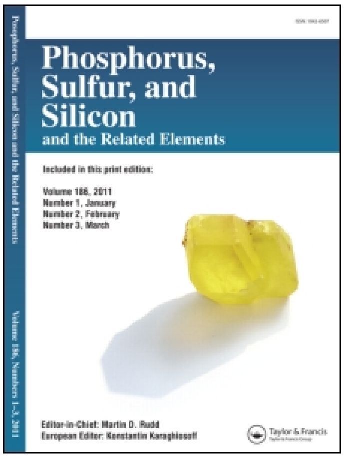


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Ring-Opening Polymerization as a Route to New Inorganic Macromolecules

Mong Liang[a]; Chris Waddling[a]; Charles Honeyman[a]; Dan Foucher[a]; Ian Manners[a]
[a] Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

To cite this Article Liang, Mong , Waddling, Chris , Honeyman, Charles , Foucher, Dan and Manners, Ian(1992) 'Ring-Opening Polymerization as a Route to New Inorganic Macromolecules', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 113 — 120

To link to this Article: DOI: 10.1080/10426509208041136

URL: http://dx.doi.org/10.1080/10426509208041136

Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 113–120
Reprints available directly from the publisher
Photocopying permitted by license only

RING-OPENING POLYMERIZATION AS A ROUTE TO NEW INORGANIC MACROMOLECULES

MONG LIANG, CHRIS WADDLING, CHARLES HONEYMAN, DAN FOUCHER, AND IAN MANNERS*
Department of Chemistry, University of Toronto, 80 St. George St.,
Toronto M5S 1A1, Ontario, Canada.

Abstract Cyclic inorganic compounds are potential precursors to new inorganic polymer systems via ring-opening polymerization. In this paper we review some of our recent work aimed at preparing inorganic polymers containing main group elements. For example, the ring-opening polymerization of the cyclic thionylphosphazenes $NSOX(NPCl_2)_2$ (X = Cl or F) is discussed. This provides a route to poly(thionylphosphazenes), a new class of stable inorganic polymers with backbones of phosphorus, nitrogen, and sulfur(VI) atoms. We also describe some of our preliminary work aimed at the investigation of the synthesis, structure, and polymerization behaviour of boracyclosiloxanes $(RBO)(R_2SiO)_n$.

INTRODUCTION

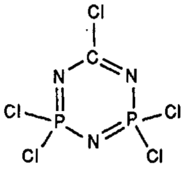
The ring-opening polymerization of cyclic organic compounds provides an important synthetic route to a variety of organic polymers of commercial significance, including polyamides, polyethers, polyolefins, and polycarbonates.[1] As a consequence of the rich abundance of different cyclic inorganic compounds a similar or even broader range of inorganic polymers might be anticipated using an analogous methodology. However, apart from cyclic phosphazenes and cyclic siloxanes, relatively few systems have been studied in detail.[2,3]

One of the aims of our research at Toronto is to explore the synthesis, structure, and polymerization behaviour of cyclic inorganic and organometallic compounds. In this paper we will discuss some of our recent work concerning rings constructed from atoms of the main-group elements.

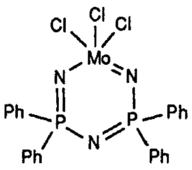
RING-OPENING POLYMERIZATION OF CYCLOTHIONYLPHOSPHAZENES

Introduction

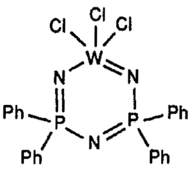
Cycloheterophosphazenes are an interesting class of inorganic species which are formally derived from the well studied, polymerizable cyclic phosphazenes by the replacement of a skeletal phosphorus atom by an atom of a heteroelement. Many examples of these small molecule compounds are now known and in the last two years the successful polymerization of species with skeletal carbon (**1**), molybdenum (**2**), or tungsten (**3**) atoms to yield stable macromolecular products has been described.[4,5]



