REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	6/20/94	FINAL June 1, 1991 - May 31, 1994

4. TITLE AND SUBTITLE

Well-defined Polyphosphazenes by Anionic Polymerization of Phosphoranimines

5. FUNDING NUMBERS

DAAL03-91-G-012

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94-21268

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P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER.

ARO 28631.24-CH

11. SUPPLEMENTARY NOTES

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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

FINAL REPORT

14. SUBJECT TERMS	15. NUMBER OF PAGES
	4
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTR.
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

A. Statement of the problem studied

Polyphosphazenes form an important class of polymers with unique properties which include a combination of high temperature stability, low temperature flexibility, low surface energy, biofriendliness, inflammability, etc. The classic synthetic approach provides very high molecular weight polymers with broad polydispersities and with no control of end groups in low yields and under extreme conditions (a few days at temperatures above 200 °C in a highly corrosive medium). The purpose of the project investigated in our laboratories was to develop alternative routes to polyphosphazenes. New synthesis should provide well defined polymers in higher yields and under milder conditions. Especially important is the control of structural features of polyphosphazenes including control of molecular weights, polydispersities, tacticities and terminal functionalities.

B. Summary of the most important results

We focused our research on catalyzed polymerization of phosphoranimines and synthesis of poly(diarylphosphazenes) via silyl azide intermediates. In addition to the synthesis, we characterized the new polymers and copolymers using various techniques including SEC, NMR, UV, VT SAXS and WAXS, X ray, electron diffraction, DSC, TGA, DMA, and dielectric relaxation.

As discovered in our laboratories, the polymerization of phosphoranimines catalyzed by nucleophiles gives well defined polymers in quantitative yield. This reaction, carried out under mild conditions (≈120 °C, 3 hours), leads quantitatively to linear polyphosphazenes with low polydispersities (M_w/M_n<1.5), moderate and tunable molecular weights (M_n≈10,000 to 200,000) and controlled end groups. It has been also shown that the catalyzed polymerization of phosphoranimines can be successfully used for the synthesis of random copolymers and the first block copolymers between two different polyphosphazenes. This method has opened new synthetic avenues for polyphosphazenes and their attachment to various organic polymers.

Polyphospazenes have been also prepared by thermal polymerization of phosphine azides (≈70 °C). Phosphine azides are formed by the anion catalyzed exchange reaction of chloro and alkoxy phosphines with trimethylsilyl azide. For example, diphenylphosphine azide leads quantitatively to poly (diphenylphosphazene). However, due to high crystallinity, this polymer is poorly soluble at degrees of polymerization exceeding n=5. In order to suppress crystallinity we prepared phenyl-*o*-tolyl chloro phosphine as well as the corresponding trifluoroethoxy derivative. Exchange with trimethylsilyl azide provides new phosphine azides which decompose to form first soluble diaryl polyphosphazenes. These polymers can not be prepared by the ring opening and substitution method. They can neither be prepared from phosphoranimines. Copolymers and homopolymers of poly(diarylphosphazenes) show various crystalline phases and a columnar hexagonal mesophase. These polymers are thermally stable up to 400 °C.

Preliminary results indicate possibility of controlling end groups in polyphosphazenes synthesized from phosphoranimines. This enables preparation of new hybrid copolymers between polyphosphazenes and various organic copolymers which will retain useful properties of polyphosphazenes but considerably reduce their cost and may lead to new applications of the interest to the Army. This was outlined in a renewal proposal **"Synthesis, Characterization and Potential Applications of New Materials from Functionalized Polyphosphazenes" submitted** to ARO in February 1994. More extensive summary of the accomplishments of the present studies (9 pages) was included as an appendix to the renewal proposal.

C. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP

Published:

1. "New Synthetic Routes towards Polyphosphazenes", K. Matyjaszewski, M. Cypryk, J. Dauth, R. Montague, M. White, *Makromol. Chem. Macromol. Symp.*, 54/55, 13 (1992)

2. "Synthesis of Poly(phenyltrifluoroethoxyphosphazene) by Direct Reaction of Silyl Azide with Phosphonite", K. Matyjaszewski, R. Montague, J. Dauth, O. Nuyken, *J. Polym. Sci., Chem.*, 30, 813 (1992)

3. "Catalysts and Initiators as Instruments Controlling Structure of Polymers with Inorganic Backbone", K. Matyjaszewski, ACS Symp. Ser. , 496, Chapter 17 (1992)

4. "Synthesis of Well-Defined Polysilanes and Polyphosphazenes", K. Matyjaszewski, *ACS Polymer Preprints*, 33 (1), 178 (1992)

