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The preparation of organofunctional cyclotriphosphazenes and the copolymerization of one of these materials, 2-[2-propenyl]pentafluorocyclotriphosphazene, with styrene to produce fire retardent styrene copolymers is described. The physical and chemical properties of the new copolymers are discussed.

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Novel Propenylfluorophosphazene-Styrene Copolymers

by

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Industrial and Engineering Chemistry
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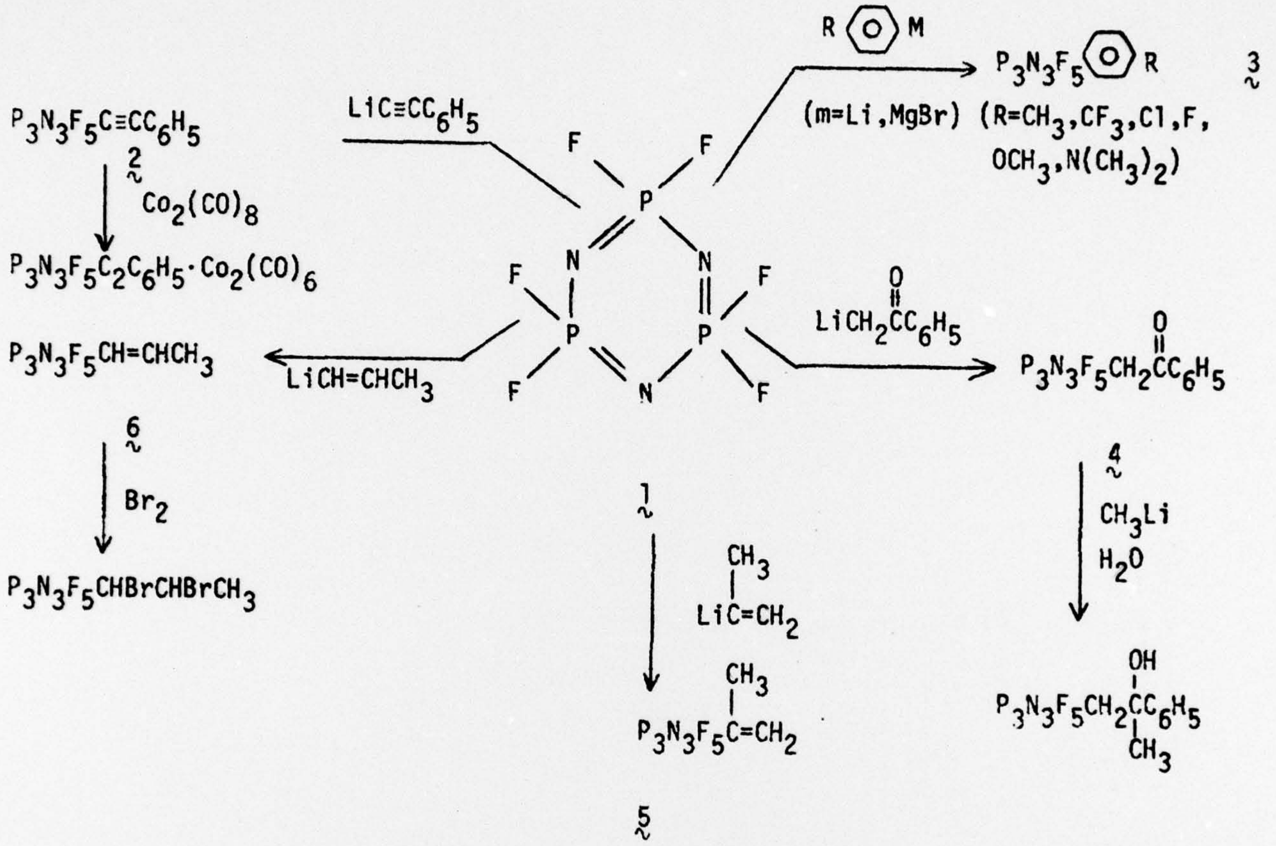
Phosphazene derivatives continue to attract the attention of chemists interested in both basic and applied research. The problems of structure, bonding and reactivity provide exciting challenges to the understanding of phosphazene chemistry (Allcock, 1972; Krishnamurthy et.al., 1978) and the existence of a variety of useful properties such as fire retardency and formation of thermally stable polymers indicates the applications potential of these systems (Singler et.al., 1975; Allcock, 1977).

