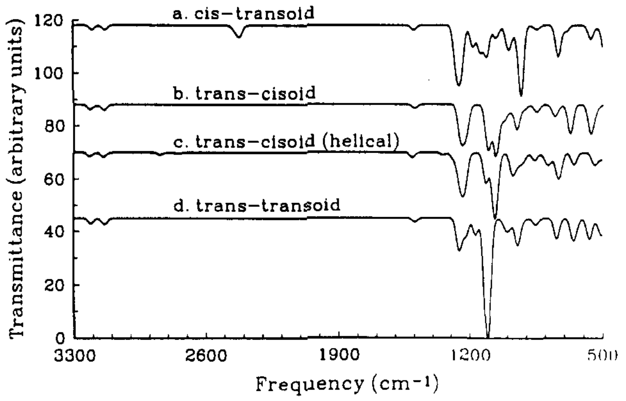


Figure 2. Calculated IR spectra for the various polymer conformations in Chart Ia–c.

C_2H_4 (0.23 mdyne/Å). Although the smaller value of the rotational constant for the oxothiazene could be interpreted in terms of a more torsionally flexible SN double bond, the influence of nonbonding steric interactions on torsional mobility must also be considered. In order to obtain a clearer picture of flexibility and bonding in oxothiazenes, calculations on poly(dimethylphosphazene), $(Me_2PN)_n$, are under way. Torsional barriers and rotational force constants for this polymer (with a T_g at −46 °C) should allow a more direct comparison with poly(methyloxothiazene).

An interesting situation arises on the question of relative inherent flexibilities of the phosphazene and oxothiazene backbones. The high chain flexibility in poly(phosphazenes) has been attributed to the freedom that a nitrogen p-orbital enjoys in being able to overlap with any of several phosphorus d-orbitals as the N═P bond undergoes torsional motion.[13] Thus, the double bond remains relatively free of torsional strain. The chemical bonding situation in poly(oxothiazenes) is very similar, except that two $p\pi$–$d\pi$ bonds are involved for each sulfur atom in every repeat unit. It is conceivable that the geometry requirements for optimum orbital overlap in the two π bonds during skeletal torsional motion may reduce inherent chain flexibility in poly(oxothiazenes).

(b) Infrared Spectra. Before discussing bonding aspects in poly(oxothiazenes), it is useful to compare the calculated IR spectra with that obtained experimentally for poly(methyloxothiazene) using a KBr disc of the polymer. Because of the scarcity of infrared data on oxothiazene structures, the analysis provided here is based mainly on our theoretical calculations.

For simplicity of computation, only the most stable (udu), helical conformation from Chart Ic, with the substituents as shown, was used for the IR calculation. For Chart Ia and Ib as well as for planar Ic all the methyl groups were substituted with H atoms for the calculation. The experimental IR spectrum as well as the calculated spectra for the various conformations in Chart I are shown in Figures 1 and 2, respectively.

It is well-known that the IR frequencies obtained from Hartree–Fock type calculations are usually 10–20% too high when compared with experiment. Therefore, we have scaled the calculated frequencies by 0.85 in Figure 2. Also, Gaussian functions with a half-width of 20 cm^{-1} have been used to represent the calculated "line" intensities in such a way that the area under a Gaussian function is equal to the calculated intensity of that peak.

Comparing with the experimental IR spectrum, it is clear that the calculated spectrum (Figure 2c) based on the helical conformation of Chart Ic, provides the closest agreement with the experimental spectrum. The strongest four peaks found experimentally are quite well reproduced from conformation Chart Ic, but not from Chart I (part a or b), strongly suggesting a trans–cis, helical conformation for polymer **4a**. Using an IR group contribution program developed in our laboratory,[34] we have identified the experimental peak occurring at 1244 cm^{-1} (calculated at 1227 cm^{-1}) to be associated with the S═O group. This value falls slightly outside the range commonly assigned to the S═O group in sulfones. A doublet of very low intensity is seen around 2800 cm^{-1} only in Figure 2c (which incorporates the Me group in calculations). This matches the experimental doublet due to C–H stretching at 3028 and 2934 cm^{-1}.