1

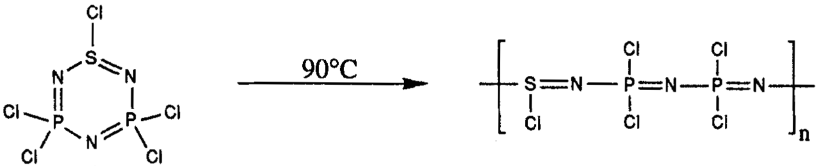


2



3

Even more recently, the ring-opening polymerization of a cyclic thiophosphazene (**4**) which contains a skeletal sulfur(IV) atom was reported.[6] However, in this case, the sulfur-nitrogen bonds present in the poly(thiophosphazene) backbone appear to possess intrinsic hydrolytic sensitivity and, to date, reasonably stable polymers have only been isolated when very bulky side group substituents are present.[6]



4 **5**

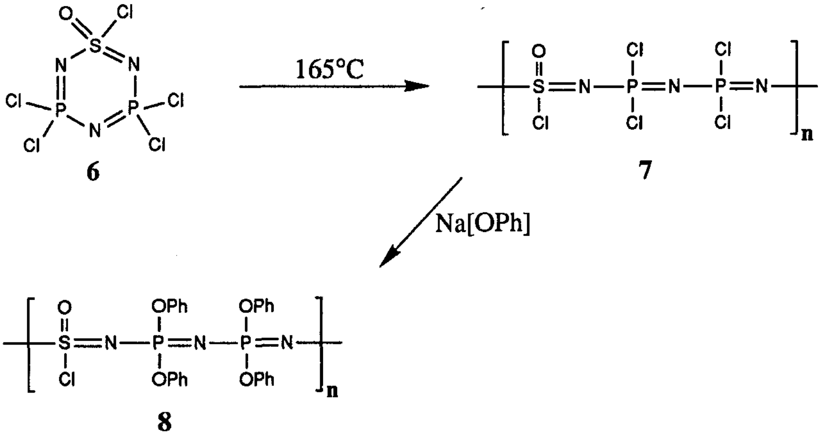
At Toronto we have explored the polymerization behavior of the cyclic thionylphosphazene **6** which contains a skeletal, high oxidation state sulfur(VI) atom.[7] Cyclic species such as **6** have been known for almost 20 years but, to our knowledge, no detailed polymerization studies have been reported.[8] Furthermore, from literature reports, many cyclothionylphosphazenes (also known as cyclothiaphosphazenes) appear to show much greater stability towards hydrolysis compared to their sulfur(IV) analogues.

Ring-Opening Polymerization of the Cyclic Thionylphosphazene 6

Several aspects of the chemistry of cyclic thionylphosphazenes have been well-studied.[8] However, no reports of well-characterized polymers derived from this ring-system have appeared.

The cyclothionylphosphazene **6** is a white, crystalline, slightly moisture-sensitive solid which can be prepared by a number of methods.[8] In our preliminary work, a low yield two-step procedure was used involving the reaction of PCl_5 with NH_4Cl to give $[Cl_3P{=}N{=}PCl_3]\,[PCl_6]$ followed by a (3 + 3) cyclocondensation with $H_2NSO_2NH_2$.[9] Recent work from our laboratory has shown that the salt $[Cl_3P{=}N{=}PCl_3]\,[PCl_6]$ can also be prepared conveniently via the reaction of two-equivalents of PCl_5 with $Cl_3P{=}NSiMe_3$ with the elimination of Me_3SiCl, a process that circumvents the need for high boiling point toxic solvents.[10]

