

NEW FIRE-RESISTANT POLYMERS FOR AIRCRAFT INTERIORS

Harry R. Allcock,* Catherine M. Ambler, Jonathan P. Taylor, Thomas J. Hartle, E. Clay Kellam,
Robbyn L. Prange, Michael B. McIntosh, and Michael M. Coleman

Departments of Chemistry and Materials Science and Engineering

The Pennsylvania Sate University

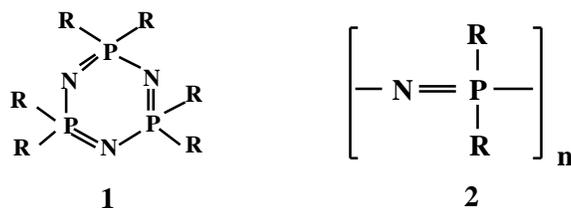
University Park, Pennsylvania 16802

Introduction

The purpose of this research is to design and find ways to synthesize new polymers that have the following characteristics: (a) non-flammable materials for stand-alone applications in aircraft interiors, and/or (b) polymers that can be incorporated into existing polymeric materials to convert them from flammable to non-flammable blends, interpenetrating networks (IPN's), or other composites.

The presence of pentavalent phosphorus in a polymer is one of the most effective and safest methods for preventing combustion. Phosphorus compounds are good fire retardants for two reasons. First, they interfere with the free radical reactions that are required to maintain a fire. Second, they generate a char at high temperatures which serves to starve the fire of oxygen and quenches the flames. The presence of nitrogen and phosphorus together in a material accentuates this effect.

A broad group of compounds known as phosphazenes are excellent fire-retardants for organic polymers. These compounds are based on a molecular skeleton of alternating phosphorus and nitrogen atoms, with two organic or inorganic side groups (**R**) attached to each phosphorus. Two of the many different molecular architectures within the phosphazene platform are shown as structures **1** and **2**.



Types **1** and **2** phosphazenes are highly effective fire-retardant species. Cyclic trimers of type **1** have been used as non-bonded additives in a wide range of polymers. However, because these additives are small molecules, they are susceptible to diffusion from the host polymer over the long term with a consequent loss of effectiveness. High polymers of type **2** have been developed as fire-resistant elastomers for use as heat-, sound-, and electrical-insulators in military applications.

We have developed six new approaches to producing previously unknown polymers of interest as fire-resistant materials for aircraft interiors. These are as follows: (1) new linear polyphosphazenes with controlled chain lengths and narrow molecular weight distributions produced by a unique living cationic polymerization;¹⁻¹⁰ (2) block copolymers of phosphazenes with organic polymers in either di-block or tri-block configurations;¹¹⁻¹⁵ (3) organic polymers with either linear type-**2** phosphazene side chains or cyclic phosphazene side units of type **2** arrayed along an organic polymer chain;^{14,16-18} (4) cycloliner polymers comprised of phosphazene rings

linked together by organic oligomeric chains;¹⁹ (5) polymeric or cyclic phosphazenes bonded covalently into polyurethanes;²⁰ and (6) linear polyphosphazenes of type **2** with phosphate-containing side groups to supplement the fire retardance of the main chain.²¹ The synthesis of these polymers will be described in turn, and this is followed by a brief summary of the results of laboratory-level fire-resistance evaluations.

Synthesis of Less Expensive Polyphosphazenes with Controlled Molecular Weights and Architectures.¹⁻¹⁰

(a) Living Cationic Polymerization. We have developed a new polymerization approach to polyphosphazenes that allows hitherto unavailable molecular weight control, offers the promise of reduced costs, and allows synthesis of star-shaped macromolecules and block and graft copolymers. Two anticipated advantages of this approach are the access it provides to relatively inexpensive polyphosphazenes for stand-alone applications, and to polymers with side groups that are appropriate for combining with classical organic polymers in the form of compatible blends and interpenetrating polymer networks.

The synthesis involves the condensation polymerization of a phosphoranimine such as **3** or **4** at room temperature in the presence of a cationic initiator such as PCl_5 . The overall process is summarized in Scheme I.