The experimentally observed peaks at 1108, 1016, and 920 cm^{-1} are very well reproduced in the calculations at 1100, 1050, and 970 cm^{-1}, respectively. Our assignment program indicates that these are due to the terminal and internal asymmetric S═N–S stretching, the low calculated intensity at 970 cm^{-1} being a result of the chain-length limitation in the calculation. Calculated symmetric S═N–S stretching for the trans–cis conformations occur in the range 670–795 cm^{-1}, and this is most likely reflected by the peak at 808 cm^{-1} observed experimentally. These sets of asymmetric and symmetric S═N–S stretching are very similar to those that occur in phosphazenes: symmetric P═N–P stretching at 750–950 cm^{-1} and asymmetric P═N–P stretching at 1200–1400 cm^{-1}. The split, however, is much less in oxothiazenes when compared with phosphazenes, indicating stronger coupling of the single and double bonds in the latter. Compared with the "NS" molecule, which has a stretching frequency at 1218 cm^{-1},[35] the sulfur–nitrogen bonds in poly(oxothiazenes) are weaker, as might be expected.

(c) Bonding. The calculated central N–S single bond length is 1.60 Å, slightly longer than the central S═N double bond length of 1.56 Å. Since the corresponding calculated bond lengths in the hypothetical "monomeric" slice of the backbone (Chart Id) are 1.64 and 1.51 Å, respectively, this may be indicative of some π-island type delocalization in oxothiazene polymers as has been proposed for phosphazene polymers. However, the characters of alternating single and double bonds are probably maintained to quite a large degree, as evidenced by the fact that rotation around a double bond is about four times more difficult in comparison with rotation around a single bond.

It is well-known that symmetrically substituted cyclotriphosphazenes show equal PN bond lengths around the ring. Thus, it was of interest to examine if the same would be true of the as yet unprepared trimethylcyclotrioxothiazene. By carrying out the Hartree–Fock calculations at the same level of accuracy as before, we found that, indeed, the NS bond lengths in this methyl trimer are all equal to each other (1.57 Å), as is also known experimentally for α-[NS(O)Cl]$_3$. However, unlike the "cis", chair form of α-[NS(O)Cl]$_3$, we found a slightly puckered chair, axial–equatorial–axial form to be the most stable for [NS(O)-

---

[34] Lie, G. C.; Grigoras, S.; Lane, T. H., unpublished work.

[35] For experimental results, see: Huber, K. P.; Herzberg, G. In *Constants of Diatomic Molecules*; Van Nostrand: New York, 1979. For theoretical calculations, see: Lie, G. C.; Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1985**, *82*, 2672.

Me]$_3$. The NSN and SNS bond angles in [NS(O)Me]$_3$ were found to be 110° and 120°, respectively.

The SNS bond angles sustained by the inner two N atoms in Chart Ic are 125° and 122°, respectively. These values are very close to those found in many cyclo- and polyphosphazenes and indicate that the hybridization of the N atom is of the sp^2 type. Bannister and Durrant[36,37] have found an interesting relationship between the S–N bond length and the bond angle at nitrogen, A, for acyclic compounds:

$$d_{\mathrm{SN}} = 180 - 0.160\mathrm{A}$$

Using an average SNS bond angle of 123.5°, the equation yields 1.6 Å for the N–S bond length, very close to our calculated values. The NSN bond angle at the central S atom was found to be 103°. It is noteworthy that the situation here is very different from that found in the polyphosphazenes, where the skeletal bond angle at phosphorus is typically about 120°. The significantly smaller skeletal bond angle at sulfur may reflect the accommodations necessary for optimum orbital overlap in the two π bonds, as mentioned earlier. The effect of the smaller skeletal bond angle at sulfur on chain flexibility could be profound, since the smaller angle would increase substituent–backbone steric interactions.

Conclusion

We have been able to conceptualize, develop, and utilize new condensation reactions in sulfur chemistry for the synthesis of a class of sulfur–nitrogen based polymers that are structurally analogous to poly(alkyl/arylphosphazenes). The polycondensation process, patterned after the well-known condensation of *N*-silylphosphoranimines to polyphosphazenes, suggests that the route may provide a general method for the synthesis of new polymer backbones –N═E– where E is a suitable main-group element or metal bearing a variety of substituents. It was also shown that not only the β-elimination of a silyl ether but also the β-elimination of a suitable carbinol may be utilized in the polycondensation process.