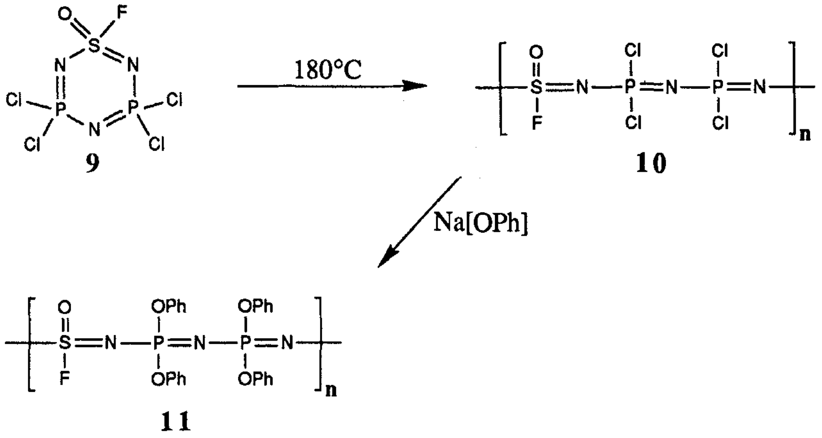
When compound **6** is heated at 165°C ring-opening polymerization occurs to yield the poly(thionylphosphazene) **7** as a hydrolytically sensitive material.[7] Treatment of this polymer with sodium phenoxide affords the substituted polymer **8**. This polymer appears indefinitely stable to atmospheric moisture and is a colourless elastomeric material which slowly undergoes viscous flow when uncrosslinked. In the crosslinked state this polymer displays rubbery behaviour.



Ring-Opening Polymerization of the Fluorinated Cyclothionylphosphazene 9

An important feature of the substitution process used to prepare **8** is the retention of the chlorine atom bonded to sulphur. We therefore reasoned that the ring-opening polymerization of cyclic thionylphosphazenes which possess a fluorine substituent at sulphur should provide access to novel inorganic fluoropolymers in which the sulphur-fluorine bonds remain intact in subsequent macromolecular substitution reactions.

The fluorinated cyclic thionylphosphazene **9** can be prepared via the reaction of **6** with AgF_2.[11] When this species is heated at 180°C ring-opening polymerization to yield the poly(thionylphosphazene) **10** occurs. This transformation represents the first example of the ring-opening polymerization of a cycloheterophosphazene with fluorine substituents.[12] Polymer **10**, like polymer **7**, also undergoes exclusive substitution of the chlorine atoms at phosphorus, affording the hydrolytically stable fluorinated poly(thionylphosphazene) **11**. Polymer **11** is a very rare example of a moisture stable inorganic polymer with fluorine substituents bonded directly to the polymer backbone. This species is expected to exhibit unusual material properties which are currently under investigation. In addition, considerable prospective tunability and versatility exists with fluorinated poly(thionylphosphazenes) as, in principle, a variety of substituents might be attached to phosphorus by carrying out substitution chemistry on **10**.



Regiospecific Nucleophilic Substitution Reactions of Cyclic and Polymeric Thionylphosphazenes

One of the most interesting features to emerge so far from the thionylphosphazene polymerization chemistry that we have developed is the regiospecific nucleophilic substitution detected for the macromolecules **7** and **10**. Interestingly, the replacement of the chlorine atoms bonded to phosphorus rather than the halogen atoms at sulfur is in stark contrast to the behavior of the sulfur(IV) analogue, the poly(thiophosphazene) **5**, where nucleophilic substitution takes place preferentially at sulfur.[6] The higher reactivity of the phosphorus-halogen bonds of cyclothionylphosphazenes towards certain nucleophiles has been previously noted[8] and was confirmed in our studies of the reactions of the small molecules **6** and **9** with sodium aryloxides. For example, reaction of **6** with excess sodium phenoxide at room temperature (dioxane, 24 h) affords mainly $NSOCl\{NP(OPh)_2\}_2$ and the complete formation of the fully substituted species $NSO(OPh)\{NP(OPh)_2\}_2$ is only achieved at elevated temperatures (dioxane, 60°C, 24 h).[7] Similarly, reaction of **9** with excess sodium phenoxide at room temperature (dioxane, 24 h) yields only $NSOF\{NP(OPh)_2\}_2$. However, in this case formation of the fully substituted species $NSO(OPh)\{NP(OPh)_2\}_2$ is not detected even at elevated temperatures (dioxane, 60°C, 72 h).[12]

Reactions of Cyclic and Polymeric Thionylphosphazenes with Amines

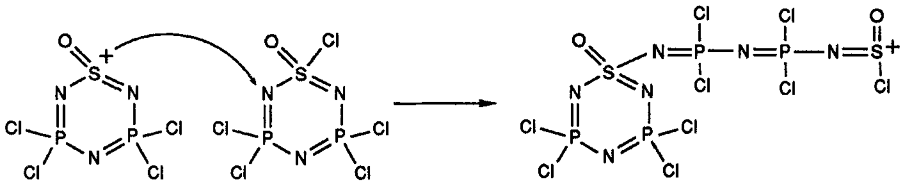
We have begun to explore the reactions of cyclic and polymeric thionylphosphazenes with amines in order to prepare new types of polymers and to compare the detected regiospecificity with that found for aryloxides.