Scheme I

Initiation



Chain Growth



Halogen Replacement



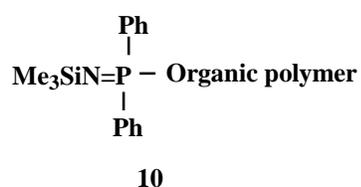
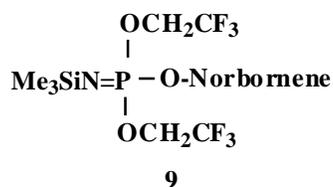
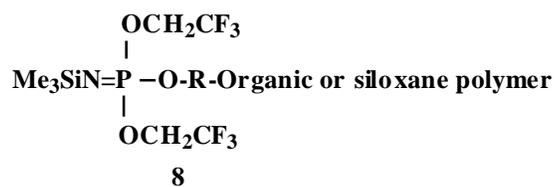
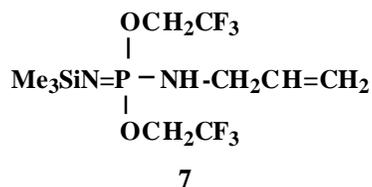
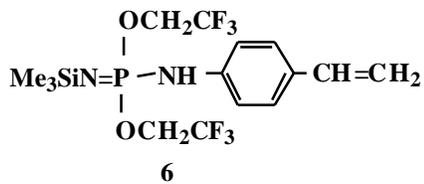
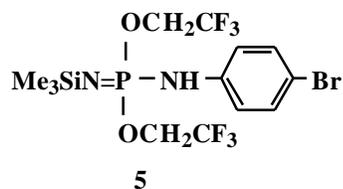
Use of this reaction sequence provides access to a wide variety of polymers with different side groups (for fire retardance and compatibility with other polymers in blends and IPN's). The Me_3SiCl released at each step in the polymerization can be recycled into the monomer synthesis reaction. Hence, cost savings can be made. The length of each polymer chain depends on the overall ratio of monomer to initiator, and can be controlled over a wide range. Chain lengths can also be limited by the addition of a phosphoranimine terminator at any stage in the polymerization. Finally, no heat is required, and the conversion of monomer to polymer is virtually 100% efficient, which is another other factor that is beneficial to the overall economics of the process.

(b) *Phosphazene-Phosphazene Block Copolymers.* Because this is a living polymerization, and because monomers of types **3** and **4** participate, it is possible to polymerize one monomer and then use the active chain end of that polymer to initiate polymerization of a second phosphazene monomer to produce block copolymers. This further increases the opportunities for the production of fire-resistant and compatible macromolecules.

(c) *Star-Geometry Polymers.*⁴ Star-geometry polyphosphazenes are of interest as compatible, non-crystallizing, fire retardant additives for organic polymers. We have produced examples of this architecture by the reaction of $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ with $\text{BrP}(\text{OR})_2=\text{NSiMe}_3$ to give the trifunctional phosphoranimine, $\text{N}[\text{CH}_2\text{CH}_2\text{NHP}(\text{OR})_2=\text{NSiMe}_3]_3$. Treatment of this compound with a trace of PCl_5 and the monomer $\text{Me}_3\text{SiN}=\text{PCl}_3$ then induces growth of three polyphosphazene arms from the central core. Replacement of the chlorine atoms by appropriate organic groups yields the fire-retardant star polymer.

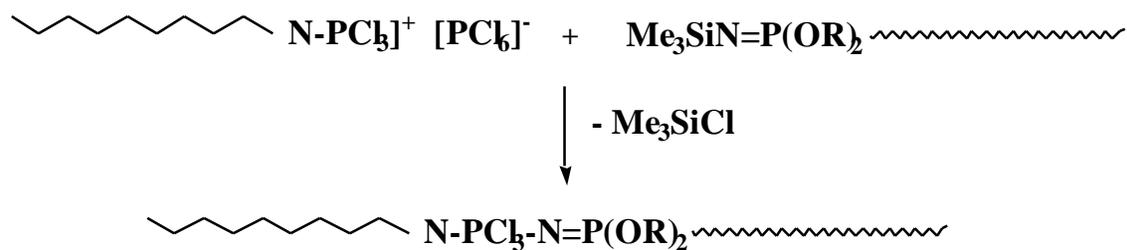
Block Copolymers of Polyphosphazenes with Organic Polymers¹¹⁻¹⁵

(a) *General Considerations.* Block copolymers that incorporate polyphosphazenes along with inexpensive organic polymers have the potential to utilize the benefits of both the phosphazene and the organic polymer while generating a fire resistant material. A number of different techniques have been developed in our program to synthesize such hitherto inaccessible materials. All these methods use features of the living cationic polymerization described in the last section, and especially the use of functional phosphoranimines as polymerization initiators or terminators. Such phosphoranimines bear a reactive site as shown in structures **5-10**.



Specifically, a functional phosphoranimine can be treated with PCl_5 and used as an initiator for the growth of a polyphosphazene chain, in which case, after replacement of the chlorine atoms in the polymer by organic groups, the terminal functional site is used to connect the polyphosphazene to the terminus of an organic polymer. Alternatively, a living cationic polymerization such as the process shown in Scheme I, is terminated by a phosphoranimine that bears a functional site. Moreover, if that terminating phosphoranimine is already linked to the end of an organic polymer chain the termination process gives a block copolymer directly. This process is illustrated in Scheme II.

