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ALPHA-METHYLSTYRL- AND STYRLPHOSPHAZENE MONOMERS AND
POLYMERS(U) VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY
C W ALLEN ET AL. 03 OCT 86 TR-3 N00014-85-K-0558

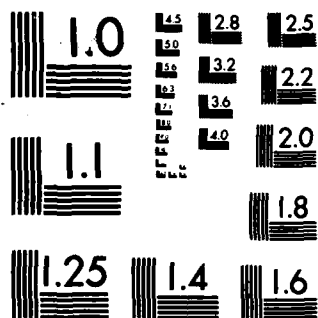
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Contract N00014-85-K-0558

Task No. NR413C012-01

TECHNICAL REPORT NO. 3

α -Methylstyryl- and Styrylphosphazene Monomers and Polymers

by

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Accepted for Publication

in

Phosphorus and Sulfur

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October 3, 1986

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Available for public release. Distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 3		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Vermont	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Cook Physical Science Building Burlington, VT 05405		7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
10c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 N. Quincy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. N00014-85	PROJECT NO. K-0558
		TASK NO. 413C012	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) α -Methyl- and Styrylphosphazene Monomers and Polymers			
12. PERSONAL AUTHOR(S) Christopher W. Allen and Jonathan C. Shaw			
13a. TYPE OF REPORT Preprint	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 1986/10/3	15. PAGE COUNT 4
16. SUPPLEMENTARY NOTATION Accepted for publication in Phosphorus and Sulfur			
COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
GROUP	SUB-GROUP	cyclophosphazenes homopolymers	
		arylphosphazenes reactivity ratios	
		copolymers nmr	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) ABSTRACT: The synthesis of the <i>m</i> and <i>p</i> -methylstyryl-phosphazenes, $N_3P_3F_6$ (1,2) is reported. At the bis stage of substitution, all isomers are observed with the <i>cis</i> non-geminal species predominating. The mono α -methylstyryl derivatives enter into facile copolymerization reactions wherein both terminal and penultimate mechanisms are observed. The synthesis and homopolymerization of styrylpentafluorocyclotriphosphazene is also reported.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL



Accession For	
NTIS	☒
ERIC	☐
Unpublished	☐
Identification	
Institution/	
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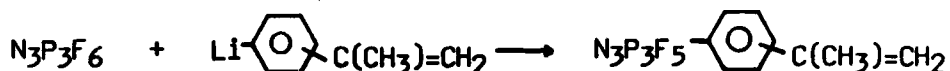
α -METHYLSTYRL-AND STYRLPHOSPHAZENE MONOMERS AND POLYMERS

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Abstract The synthesis of the *m* and *p* α -methylstyryl-phosphazenes, $N_3P_3F_6-n[C_6H_4C(CH_3)=CH_2]_n$ ($n=1,2$) is reported. At the bis stage of substitution, all isomers are observed with the *cis* non-geminal species predominating. The mono α -methylstyryl derivatives enter into facile copolymerization reactions wherein both terminal and penultimate mechanisms are observed. The synthesis and homopolymerization of styrylpentafluorocyclotriphosphazene is also reported.