The problem of construction of non-flammable synthetic polymer systems is one of contemporary technological significance (Granzow, 1978). Traditionally, flame retardents have been additives such as antimony oxychloride, phosphate esters or cyclophosphazenes. More recent efforts have involved non-flammable polymers such as polyphosphazenes. There are difficulties associated with each of these approaches. The possibility exists for the additives to leach out over time and the additives may represent biohazards. Wide scale utilization of the polyphosphazenes has yet to be achieved. An alternative approach to those described above is the incorporation of the flame retardent into the polymer backbone. In this communication we would like to describe how our interest in organofunctional cyclophosphazenes has led to incorporation of the fire retardent properties of the phosphazene unit into traditional organic polymers.

Organophosphazenes are most commonly prepared by the reactions of organometallic reagents with hexafluorocyclotriphosphazene, $P_3N_3F_6$ (1). Recently, interest has developed in the synthesis and reactions of organofunctional phosphazenes (Scheme I).

Scheme I.

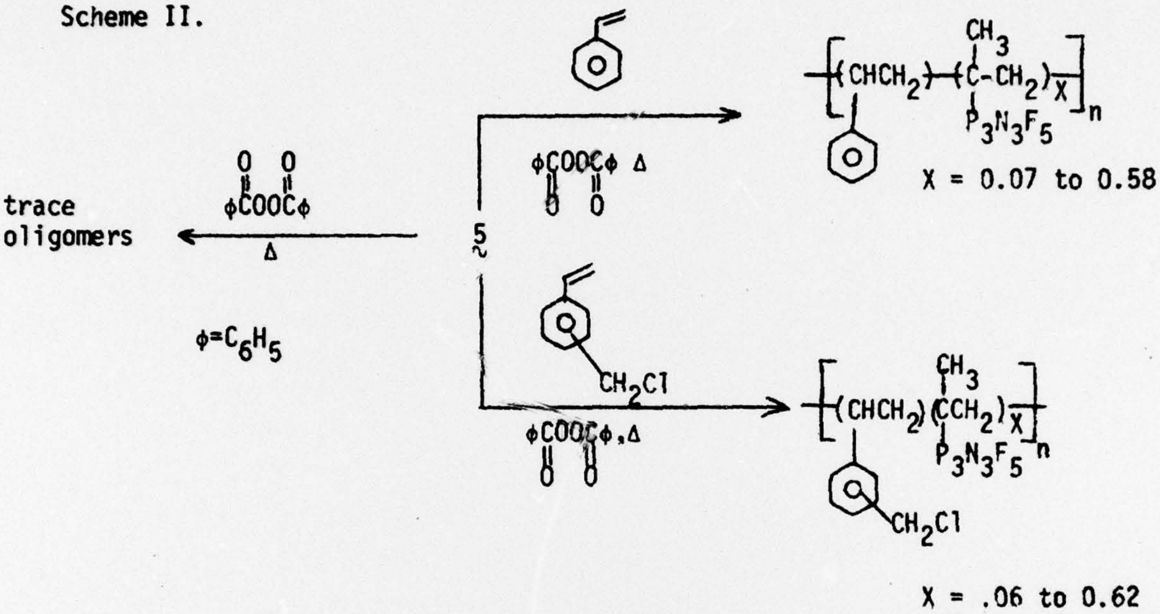


The aim of our work in this area has been expanding the variety of available organophosphazenes *via* synthetic transformations of the exocyclic group. Thus the synthesis and reactions of acetylenic (2) (Chivers, 1971), substituted aryl (3) (Allen, et.al., 1977), β-keto (4) (DuPont and Allen, 1977) and most recently propenyl (5, 6) (DuPont and Allen, 1978a) phosphazene derivatives have been reported.

Upon examining 2-[2-propenyl]pentafluorocyclotriphosphazene (5), one can consider it to be, on a superficial level, an inorganic relative of styrene. While we considered this, admittedly strained, analogy, we began to wonder if this material could enter into the broad range of polymer chemistry which is based on styrene.

We chose to explore radical polymerization as our entry into these systems as is shown in Scheme II, (DuPont and Allen, 1978b). While attempted homopolymerization of 5 led only to minute amounts of oligomers, copolymerization with styrene based monomers led to the desired propenylphosphazene/styrene copolymers. By changing the ratio of monomers in the monomer feed, polymers of variable composition incorporating up to 40 mole percent of the phosphazene can be prepared. Approximate reactivity ratio data indicate that the reactivity of the olefinic center in 5 is reduced by the strongly electron withdrawing phosphazene function.

Scheme II.