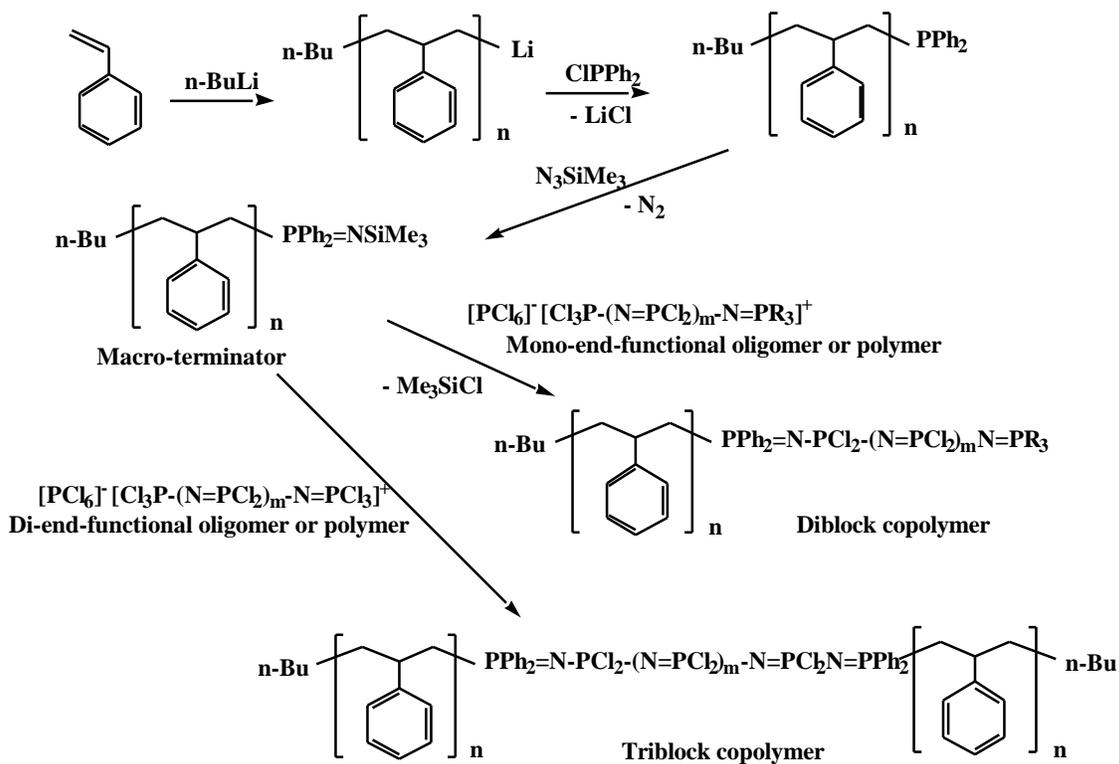
Scheme II



The following examples illustrate these principles.

(b) *Polystyrene-Polyphosphazene Block Copolymers*.¹⁴ Anionically-produced polystyrene can be end-functionalized with a phosphine unit (Scheme III). This end unit reacts with Me_2SiN_3 to produce a terminal phosphoranimine. The resultant macromolecule is then employed as a macro-terminator for living poly(dichlorophosphazene). Replacement of the chlorine atoms in the resultant block copolymer completes the process.