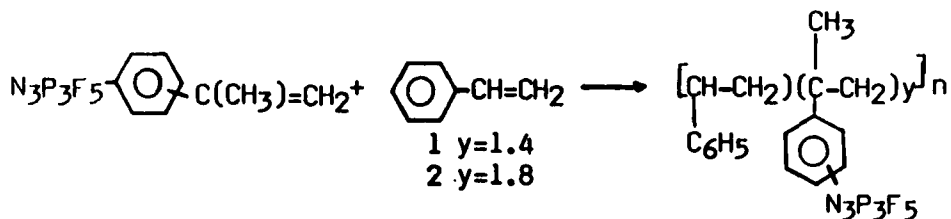
Recent work has shown that the range of synthesis of new and interesting cyclo- and polyphosphazene derivatives can be dramatically enhanced by incorporation of an organofunctional unit as a substituent on a phosphorus atom.¹ This substituent can serve as the site for various synthetic transformations leading to new monomeric and polymeric phosphazenes. The use of the para-aminophenoxy substituent as an organofunctional unit has been explored in detail by the Allcock group² and by Kumar et. al.³ We have focused our investigations on alkenyl^{4,5} and alkynyl⁶ substituents. The alkenyl phosphazenes represent novel olefinic monomers which allow for the incorporation, via copolymerization, of the cyclophosphazenes and many of their useful properties into traditional organic polymers.⁷ We have been conducting a systematic study of the synthesis, spectroscopic properties and reactivity of olefins directly bonded to the cyclophosphazene moiety^{5,8} and those separated from the phosphorus atom by a spacer group.^{4,9} This particular series of investigations involves olefinic groups separated from the cyclophosphazene by a phenyl group.

The first system to be investigated was the α -methylstyrene system. Both the meta (1) and para (2) α -methylstyrylpentafluorocyclotriphosphazenes were prepared from hexafluorocyclotriphosphazene and the appropriate lithium reagent. All new materials were characterized by elemental analysis, mass spectrometry, ir and nmr (¹H, ¹³C, ¹⁹F, ³¹P) spectroscopy. The chemical



shifts of the vinylidene, $=\text{CH}_2$ protons are identical in 1 and 2 suggesting the absence of significant mesomeric electron withdrawal from the aryl unit by the phosphazene. The difference in the β -vinyl carbon chemical shifts fall between those observed in systems with significant mesomeric interactions and those where such interactions cannot occur. This observation indicates either low degrees of mesomeric interaction or the more likely effect of electrostatic stabilization of aryl charge density by the positive phosphorus center. At the stage of bis substitution, all three isomers of $\text{N}_3\text{P}_3\text{F}_4[\text{C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2]_2$ are formed. These systems were characterized by GC-mass spectrometry and nmr spectroscopy. The ratio of geminal to cis-non-geminal to trans-non-geminal isomers is 1:6.1:1.5 for the para- α -methylstyryl derivatives and 1:2.8:1.1 in the meta system. Although the predominance of non-geminal isomers can be ascribed to steric effects, the preferential formation of the cis isomer is counter-intuitive. This observation may be rationalized by postulating an electrostatic attraction between the electron poor aryl ring on the phosphazene and the electron rich aryl ring in the lithium reagent thus favoring a cis attack. The decreased amount of the cis isomer in the meta derivative can be ascribed to the steric effect of the meta substituent.

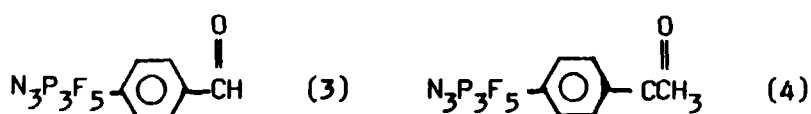
Both 1 and 2 enter into facile copolymerization reactions with styrene or para-chlorostyrene. The phosphazene incorporation in the copolymer is the highest observed for alkenyl-



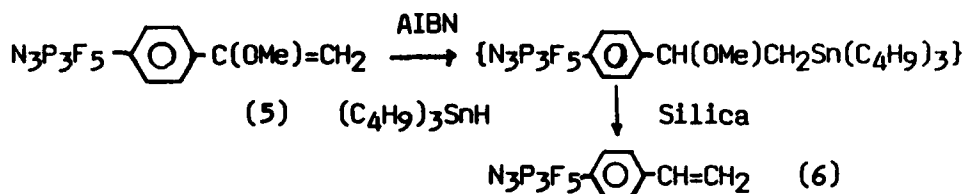
phosphazene monomers. The maximum degrees of incorporation achieved requires that there are regions of at least two phosphazene units linked together. This structural feature has not been previously observed in organophosphazene copolymers. Both of these observations are related to the moderation of the phosphazene induced olefin polarity by the aryl spacer group interposed between the two functionalities in question. Semiquantitative information on the magnitude of this effect has been obtained from the reactivity ratios and Alfrey-Price (Q,e) parameters for 1 and 2. The reactivity ratios (r_2) of 1 and 2 as calculated by the Mortimer-Tidwell non-linear least squares approach are within the 95% joint confidence limits of each other suggesting similar