5. "Synthesis and Polymerization of Mixed Phosphoranimines", K. Matyjaszewski, M. S. Lindenberg, M. L. White, *ACS Polymer Preprints*, 33 (1), 1096 (1992)

6. "Fluoride Initiated Polymerization of Fluoroalkoxy Phosphoranimine", K. Matyjaszewski, J. B. Green, R. A. Montague *ACS Polymer Preprints*, 33(2), 174 (1992)

7. "Synthesis of Polyphosphazene Copolymers Using Anionic Initiators", K. Matyjaszewski, M. S. Lindenberg, J. S. Spearman, M. L. White, *ACS Polymer Preprints*, 33(2), 176 (1992)

8. "Chain Terminators for Polyphosphazenes", R. A. Montague, F. Burkus II, K. Matyjaszewski, *ACS Polym. Preprints* , 34(1), 316 (1993)

9. "Synthesis of Polyphosphazene Random and Block Copolymers", K. Matyjaszewski, M. S. Lindenberg, M. K. Moore, M. L. White, *ACS Polym. Preprints* , 34(1), 274 (1993)

10. "Synthesis of Polyphosphazene Block Copolymers with Alkoxyethoxy and Trifluoroethoxy Groups", K. Matyjaszewski, M. K. Moore, M. L. White, *Macromolecules*, 26, 6741 (1993)

11. "Synthesis of Poly(phenyl-o-tolyl-phosphazene) via Reaction of Trimethylsilyl Azide with Phenyl-o-tolyl-2,2,2-trifluoroethylphosphinite", U. Franz, O. Nuyken, K. Matyjaszewski, *Macromolecules* , 26, 3723 (1993)

12. "Synthesis of Polyphosphazene Random Copolymers Bearing Alkoxyethoxy and Trifluoroethoxy Functional Groups", K. Matyjaszewski, M. S. Lindenberg, M. K. Moore, M. L. White, M. Kojima, *J. Inorg. & Organomet. Polym.*, 3, 317 (1993)

13. "Synthesis and Characterization of Poly(phenyl-p-tolylphosphazene) Prepared via Spontaneous Polymerization of Phenyl-p-tolylphosphine Azide", U. Franz, O. Nuyken, K. Matyjaszewski, *Macromol. Rapid Commun.*, 15, 169 (1994)

14. "Synthesis of Polyphosphazene Polymers Bearing Alkoxyehtoxy and Trifluoroethoxy Groups", K. Matyjaszewski, M. S. Lindenberg, M. S. Moore, M. L. White, *J. Polym. Sci., Chem*, 32, 465 (1994)

15. "Novel Structural and Thermotropic Behavior of Poly(diphenylphosphazene)", M. Kojima, J. Magill, M. Cypryk, U. Franz, M. White, K. Matyjaszewski, *Macromol. Chem. Phys.*, 195, 1823 (1994)

16. "Thermal Properties of Copolyphosphazenes", F. Burkus, M. White, K. Matyjaszewski, *ACS Polym. Preprints*, 35(1), 805 (1994)

17. "Polymerization of Phosphoranimines with Various Silyl Substituents" F. Burkus, R. Montague, K. Matyjaszewski, *ACS Polym. Preprints*, 35(1), 460 (1994)

Submitted:

18. "Polyphosphazene Random and Block Copolymers with Alkoxyalkoxy and Trifluoroethoxy Groups", M. White, K. Matyjaszewski, *ACS Symposium Series*, submitted

19. "Synthesis of Polyphosphazenes from Phosphoranimines and Phosphine Azides", K. Matyjaszewski, U. Franz, R. A. Montague, M. L. White, *Polymer*, in press

20. "Novel Thermotropic Behavior of (Diphenyl/Phenyl-o-tolyl Phosphazene) Random Copolymers", M. Kojima, J. Magill, U. Franz, M. L. White, K. Matyjaszewski, *Makromol. Chem.*, submitted

21. "Morphology of Poly(methoxyethoxy/trifluoroethoxy)phosphazene Copolymers", M. Kojima, J. Magill, M. White, K. Matyjaszewski, *Makromol. Chem.*, submitted

D. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJESCT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

Personel supported during the reported period:
Principal investigator: K. Matyjaszewski
Graduate students: R. A. Montague , J. Dauth, U. Franz, J. Sarver, M. White
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M. Moore (BSc), M. Linderberg (BSc), F. Burkus (BSc), J. Green (BSc), C. Reddick (BSc), J. Spearman (BSc)

REPORT OF INVENTIONS:

1. Catalyzed polymerization of phosphoranimines.
2. New linear polyphosphazenes with controllable molecular weights and low polydispersities.
3. End functionalization of polyphosphazenes.
4. Block copolyphosphazenes.
5. Soluble poly(diarylphosphazenes).