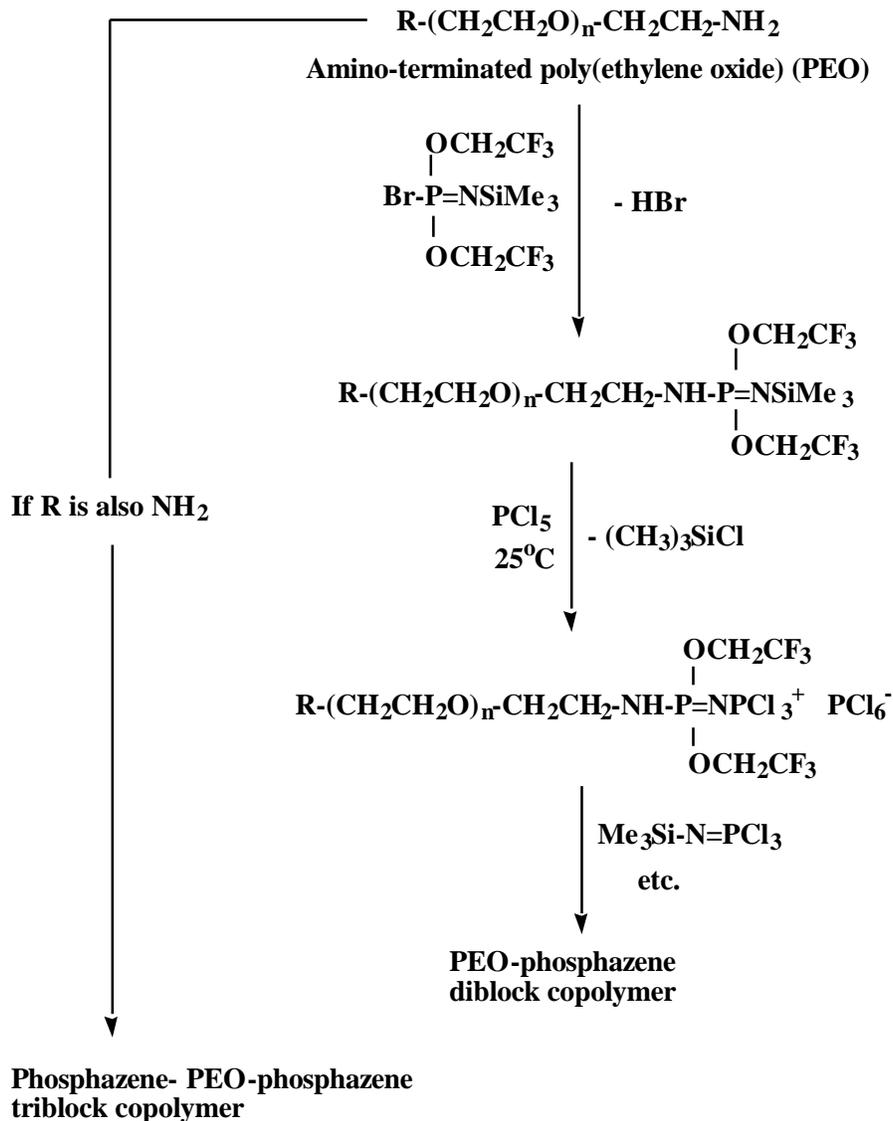
Scheme III



G-994

(c) *Poly(ethylene oxide)-Polyphosphazene Block Copolymers..*⁸ Poly(ethylene oxide) can be obtained commercially with amino end groups. These react with $\text{BrP}(\text{OR})_2=\text{NSiMe}_3$ to place phosphoranimine initiator sites at one or both ends of the poly(ethylene oxide) chain (Scheme IV). Initiation with PCl_5 followed by treatment with $\text{Me}_3\text{SiN}=\text{PCl}_3$ then generates a polyphosphazene chain from that site. Di- or tri-block copolymers are formed depending on whether a mono- or di-amino-end-terminated organic polymer is used.

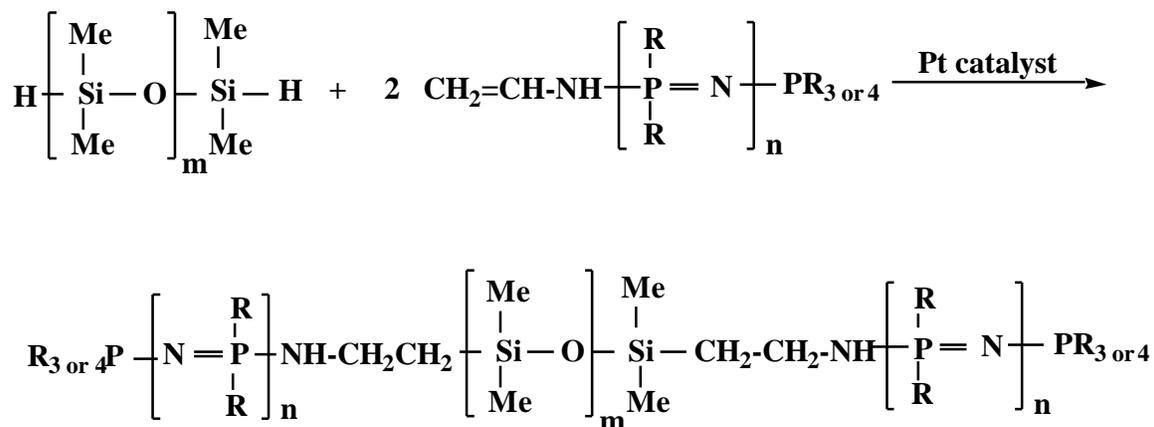
Scheme IV



(d) *Poly(dimethylsiloxane)-Polyphosphazene Block Copolymers.*^{12,15} Functional phosphoranimine **7** has been used as an initiator species for the growth of a poly(dichlorophosphazene) chain (Scheme V). After the chlorine atoms have been replaced by alkoxy, aryloxy, or amino groups, the allyl end units are then linked by hydrosilylation to hydrido-

terminated poly(dimethylsiloxane). These hybrid phosphazene-silicone polymers represent a new generation of macromolecules that could be useful as fire-resistant elastomers and adhesives.

Scheme V



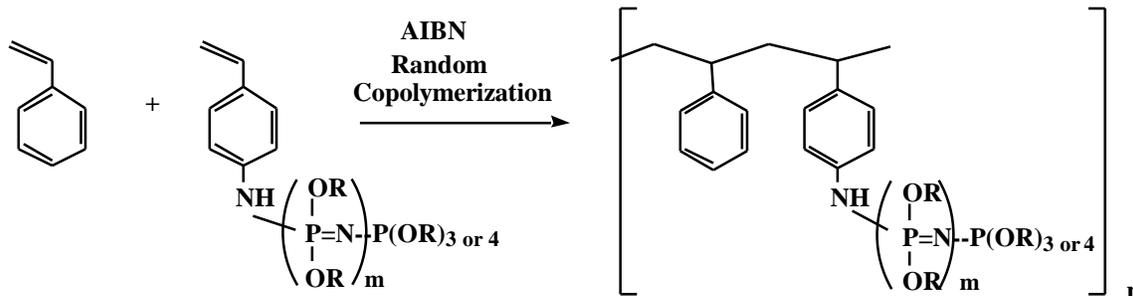
Polyphosphazene-*block*-polysiloxane-*block*-polyphosphazene copolymer