The polycondensation method discussed in this paper appears to yield poly(oxothiazenes) of relatively high molecular weight. Further, the condensation of *N*-silylsulfonimidates is catalyzed by either Lewis acids or bases. Since significant differences in molecular weights of the polymers are observed in certain cases depending on the "monomer" used, it appears likely that at least a fair degree of molecular weight control can be exercised with appropriate combinations of "monomer", solvent, catalyst, and reaction conditions. The lower alkyl and aryl substituted polymers are thermoplastics, but indications are that the oxothiazene backbone is flexible, even though this flexibility may be lower than that of the phosphazene backbone. The nature and extent of the possible influence of the S═O side-group and a "small" NSN skeletal bond angle on chain flexibility will likely become clearer with further development of this polymer system.

Experimental Section

Materials and General Procedures. The following reagents and solvents (of at least 99% purity whenever available) were obtained from commercial sources and used without further purification unless otherwise noted: CF$_3$CH$_2$OH, PhOH, anhydrous EtOH, anhydrous MeOH, anhydrous AlCl$_3$, BF$_3$·Et$_2$O, FeCl$_3$, WCl$_6$, Sn(octoate)$_2$, anhydrous KF, TAS-F, LiOPh, toluene, 2-propanol, both ACS grade and anhydrous DMF, DMSO, MeNO$_2$, CH$_2$Cl$_2$, CHCl$_3$, anhydrous THF, hexanes, C$_6$H$_6$, and Et$_2$O. The *N*-silylsulfonimidates **3** were synthesized and purified as described in the preceding paper in this issue. Chloroform and dichloromethane were distilled from P$_2$O$_5$, while benzene and diethyl ether were distilled from CaH$_2$. All syntheses and extended manipulations involving air- or moisture-sensitive species were carried out under an atmosphere of dry nitrogen. In particular, the solid catalysts used for sulfonimidate polymerizations were handled in a nitrogen-filled glove bag. Proton and ^{13}C NMR spectra were recorded on Varian EM-390 or VXR-200 and VXR-200 spectrometers, respectively. Chemical shifts are relative to tetramethylsilane for ^{1}H and ^{13}C signals. The IR spectrum of **4a** was obtained as a KBr disc on a Perkin-Elmer 1640 spectrometer. Molecular weights of all oxothiazene polymers were obtained by GPC with 0.5% w/v solutions in DMF at 90 °C (against polystyrene standards using 10^3, 10^4 and 10^5 Å μ-Styragel columns on a Waters 150C GPC instrument, at a flow rate of 2 mL/min). Elemental analyses were performed by Galbraith Labs. Inc., Knoxville, TN.

General Procedure for the Thermal Condensation of 3 to 4. The *N*-silylsulfonimidates 3 (2.5–25 g, ca. 0.007–0.1 mol) were either distilled directly into precleaned and preweighed heavy-walled glass ampules of 12–70 mL volume or were simply poured in with no more than approximately 30–40% of the ampule filled in any case. Typically, 0.015 mol **3** was used, and larger scale (0.05–0.10 mol) condensations were employed mainly for **3b**. For the synthesis of copolymer **5**, the two "monomers" **3b** and **3e** were weighed into the ampule via pipet. The sulfonimidates were then subjected to 2–3 standard freeze–pump–thaw cycles for degassing. Following this, the ampules were sealed, wrapped in glass wool, and placed within a screw-capped metal pipe (with a hole in at least one of the caps for unexpected pressure release), and the assembly placed in a thermoregulated oven at the study temperatures between 120 and 170 °C.

For catalyzed condensations (which used 0.05 mol % catalyst, based on **3**, in all cases), both **3** and the solid catalyst were weighed into the ampule in a glove bag under nitrogen atmosphere. Boron trifluoride etherate was transferred via syringe to the ampule containing previously degassed **3**, through a septum on a special side-arm on the ampule.

Following the heating period, the ampules were allowed to cool to room temperature, opened after freezing in liquid nitrogen, quickly attached to a vacuum line, and allowed to reach room temperature there under a static vacuum. The liquid contents of the ampule were then either transferred to a preweighed flask on the vacuum line using trap-to-trap distillation techniques or were carefully transferred to a nitrogen-filled flask. Analysis of the liquid by ^{1}H NMR (in conjunction with its weight where Me$_3$SiOCH$_2$CF$_3$ was removed from the ampule by trap-to-trap distillation) yielded the extent of condensation of **3**.