The cyclic thionylphosphazene **6** reacts with methylamine or aniline to yield products which are fully substituted both at a phosphorus and sulfur. Preliminary results indicate that these reactions can also be carried out at the polymer level with **7** to yield stable products.[13]

Thionylphosphazene Ring-Opening Polymerization Mechanism

The most likely polymerization mechanism for **6** or **9** is a cationic, chain growth process. A similar mechanism is common for many cyclic organic molecules and is believed to operate for cyclic phosphazenes.[2] Two possible initiation steps might be envisaged. First, ionization of a S-Cl bond, and second, ionization of a P-Cl bond. Studies by Van de Grampel suggest that the nucleophilic substitution reactions of **6** with amines a proceed via an S_N1 mechanism at sulphur, and an S_N2 process at phosphorus.[8] This would tend to indicate that the first alternative, which is identical to the first step of an S_N1 process, is the more feasible.

If we speculate that the first alternative is correct, chain propagation might occur via attack of the thionylphosphazene cation on another molecule of **6** to give a cationic cyclolinear species which could then continue chain propagation.



Chain termination could occur by cation-anion recombination, and chain transfer by the cationic active site abstracting a chloride anion from an adjacent polymer chain. The polymerization may actually be living but this remains to be determined. Further work aimed at addressing these problems and investigating the material properties and applications of poly(thionylphosphazenes) is in progress.

SYNTHESIS, STRUCTURE, AND POLYMERIZATION BEHAVIOUR OF HETEROCYCLOSILOXANES

Introduction

Cyclosiloxanes comprise a well studied group of small molecules many of which polymerize to yield polyorganosiloxanes (silicones). At present, these macromolecules represent the most commercially useful class of inorganic polymers with applications as high performance oils, speciality elastomers, adhesives, and biomaterials.[3] At Toronto we are interested in the synthesis, structure, and polymerization behaviour of cycloheterosiloxanes, which contain an atom of a third main group or transition metal heteroelement in addition to silicon and oxygen.[14] Most aspects of the chemistry of these species are virtually unexplored. However, the polymerization of compounds of this type would be of considerable interest as the resulting macromolecules should possess properties that complement and broaden those accessible with the conventional silicone polymer system.

Synthesis and Structure of Cycloborasiloxanes

We are particularly interested in the idea that additional ring-strain might be imparted to silicone rings via the incorporation of small skeletal heteroatoms such as boron. We have therefore prepared a range of boracyclosiloxanes such as the six-membered ring compound $PhBO(Ph_2SiO)_2$ **12**. This compound is readily accessible via the reaction of phenylboric acid with 1,2-dichlorotetraphenyldisiloxane in the presence of a hydrogen halide acceptor.[15]

The X-ray structure of this species (Figure 1) shows that the structural consequences of replacing a silicon atom (covalent radius 1.17 A) by a smaller boron atom (covalent radius 0.80 A) are dramatic. This causes a considerable decrease of 0.26 A in the distance between the two oxygen atoms O1 and O1' compared to the situation in $Si_3O_3Ph_6$.[16] This contraction can be readily appreciated by noting the non-parallel nature of the Si-O1 and Si'-O1' bonds (see Figure 1). The enforced decrease in the O1-O1' distance leads to a marked contraction of the Si-O2-Si' bond angle to 127.1(1)° compared to the value of 131.8(8)° in $Si_3O_3Ph_6$. The presence of considerable angle-strain in **1** is further emphasized by a consideration of the much larger Si-O-Si bond angles in $Si_4O_4Ph_8$ [152.3(2)° and 167.4(2)°][17] and unconstrained, linear disiloxanes such as $Me_3SiOSiMe_3$ [148.8(1)°][18].

