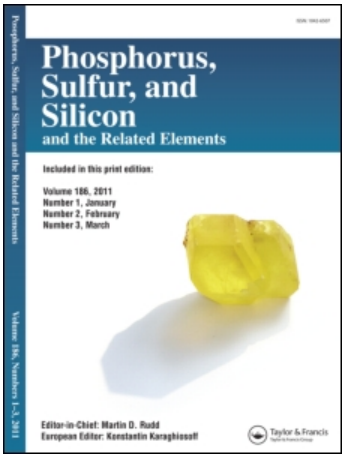

Phosphorus, Sulfur, and Silicon and the Related Elements

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SULFUR(VI)-NITROGEN-PHOSPHORUS MACROCYCLES AND POLYMERS

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Abstract Cyclic thionylphosphazenes **1** undergo thermal ring-opening Polymerization (TROP) to yield poly(thionylphosphazenes) **2** with backbones of four coordinate sulfur(VI), nitrogen, and phosphorus atoms. During TROP of **1**, macrocycles with analogous skeletal compositions were also formed. Isolation, characterization and thermolysis studies of these species are described.

INTRODUCTION

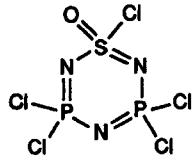
Cyclic compounds which contain inorganic elements as part of the ring skeleton are of considerable interest with respect to their structure, reactivity, solid state properties, and as precursors to new inorganic and organometallic polymer systems. In this paper we report the isolation and identification of byproducts formed during TROP of **1** which represent the first examples of macrocyclic species with sulfur(VI)-nitrogen-phosphorus skeletons. Additionally, we describe the polymerization behavior of these macrocycles.

SULFUR(VI)-NITROGEN-PHOSPHORUS MACROCYCLICS

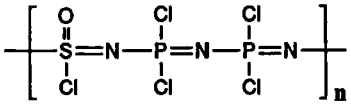
TROP of thionylphosphazene **1** yields the poly(thionylphosphazene) **2** together with small amounts of macrocyclic material which can be detected by ^{31}P NMR and

mass spectrometry.[1, 2] Macrocycles were successfully isolated via fractional sublimation after **2** had been removed by precipitation. The white crystalline sublimate showed two ^{31}P NMR resonances in a 1.2:1 ratio at -8.1 and -8.3 ppm in hexanes. An X-ray quality crystal was obtained from a hexanes solution at ambient temperature.

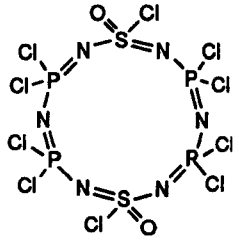
Remarkably, single crystal X-ray diffraction analysis found a 2:1 mixture of cis and trans isomers of the symmetrical 12-membered ring **3** with molecules of the latter located at crystallographic inversion centers. Analysis of the crystal by ^{31}P NMR found resonances at -8.1 and -8.3 ppm in a 2:1 ratio. The ^{31}P NMR peaks at -8.1 and -8.3 are therefore assigned to cis and trans isomers, respectively.



1



2



3

While **3** does not undergo TROP even when heated at elevated temperatures for prolonged periods, vacuum thermolysis of a 1:1 mixture of **1** and **3** at 165 °C resulted in a decrease in the amount **3** by ^{31}P NMR accompanied by formation of poly(thionylphosphazene) **2**. This result suggests that **3** copolymerizes with **1**.

Analysis of the residue remaining after sublimation of **3** using mass spectrometry showed the presence of higher (18-36 membered) ring systems. Attempts to crystallize these higher membered ring species are underway.

ACKNOWLEDGMENTS

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REFERENCES

1. M. Liang, and I. Manners, J. Am. Chem. Soc. 113, 4044 (1991).
2. Y. Ni, A. Stammer, M. Liang, J. Massey, G. Vancso, I. Manners, Macromolecules 25, 7119 (1992).