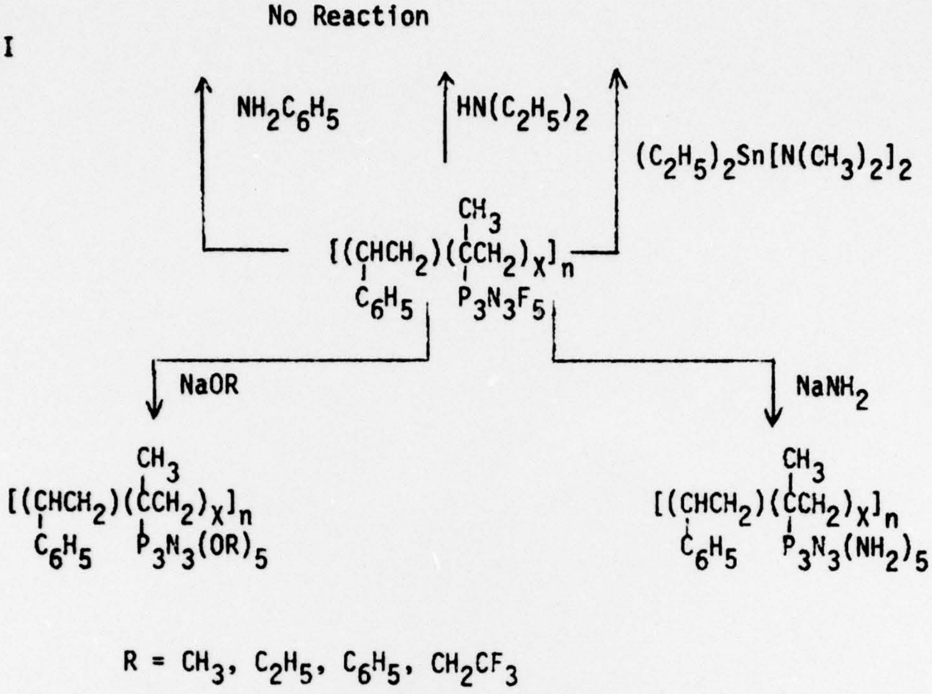
The molecular weights for the series of propenylphosphazene/styrene copolymers were determined using gel permeation chromatography with equilibrium ultracentrifugation and membrane osmometry as an occasional check. The systems are homogeneous with relatively low polydispersity values. In addition to the absolute magnitude of the figures, the variation of molecular weight with phosphazene content is of interest. The highest molecular weights ($\bar{M}_W$ = 92,000, $\bar{M}_N$ = 66,000) occur with copolymers of lowest phosphazene content (6.3%) while the lowest molecular weights ($\bar{M}_W$ = 33,000, $\bar{M}_N$ = 25,000) correspond to the highest phosphazene content (36.5%). These observations, along with the reluctance of **5** to undergo homopolymerization, strongly suggest that phosphazene unit plays a significant role in the termination steps of the polymerization process.

Initial data indicates that the thermal stability of the propenylphosphazene/styrene copolymers compares favorably to that of pure polystyrene. TGA studies show that the temperature required for 50% weight loss is 20 to 30° greater for the copolymers than for the parent organic homopolymer. A 15 to 20% decrease in molecular weight is observed if the copolymer is maintained at 120° for 24 hours. In vacuo, solid state thermolysis for 24 hours at 250° transforms the copolymer to a glassy solid with no formation of volatile species. The broadening of the phosphorus-nitrogen stretching mode in the ir spectrum of the thermolyzed product suggests opening of the phosphorus-nitrogen bond under these conditions (Allen and Sie, 1978).

The copolymers were found to be flame retardant under normal atmospheric conditions. Qualitative tests were carried out simply by holding a flame source to the powdered copolymer. Pure vinyl benzyl chloride and styrene polymers readily ignited and sustained a flame, but the copolymers ignited only with great difficulty and would easily self extinguish. This reflects the fact that the copolymers contain substantial amounts of phosphorus and nitrogen, which are well known fire retardents (Granzow, 1978).

The new copolymers are stable to dilute acid or base. This observation led us to investigate nucleophilic substitution of the phosphazene moiety in the copolymer (Allen and DuPont, 1978). As is shown in Scheme III, weak nucleophiles do not undergo reaction but strong, anionic nucleophiles lead to complete substitution of the

Scheme III



phosphorus-fluorine bonds. While the amido, phenoxy and trifluoroethoxy derivatives have flame retardent properties, the methoxy and ethoxy derivatives will burn. This observation may indicate the elimination of the volatile alcohol under thermolysis conditions.

In summary, I believe we have demonstrated that the incorporation of the phosphazene unit into traditional organic polymers leads to new, fire retardent polymers. Furthermore, the phosphazene unit provides reactive sites in the copolymer and hence provides a route (via nucleophilic substitution) to potential modification of properties of the polymer.

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