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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract USN00014-89-J-1041
R&T Code NR413c012

Polymeric Precursors to Binary Inorganic Materials

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JUL 06 1994
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94-20478

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FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is submitted	2. Federal Grant or Other Identifying Number Assigned By Federal agency	OMB Approval No.	Page	of
U. S. Naval Research	N00014-89-J-1041	0348-0039	1	1 pages

3. Recipient Organization (Name and complete address, including ZIP code)

University of Vermont
Grant & Contract Accounting, Waterman Bldg.
Burlington, Vermont 05405

4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
03-0179440	0-24810	☒ Yes ☐ No	☒ Cash ☐ Accrual

8. Funding/Grant Period (See Instructions) From: (Mionth, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
10/01/88	11/30/92	10/01/88	11/30/92

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	- 0 -	240,719.64	240,719.64
b. Recipient share of outlays	- 0 -	- 0 -	- 0 -
c. Federal share of outlays	- 0 -	240,719.64	240,719.64
d. Total unliquidated obligations			- 0 -
e. Recipient share of unliquidated obligations			- 0 -
f. Federal share of unliquidated obligations			- 0 -
g. Total Federal share *(Sum of lines c and f)*			240,719.64
h. Total Federal funds authorized for this funding period			241,189.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			469.36

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☐ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate see attached	c. Base	d. Total Amount	e. Federal Share

12. Remarks: *Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
Rosemary J. Rathbun, Director, Grant & Contract Accounting	802-656-2986
Signature of Authorized Certifying Official Rosemary Rathbun	**Date Report Submitted** 11/12/92

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11. Indirect Expense

11b. Rate		11c. Base	11d. Total Amt.	11e. Federal Share
FY 89	55.0%	28,557.20	15,706.46	15,706.46
FY 90-92	52.6%	127,087.45	66,848.00	66,848.00
FY 93	50.0%	680.35	340.18	340.18
Totals		$156,325.00	$82,894.64	$82,894.64

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BRIEF NARRATIVE REPORT

The research supported in this contract, and previous a ORN contract ("Organofunctional Phosphazenes and Organofunctional Phosphazene Polymers") has lead to the establishment of an entire new class of hybrid inorganic/organic materials. After the discovery and elaboration of this class of polymers by our group in Vermont, research in this area has attracted the interest of inorganic chemists, polymer chemists and materials scientists in the US, Canada, the UK, the Netherlands and Japan. Our work has been comprehensively reviewed in Technical Report (TR)#19. The entire area is covered in yearly comprehensive reviews of phosphazene chemistry authored by the P.I. The work supported by this contract was concerned with the preparation and polymerization of functionalized inorgainc ring systems followed by thermal decomposition reactions to provide interesting and useful materials such as boron nitride ceramics. The general approach involved a three step process which started with the affixing of a vinyl group to an inorganic ring system (with the emphasis being on cyclophosphazenes and cycloborazines). The vinyl borazine was then polymerized to form polymeric precursors to the above mentioned ceramics. In some cases, chemical modification of the polymers preceded the final step which involves the pyrolysis of the mixed inorganic/organic polymers to form the desired materials. At each stop of the process, new materials were characterized in terms of both structure and reactivity.

Inorganic rings systems examined included cyclphosphaznes, cycloborazines and silylazanes. In cyclphosphazene chemistry we have developed several new monomers and studied their polymerization behavior. These included vinylether (TR#1), ∝-methylstyrene (TR#3,4,9) styrene (TR#3), vinyloxy (TR#15) derivatives. A detailed mechanistic study of the thermal decomposition process of one of these systems, poly(vinyloxypentachlorocyclotriphosphazene), has been conducted (TR#7). Reactivity studies include both monomers and polymeric systems. Insights gained from monomer synthesis lead to the establishment of predictive schemes for substitution reactions of cyclophosphazenes (TR#16). Reactivity ratios of inorganic monomers in copolymerization have received detailed attention (TR#6,7,19). Reactions of polymers containing cyclophosphazenes have involved both nucleophilic substitution processes and redox activity of exocyclic redox centers (TR#18). In cycloborazine chemistry new vinyl and styrene derivatives have been prepared (TR#11,13) and their homo and copolymerization reactions investigated (TR#11,13,17,19). Transformation to high char yield materials has been achieved (TR#17,19). The polymerization of $N_3B_3Me_5CH=CH_2$ proceeds thermally or by δ-irradiation but not by classical radical initiation. Polymerization of $N_3B_3Me_4(CH=CH_2)_2$ or the $N_3B_3Me_{6-n}(CH=CH_2)_n$ (n=1,2) mixture can be controlled to stop at a soluble material which may be cross-linked on further heating. Pyrolysis of the cross-linked material gives an 80% char yield at 800° in air or nitrogen. The trininyl derivative can be added to a mold and heated to give shaped objects. Novel acetylene bridged borazines have also been prepared. A synthesis of monovinylcyclodsilylazanes $(Me_2Si)(NR)_2SiMeCH=CH_2$ has been achieved and the copolymerization of one of these materials (R=Ph) with styrene has been carried out.