The solid polymer remaining in the ampule was rinsed several times with CH$_2$Cl$_2$ or with hexanes depending on the insolubility of the polymer in the rinse solvent. After removal of residual rinse solvent under vacuum, the polymers were purified by two precipitations using appropriate solvent/nonsolvent combinations. For **4a** in particular, precipitation from MeNO$_2$ into toluene was required to obtain an analytically pure sample, since the polymer appears to retain 1–3% DMF even after repeated vacuum drying at 100–135 °C. In general, after precipitation all polymers were dried under vacuum at 80–100 °C for 40–70 h.

Poly(methyloxothiazene), 4a: rinse solvent for crude polymer, CH$_2$Cl$_2$; solvent/nonsolvent for purification, DMF/distilled water, DMF/toluene, or MeNO$_2$/toluene; drying temperature, 100 °C/0.5 mm; ^{1}H NMR (in DMSO-d_6) ∂ 3.45–3.50 (Me-S); ^{13}C NMR (in DMSO-d_6) ∂ 46.4 (Me-S, main triad plus outer peaks); IR (KBr disc) 3028 (w), 2934 (w), 1244 (ms), 1108 (m), 1016 (ms), 920 (ms), 808 (m). Anal. Calcd: C, 15.58; H, 3.92; N, 18.17. Found: C, 16.07; H, 3.83; N, 18.32.

Poly(ethyloxothiazene), 4b: rinse solvent for crude polymer, hexanes; solvent/nonsolvent for purification, CHCl$_3$/hexanes; drying temperature, 90 °C/0.5 mm. Anal. Calcd: C, 26.36; H, 5.53; N, 15.37. Found: C, 26.37; H, 5.63; N, 15.15.

Poly(phenyloxothiazene), 4c: rinse solvent for crude polymer, hexanes; solvent/nonsolvent for purification, CH$_2$Cl$_2$/hexanes; drying temperature, 95 °C/0.5 mm. Anal. Calcd: C, 51.78; H, 3.62; N, 10.06. Found: C, 51.97; H, 3.77; N, 9.99.

Poly(4-fluorophenyloxothiazene), 4d: rinse solvent for crude polymer, CH$_2$Cl$_2$; solvent/nonsolvent for purification, DMF/distilled water; drying temperature, 95 °C/0.5 mm. Anal. Calcd: C, 45.85; H, 2.57; N, 8.91. Found: C, 45.88; H, 2.73; N, 8.70.

Poly(methyl-co-phenyloxothiazene), 5: rinse solvent for crude polymer, hexanes; solvent/nonsolvent for purification, CHCl$_3$/hexanes; drying temperature, 100 °C/0.5 mm. Anal. Calcd (for 1:1 copolymer): C, 38.87; H, 3.73; N, 12.95. Found: C, 39.42; H, 3.65; N, 12.81.

General Procedures for the Desilylation of 3 to 7 Using Methanol. 2,2,2-Trifluoroethyl sulfonimidates 7a, 7c, 7d. A two-necked, RB flask, equipped with Teflon sleeves at the necks, a magnetic stirring bar, gas inlet, and rubber septum was flushed with nitrogen and charged with the *N*-silylsulfonimidate (0.005–0.2 mol). The flask was maintained at 20–25 °C using a water bath, while methanol (500 mol % excess) was slowly added via syringe through the rubber septum. The septum was then

---

(36) Banister, A. J.; Durrant, J. A. *J. Chem. Res.* **1978**, S 150.

(37) Banister, A. J.; Durrant, J. A. *J. Chem. Res.* **1978**, S 152.

replaced with a stopper, and the mixture was heated at 45–55 °C (35–40 °C when a 1000 mol % methanol was used) for 5 h. Excess methanol and methoxysilane were then removed under reduced pressure and below 55 °C (40 °C for 1000 mol % excess methanol) to leave behind the clear, viscous, free sulfonimidate. This was stored at −20 to −25 °C and usually thermally condensed to the oxothiazene polymer within 1–3 days.