Graft Copolymers of Linear Phosphazenes as Side Units on Organic Polymers^{14,16-18}

(a) *General Principles.* The formation of block copolymers between polyphosphazenes and organic polymers represents one effective way to combine the attributes of the two systems. Another approach is to incorporate the linear poly- or oligo-phosphazene as a side chain on the organic polymer - a so-called graft system. We have accomplished the synthesis of such polymers in two ways. Both utilize the living cationic polymerization.

(b) *Linear Polyphosphazene Grafts on Polystyrene.* The styryl-functionalized polyphosphazene shown in Scheme VI has been produced by the use of

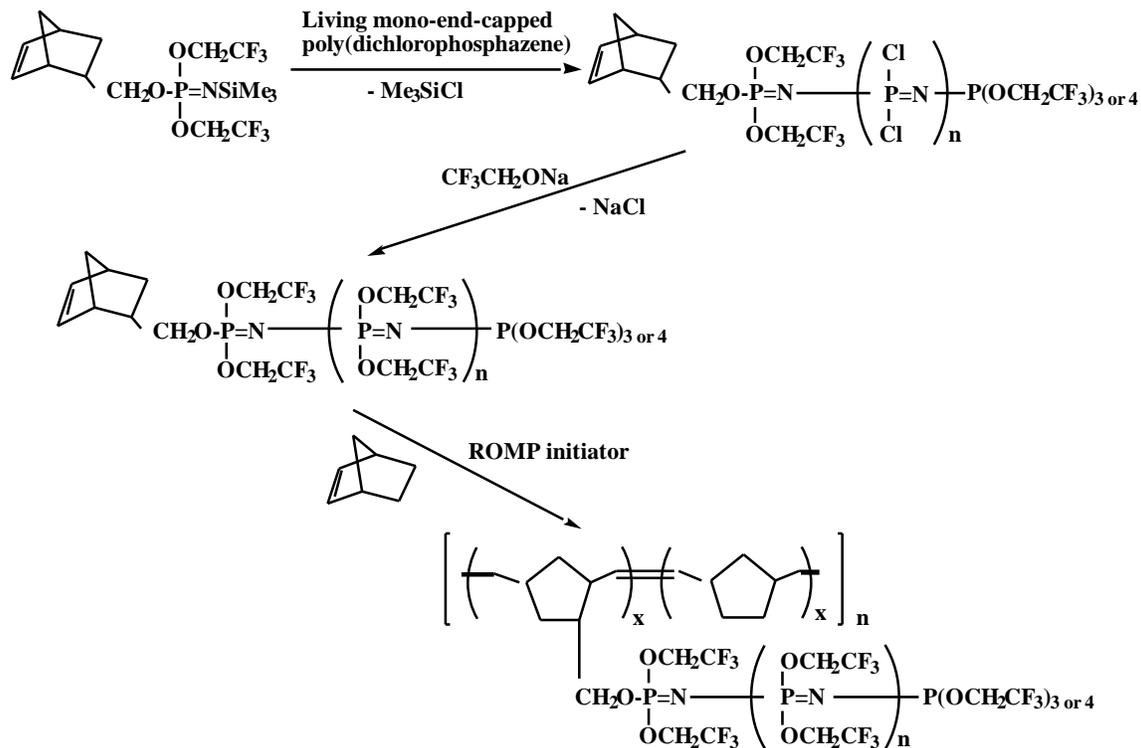
Scheme VI



$\text{CH}_2=\text{CHC}_6\text{H}_4\text{P}(\text{OR})_2=\text{NSiMe}_3$ (**6**) as a polymerization terminator or initiator for a living cationic polymerization. This polphosphazene, after replacement of the chlorine by organic side groups, can then undergo free-radical copolymerization with styrene to produce the graft copolymer structure. In principle, the end-functionalized polyphosphazene should also copolymerize with a wide range of olefinic, vinyl, and acrylic monomers, so this is potentially a powerful method to incorporate fire retardants into a broad spectrum of organic addition polymers.

(c) *Use of Ring-Opening Metathesis Polymerizations (ROMP)*. The second method developed in our program involves the first use of ROMP polymerizations to incorporate polyphosphazene side groups into an organic polymer.¹⁶ Use of the techniques discussed earlier allows norbornenyl groups to be linked to the end of a polyphosphazene chain (Scheme VII). The norbornenyl group was then polymerized with the use of an organometallic initiator to generate the graft copolymer system shown in Scheme VII. Polynorbornenes are among the most flammable macromolecules known. The phosphazene grafts impart a high level of fire resistance.