TECHNICAL REPORTS/JOURNAL ARTICLES

1. Technical Report #1: C.W. Allen and R.P. Bright "Organophosphazenes. 19. Copolymerization of 2-(2-ethonxyvinly)pentafluorocyclotriphosphazene with Styrene and Methyl Methacrylate" *Macromolecules*, **19**, 571 (1986).

2. Technical Report #2: J.C. Shaw and C.W. Allen "Organophosphazenes. 20. Carbonyl Functionalized Aryl Fluorcyclotriphosphazenes", *Synth. React. Inorg. Met. Org. Chem.*, **16**, 1207 (1986).

3. Technical Report #3: C.W. Allen and J.C. Shaw, ∝-Methylstyrl- and styriphosphazene Monomers and Polymers, *Phosphorus and Sulfur*, **30**, 97 (1987).

4. Technical Report #4: J.C. Shaw and C.W. Allen "Organophosphazenes. 21. The Synthesis of (∝-Methylethenyl)phenylfluorocyclotriphosphazenes". *Inorg. Chem.*, **25**, 4632 (1986).

5. Technical Report #5: D.E. Brown and C.W. Allen, "(Vinlyoxy)chlorocyclotetraphosphazenes. The Use of Two Dimensional ^{31}P NMR Spectroscopy in Phosphazene Chemistry", *Inorg. Chem.*, **26**, 934 (1987).

6. Technical Report #6: L. McNally and C.W. Allen, Polymerization of Main Group Vinyl Compounds" *Heteroatom*, **4**, 159 (1993).

7. Technical Report #7: C.W. Allen, "Hybrid Inorganic-Organic Polymers Derived from Organofunctional Phosphazenes: *ACS Sym. Ser.*, 1987, No. 360, 290.

8. Technical Report #8: C.W. Allen, D.E. Brown, A.W. Cordes, and S.L. Craig, "The Structure of 2,2-Bis(trimethylsilylamino)tetrachlorocyclotriphosphazene, $N_3P_3Cl_4(NHSiMe_3)_2$: *J.C.S. Dalton*, **1405**, (1988).

9. Technical Report #9: C.W. Allen, J.C. Shaw, and D.E. Brown "Organophosphazenes. 22. Copolymerization of (∝-Methlethenylphenyl)pentafluorocyclotriphosphazene with styrene and Methyl Methacrylate" *Macromolecules*, **21**, 2653 (1988).

10. Technical Report #10: C.W. Allen, "Inorganic Polymers of the Main-Group Elements" NEACT Journal, 7(1), 4 (1989).

11. Technical Report #11: L.A. Jackson and C.W. Allen "Alkenylborazenes" *Phosphorus Sulfur, Silicon*, **41**, 341 (1989).

12. Technical Report #12: C.W. Allen, D.E. Brown and K.R. Carter "Vinyloxycyclophosphaznes" *Phosphorus Sulfur, Silicon*, **41**, 311 (1989).

13. Technical Report #13: L.A. Jackson and C.W. Allen, "Organoborazines. 2. Synthesis of Alkenylcyclotriborazines". *J. Chem. Soc. Dalton Trans.*, 2423 (1989).

14. Technical Report #14: C.W. Allen, P. Malik, A. Bridges, J. Desorcie and B. Pellon,

"The Reactions of Alkynlcyclophosphazenes with Methal Carbonyls", *Phosphorus Sulfur, Silicon*, **50**, 433 (1990).

15. Technical Report #15: D.E. Brown and C.W. Allen "Homo- and Copolymerization of (Methacryloyl ethenedioxy)-pentachlorocyclotriphazene" *J. Inorg. Organomet. Polymers*, **1**, 189 (1991).

16. Technical Report #16: C.W. Allen "Regio- and Stereochemical Control in Cyclophosphazene Substitution Reactions" *Chem. Rev.*, **91**, 119 (1991).

17. Technical Report #17: L.A. Jackson and C.W. Allen, Organoborazines 3. Homo- and Copolymerization of p-Vinylphenylcyclotriborazines", *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 577 (1991).

18. Technical Report #18: C.W. Allen, K.R. Carter, M. Bahakur and D.E. Brown, "Reactions of Polymers with Pendant Cyclophosphazenes", *Polymer Preprints*, 32(3), 479 (1991).

19. Technical Report #19: C.W. Allen, "*Inorganic Rings on Carbon Chains*", in *The Chemistry of Inorganic Ring Systems, R. Steudel (Ed.) Studies in Inorganic Chemistry*, Vol. 14, Elsevier (Amsterdam), Chapter 10 (1992).

PERSONNEL SUPPORTED ON CONTRACT

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