For **7a**: ^{1}H NMR (ca. 25% v/v in $\mathrm{CDCl_3}$) ∂ 3.10 (Me-S), 3.6 (br, NH), 4.40 ($\mathrm{OC}H_2\mathrm{CF}_3$, apparent quartet $^3J_{\mathrm{FH}} = 8.3$ Hz); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ 40.0 (Me-S), 63.5 (q, $\mathrm{O}C\mathrm{H}_2\mathrm{CF}_3$, $^2J_{\mathrm{FC}} = 37.0$ Hz), 122.6 (q, $\mathrm{OCH}_2C\mathrm{F}_3$, $^1J_{\mathrm{FC}} = 277.6$ Hz).

For **7c**: ^{1}H NMR (ca. 25% v/v in $\mathrm{CDCl_3}$) ∂ 1.96 (m, $\mathrm{ClCH_2C}H_2$-$\mathrm{CH_2}$-S), 2.93 (m, $\mathrm{ClCH_2CH_2C}H_2$-S, possibly diastereotopic protons), 3.17 (t, $\mathrm{ClC}H_2\mathrm{CH_2CH_2}$-S, $^3J_{\mathrm{HH}} = 6.3$ Hz), 3.5 (br, NH), 4.03 ($\mathrm{OC}H_2$-$\mathrm{CF_3}$, apparent quartet, $^3J_{\mathrm{FH}} = 8.4$ Hz); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ 26.9 ($\mathrm{ClCH_2}C\mathrm{H_2CH_2}$-S), 42.4 ($\mathrm{ClCH_2CH_2}C\mathrm{H_2}$-S), 50.1 ($\mathrm{Cl}C\mathrm{H_2CH_2CH_2}$-S), 63.3 (q, $\mathrm{O}C\mathrm{H_2CF_3}$, $^2J_{\mathrm{FC}} = 37.0$ Hz), 122.6 (q, $\mathrm{OCH_2}C\mathrm{F_3}$, $^1J_{\mathrm{FC}} = 278.0$ Hz).

For **7d**: ^{1}H NMR (ca. 25% v/v in $\mathrm{CH_3CN}$) ∂ 7.10 (d, Ph-CH=CH-S, $^{\mathrm{trans}}J_{\mathrm{HH}} = 15.6$ Hz), 4.2–4.7 ($\mathrm{OC}H_2\mathrm{CF_3}$, apparent quartet, overlapping with NH signal), 7.4–7.9 (m, Ph-S, overlapping with Ph-CH=CH-S signal); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ 64.1 (q, $\mathrm{O}C\mathrm{H_2CF_3}$, $^2J_{\mathrm{FC}} = 36.6$ Hz), 122.2 (Ph-CH=CH-S), 122.6 (q, $\mathrm{OCH_2}C\mathrm{F_3}$, $^1J_{\mathrm{FC}} = 278.0$ Hz) [Ph; 131.8-i, 128.5-o, 129.0-m, 131.4-p].

Phenyl Sulfonimidates 7b and 7e. With a setup as for the fluoroalkoxy sulfonimidates, the flask was charged with the *N*-silylsulfonimidate **3b** or **3f** (0.01–0.03 mol). While maintaining the flask at 15–20 °C using a water bath, methanol (100–150 mol % excess for **3b**, 200 mol % excess for **3f**) was slowly added via syringe. The mixture was stirred at 22–25 °C for 2–4 h, and then volatiles were removed under reduced pressure below 35 °C, to leave behind the crystalline, solid free sulfonimidate. This was stored at −20 to −25 °C but normally condensed to the oxothiazene polymer within 1–3 days.

For **7b**: ^{1}H NMR (ca. 20% w/v in $\mathrm{CDCl_3}$) ∂ 3.11 (Me-S), 3.5 (br, NH), 7.1–7.6 (OPh); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ 39.7 (Me-S) [OPh; 149.6-i, 122.7-o, 129.8-m, 126.8-p].

For **7e**: ^{1}H NMR (ca. 20% w/v in $\mathrm{CDCl_3}$) ∂ 6.9–8.0 (m, *Ph*-S, overlapping with O*Ph*), 3.8 (br, NH); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ [Ph-S; 137.2-i, 128.2-o, 129.0-m, 133.6-p], [OPh; 150.4-i, 122.9-o, 129.6-m, 126.0-p].