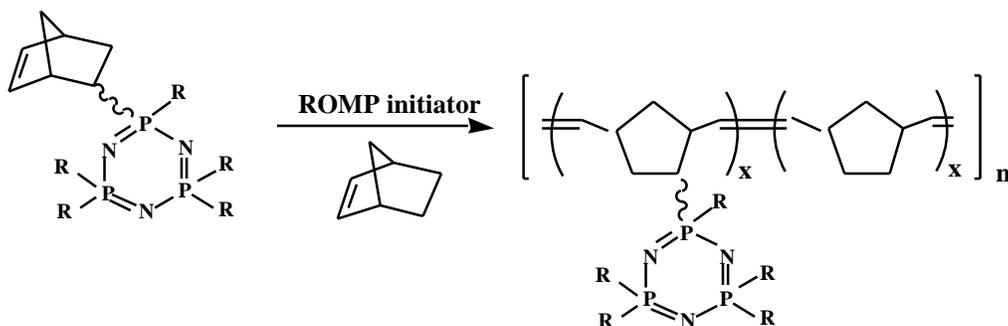
Scheme VII



Cyclophosphazene Rings as Side Groups Linked to Organic Polymer Chains

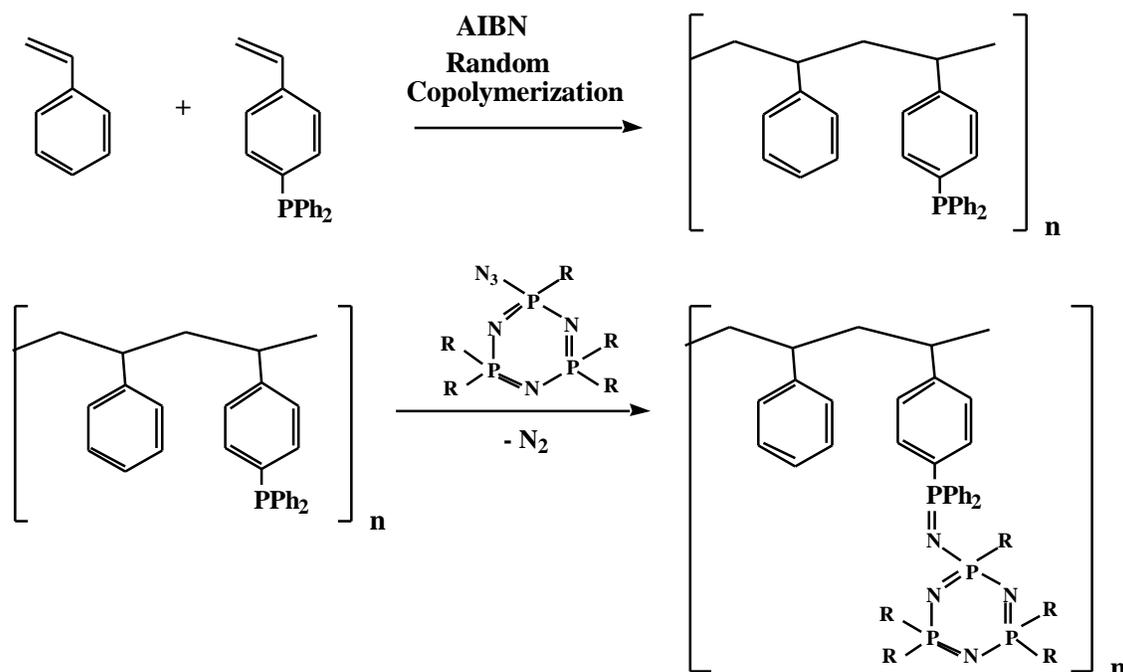
(a) *Cyclic Phosphazene Grafts Via ROMP Polymerization.*¹⁶ The ROMP technique described above also allows cyclic small-molecule units to be linked as side groups to an organic polymer chain. Thus, we have used simple substitution chemistry to connect a phosphazene ring via a short spacer group to a norbornenyl monomer. This monomer was then ROMP copolymerized with norbornene to produce the fire retardant polyoymers shown in Scheme VIII. The properties of these polymers can be readily tuned by variations in the ratios of the two monomers and by changes to the organic side groups linked to the phosphazene ring.

Scheme VIII



(b) *Linkage of Cyclic Phosphazene Side Groups to Organic Polymers Via Azide Coupling Techniques*¹⁸ We have recently synthesized a range of cyclic phosphazenes that bear one azido group per ring and five organic cosubstituent groups (Scheme IX). Polystyrene copolymers are accessible that contain both styrene and styryldiphenylphosphine monomer units. The azidocyclophosphazenes couple almost quantitatively to the the pendent phosphine units via formation of a stable phosphinimine linkage. The ratio of pendent phosphazene rings to styrene residues can be controlled over a wide range through variations in the ratios of styrene to styryldiphenylphosphine in the initial copolymerization. Again, property tuning is possible through the use of different cosubstituents on the phosphazene rings. The fire resistance of these modified polystyrenes is being investigated.