reactivity. The reactivity ratio for styrene (r_1) as well as r_2 are both less than one indicating an alternative tendency. This suggests the possibility of an electrostatic interaction between the nucleophilic styryl group and the electrophilic phosphazene. The calculated Q values for 1 and 2 are reduced from styrene showing a reduction in mesomeric interactions. The calculated e values are significantly higher than that of styrene or nitrostyrene reflecting the highly polar nature of 1 and 2. The thermal decomposition of the copolymers of 1 and 2 when studied by TGA show a two step unzipping process corresponding to phosphazene and styrene loss respectively as the temperature increases. The decomposition of the copolymers of 1 begins before similar event for copolymers of 2 indicating a role for steric destabilization in the meta substituted derivatives. The copolymers of 1 and 2 with methyl methacrylate were also obtained. Attempts to calculate reactivity ratios lead to solutions with very large 95% joint confidence limits in the phosphazene monomer. We were, however, able to achieve a good fit of the data using a penultimate model. Thus, in these systems, the reactivity of the terminal radical is significantly modified by the presence of a phosphazene function in the penultimate position.

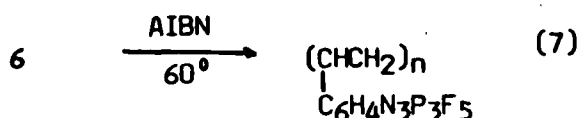
Although a broad spectrum of copolymers could be prepared from 1 or 2, all attempts (radical, cationic, anionic) at homopolymerization were unsuccessful. We therefore turned our attention to the preparation of a phosphazene bearing a styrene, rather than an α -methylstyrene, substituent. Since anionic polymerization of styrene is initiated by organolithium reagents, indirect routes were explored. Aryl pentafluorocyclotriphosphazenes with carbonyl groups in the para position (3,4) were prepared from para-bromobenzaldehyde and para-bromoacetophenone by first converting the carbonyl to the acetal and then preparing the lithium



reagent. After coupling with $\text{N}_3\text{P}_3\text{F}_6$ the protecting group was removed to give 3 and 4. However, the Wittig reaction on 3 gave only degradation products as did the reduction of 4 to the alcohol. An alternative route was developed starting from an α -methoxystyryl phosphazene (5). Interestingly, 5 was unreactive with respect to borohydride or aluminum hydride addition. Fortunately, hydrostanation of 5 proceeded smoothly and β -elimination of tributyltinmethoxide from the resulting organotin derivative occurred spontaneously on silica gel giving rise to the styrylpentafluorocyclotriphosphazene (6).



The ^{13}C chemical shift of the vinylidene carbon in 6 occurs further downfield than even 4-nitrostyrene, making 6 amongst the most electron deficient styrene derivatives known. Polymerization of 6 via radical initiation proceeded smoothly to give the homopolymer (7), a polymer having a carbon chain backbone and an inorganic surface. The molecular weights of 7 are 102,000 and



374,000 for M_n and M_w respectively. Thermal decomposition of 7, as monitored by TGA, starts about 80° higher than that for polystyrene and the polymer retains fifteen to thirty percent of its original weight at temperatures of 900° to 1100°C . This observation suggests the possibility of thermal decomposition of carbon chain polymers with inorganic surfaces as a potentially new route to ceramic materials.

Acknowledgements

This work was supported in part by the Office of Naval Research.

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