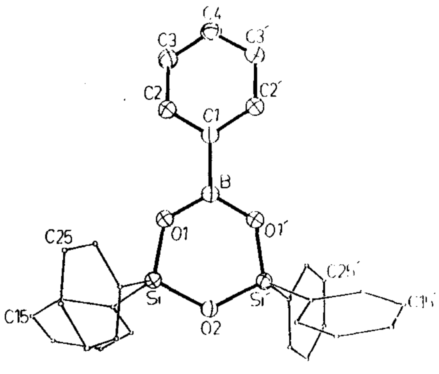


FIGURE 1 The Molecular Structure of $PhBO(Ph_2SiO)_2$ **12**

Preliminary results suggest that these species such as **12** undergo extremely facile equilibration reactions to yield larger macrocyclic products both at ambient and at elevated temperatures. Full details these studies will be reported in forthcoming publications.[15]

ACKNOWLEDGEMENTS

We thank the University of Toronto, the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Ontario Centre for Materials Research for financial support of our programme.

REFERENCES

1. "Ring Opening Polymerization" Edited by K.J. Ivin and T. Saegusa, Elsevier, New York, 1984.
2. See H. R. Allcock in Inorganic and Organometallic Polymers, edited by M. Zeldin , K. Wynne, H. R. Allcock, ACS Symp.Ser. 360, Washington D.C. (1988).
3. See J. C, Saam in Silicon-Based Polymer Science edited by J.M. Zeigler, and F. W. G. Fearon, Advances in Chemistry 224, American Chemical Society, Washington D.C.(1990).
4. a) I. Manners, G. Renner, H. R. Allcock, O. Nuyken, J. Am. Chem. Soc., 111, 5478, (1989) b) S. M. Coley, I. Manners, G. Renner, H. R. Allcock, O. Nuyken, Macromolecules, 24, 2024 (1991).
5. H. W. Roesky, M. Lucke, Angew. Chem. Int. Ed. Engl., 28, 493, (1989).
6. J. A. Dodge, I. Manners, H. R. Allcock, G. Renner, O. Nuyken, J. Am. Chem. Soc., 112, 1268, (1990).
7. a) M. Liang, I. Manners, J. Am. Chem. Soc. 113, 4044, (1991).
   b) M. Liang, C. Waddling, I. Manners, Polymer Prepr. (Am. Chem. Soc. Div. Polym. Chem.) (1991), in press.
8. J. C. Van de Grampel, Rev. Inorg. Chem. 3, 1 (1981).
9. U. Klingebiel, and O. Glemser, Z. Naturforsch. 27b, 467 (1972).
10. C. Honeyman, I. Manners, unpublished results.
11. H. H. Baalman, J. C. Van de Grampel, Recl. Trav. Chim., 92, 1237, (1973).
12. M. Liang and I. Manners, Manuscript in Preparation.
13. C. Waddling, T. Angelakos, M. Liang, I. Manners, Manuscript in Preparation.
14. For recent work on heterosiloxanes, see for example, a) A. Haoudi-Mazzah, A. Mazzah, H. Schmid, M. Noltemeyer, and H. W. Roesky, Z. Naturforsch., 46b, 587, (1991) b) M. A. Hossain, M.B. Hursthouse, M. A. Mazid, and A.C. Sullivan , J. Chem. Soc., Chem. Commun. 1305, (1988). c) M. B. Hursthouse, M. A. Mazid, M. Motevalli, M. Sanganee, and A. C. Sullivan J. Organomet. Chem., 381, C43 (1990), d) U. Wannagat, G. Eisele, Z. Naturforsch., 33b, 475, (1978).
15. a) D. Foucher, A. Lough, and I. Manners, J. Organomet. Chem. (1991), in press.
    b) D. Foucher, A. Lough, and I. Manners, Manuscript in Preparation.
16. N. G. Bokii, G. N. Zakharova, and Y. T. Struchov, Zhur. Struktur. Khim., 13, 291, (1972).
17. M. A. Hossain, M. B. Hursthouse, and K. M. A. Malik, Acta Cryst., B35, 522, (1979).
18. M.J. Barrow, E.A.V. Ebsworth, and M. M. Harding, Acta Cryst. , B35, 2093 (1979).