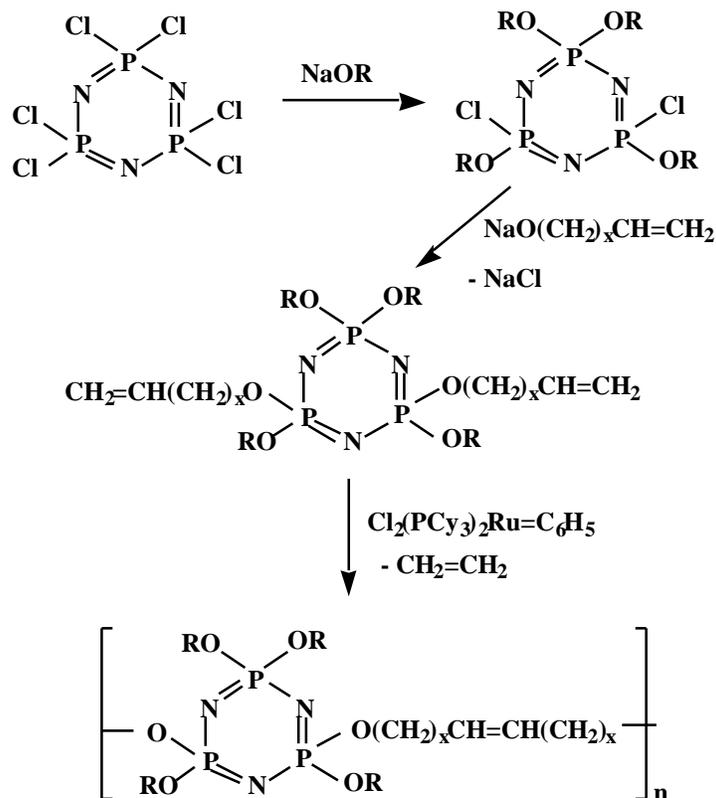
Scheme IX



Cycloliner Polymers by ADMET Polymerization¹⁹

An alternative way to incorporate cyclic phosphazene residues into an organic polymer chain has been devised. This involves the synthesis of cycloliner polymers by the linkage of phosphazene rings by organic chains using the ADMET polymerization technique. This is illustrated in Scheme X. Two non-geminal alkene groups with terminal unsaturation are linked to a cyclophosphazene ring. Treatment of this compound with an organometallic catalyst then causes acyclic diene metathesis polymerization with concurrent elimination of ethylene. In general, the polymers have six or more methylene groups connecting the chain of rings. The other substituents on the phosphazene rings allow control over both the physical properties and the fire-resistance. This is a new method for preparing fire-resistant polymers that could be useful both as stand-alone materials and as polymeric additives to long existing organic polymeric materials.