Ethyl Sulfonimidate 7f. A two-necked flask equipped as above, was charged with **3g** (0.02 mol, 3.90 g) and dry KF (0.0001 mol, 0.0058 g). The flask was maintained at 20–25 °C and methanol (0.12 mol, 4.9 mL) was slowly added via syringe. The mixture was heated at 50–52 °C for 5 h. Volatiles were then removed under reduced pressure at 45 °C. This left the free sulfonimidate **7f** as a clear, colorless liquid.

For **7f**: ^{1}H NMR (ca. 25% v/v in $\mathrm{CDCl_3}$) ∂ 2.88 (Me-S), 3.1 (br, NH), 1.21 (t, $\mathrm{OCH_2C}H_3$, $J_{\mathrm{HH}} = 7.2$ Hz), 4.02 ($\mathrm{OC}H_2\mathrm{CH_3}$, apparent quartet); ^{13}C NMR (in $\mathrm{CDCl_3}$) ∂ 39.1 (Me-S), 14.4 ($\mathrm{OCH_2}C\mathrm{H_3}$), 63.8 ($\mathrm{O}C\mathrm{H_2CH_3}$).

General Procedure for the Thermal Polycondensation of 7a–e. The flask containing the free sulfonimidate (0.005–0.2 mol) was fitted with a magnetic stirring bar or a mechanical stirrer (and reflux condenser for 2,2,2-trifluoroethyl sulfonimidates) and Teflon sleeves at the necks and was connected to a preweighed trap held at −78 °C. The whole assembly was maintained under nitrogen. Typically, 0.005–0.01 mol of **7** was used; larger scale (0.2 mol) condensations have been carried out only with **7a**. For solution polymerizations, DMF (anhydrous) was added to the flask to make a 1–3 molar solution of the sulfonimidate. For neat polymerizations, the pressure was usually reduced (to about 10 mmHg for **7a**, **7c** and **7d** and to 1–2 mmHg for **7b** and **7e**) in order to facilitate removal of the alcohol byproduct of the condensation to the −78 °C trap. The flask was then gradually heated to 85–120 °C (not above 95 °C for solution polymerization in DMF) and maintained at that temperature for 1–3 h. Exothermic condensation usually began between 85 and 105 °C and appeared to be practically over within 20 min. Usually, at this point the pressure was reduced to about 0.2 mmHg to remove as much alcohol as possible, particularly for phenyl sulfonimidate condensations.

At the end of the heating period, the flask was cooled to room temperature, and the crude polymer was rinsed with a solvent that dissolved any uncondensed precursor/residual condensation byproduct but not the polymer and then purified by two precipitations from appropriate solvents as described earlier for polymers obtained from **3**. In all cases, condensation of the free sulfonimidate was found to be near-quantitative based on the weight of the alcohol obtained and ^{1}H NMR analysis of both the trapped alcohol and the residue in the flask.

Poly(3-chloropropyloxothiazene), 4e: rinse solvent for crude polymer, benzene; solvent/nonsolvent for purification, first precipitation, $\mathrm{CH_2Cl_2}$/hexanes; second precipitation, DMF/distilled water; drying temperature, 90 °C/0.5 mm. Anal. Calcd: C, 25.81; H, 4.33; N, 10.03. Found: C, 26.21; H, 4.38; N, 10.06.

Poly(β-styryloxothiazene), 4f: rinse solvent for crude polymer, none; solvent/nonsolvent for purification, $\mathrm{CH_2Cl_2}$/hexanes; drying temperature, 100 °C/0.5 mm. Anal. Calcd: C, 58.16; H, 4.27; N, 8.48. Found: C, 57.00; H, 4.46; N, 8.06.

Poly(methyl-co-phenyloxothiazene), 5: rinse solvent for crude polymer, none; solvent/nonsolvent for purification, DMF/distilled water; drying temperature, 95 °C/0.5 mm. Anal. Calcd (for 1:1 copolymer): C, 38.87; H, 3.73; N, 12.95. Found: C, 39.89; H, 4.03; N, 12.55.

Acknowledgment. This work was supported by the Dow Corning Corporation. We also thank Dr. Michael Owen and Shirley Wackerle of Dow Corning, Midland, Michigan for providing the surface tension and contact angle measurement data for poly(methyloxothiazene).