Scheme X



OR = OC₆H₅ or OCH₂CH₂OCH₂CH₂OCH₃

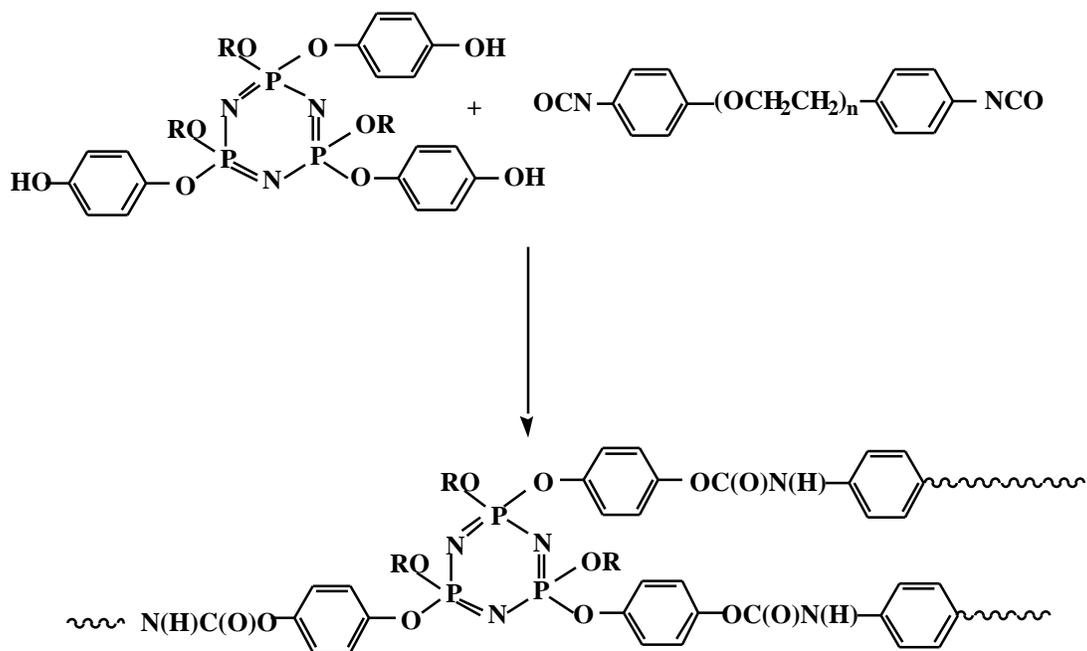
x = 4-9

Cy = cyclohexyl

Incorporation of Cyclophosphazene Fire Retardants into Polyurethanes

In earlier studies²⁰ we developed a method to incorporate high polymeric phosphazenes into polyurethanes. These IPN's showed impressive fire resistance at the 20% phosphazene (2% phosphorus) level. We have now examined the possibility that *cyclic* phosphazenes might be incorporated into polyurethanes to achieve similar effects using lower cost materials. The overall approach is shown in Scheme XI.

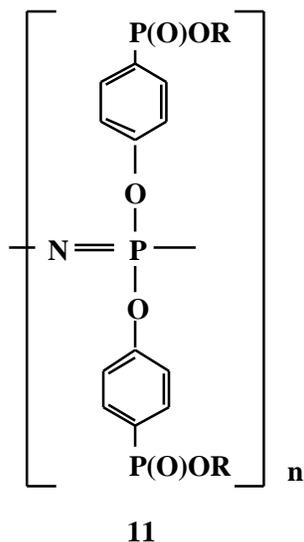
Scheme XI



These hybrid structures show considerable promise for fire-resistant applications in aircraft. As little as 10-20% of the cyclophosphazene generates a limiting oxygen index up to 32 and provides 10-30% char at 800°C during attempted combustion

Polyphosphazenes With Phosphate-Type Side Groups²¹

Organophosphates are widely used as fire retardants. Their main defects are their propensity to diffuse from the polymeric host, their volatility at moderate temperatures, and their tendency to plasticize the host polymer and lower its glass transition temperature. We have developed ways to link fire-retardant phosphate esters to the organic side groups of high polymeric linear phosphazenes in an attempt to both enhance the fire retardance of the phosphazene polymer and prevent the diffusion and volatilization of the organophosphate. (structure **11**)



This work is still on-going, but model compound research with phosphazene cyclic trimers that bear phosphate ester side groups showed that these have distinctly higher limiting oxygen indices (ie. they are more effective flame retardants) than the phosphate esters themselves. A translation of this work to the high polymer level is continuing.

Summary of Fire-Resistance Evaluations

Two methods of thermal analysis are currently employed in our laboratory for the evaluation of fire resistance. These include (1) limiting oxygen index testing (LOI) and (2) thermogravimetric analysis (TGA).

LOI provides a comparison value which indicates the oxygen concentration needed to sustain combustion. A material will self extinguish if the LOI is higher than the normal atmospheric 20% oxygen concentration. This system of analysis offers some insight into the vapor

phase mechanisms of fire resistance. LOI measurements were obtained using a modified ASTM limiting oxygen index apparatus.

Condensed phase fire retardant mechanisms can be better studied through TGA techniques. In such studies, a material is thermally degraded over a predetermined temperature range at a constant rate of temperature increase. Sample weight loss and onset of decomposition can be measured, and this provides indications of thermal stability and char residue yields. Our research employs a Perkin-Elmer TGA 7 thermogravimetric analyzer and involves the application of heat to samples over the range of 50°C to 800°C at a rate of 10°/min. The tests are conducted in a nitrogen atmosphere.

These evaluation studies are ongoing, but a summary of fire-related data for recently synthesized materials is as follows. In general, phosphazene polymers with aryloxy side groups provide the best char yields, some of the highest LOI values, and the best overall combination of fire resistance and economic potential. The diphenoxyphosphazene polymer, $[N=P(OPh)_2]_n$, shows a high remaining char weight of about 90% at 500°C and over 20% at 800°C. The benefits of aryloxy substituents are further supported by the high LOI values for aryloxy side-group derivatives that bear alkyl or chloro-substituents, which are in the range of 32-60. Short alkoxy side groups, such as iso-propoxy, n-propoxy, or n-butoxy, allow the fire-quenching benefits of the phosphazene backbone to become manifest, with char yields near 30% and LOI values in the range of 25, but side chains with longer alkyl components lower the LOI to below 20.. Heavily fluorinated alkoxy groups, such as $[N=P(OCH_2(CF_2)_3CF_2H)_2]_n$ demonstrate very high rankings in each category of testing (char yields as high as 50-96% at 500°C and LOI values

well above 40. The norbornene polymers with cyclophosphazene side groups show char yields above 40%, while polyphosphazenes with aryloxyphosphate side units have char yields in excess of 60%. The fire-retardant effects of both IPN-based polyphosphazenes and bonded cyclophosphazenes on polyurethanes are also impressive. The evaluation work is continuing for all the polymers mentioned in this report, but the char yields and LOI values obtained so far indicate that many of the polymers being produced in this work have a significant potential as fire resistant materials.

Acknowledgments

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