CC/NUMBER 46
This Week's Citation Classic ®
NOVEMBER 18, 1991

Allcock H R, Kugel R L & Valan K J. Phosphonitrilic compounds. VI. High molecular weight poly(alkoxy- and aryloxyphosphazenes). *Inorg. Chem.* 5:1709-15, 1966.
[Central Research Division, American Cyanamid Co., Stamford, CT]

A method is described for the synthesis of the first stable poly(organophosphazenes). The method involves the ring-opening-polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to a soluble, high molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$, followed by macromolecular substitution reactions with organic nucleophiles to replace the chlorine atoms by organic side groups. The resultant polymers are stable to water and other reagents and have properties that can be controlled by the types of side groups introduced during the substitution process. [The *SCI*® indicates that this paper has been cited in more than 210 publications.]

Polymers Based on the Inorganic Elements

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This paper had its origins six years prior to publication. As a graduate student in England working in the field of organosilicon chemistry, I was aware of the development in the US of organosiloxane (silicone) polymers and of their remarkable properties. I became intrigued with the idea that other highly stable polymers might be accessible based on elements other than silicon.

For this reason, I decided to gain some experience in another field and spent a year as a postdoctoral fellow at Purdue University working with small molecule organo-phosphorus-nitrogen compounds, then called "phosphonitriles." These seemed like ideal precursors to polymers, with a phosphorus-nitrogen backbone, but we were unable to convert any of them to high polymers. It became clear that I did not know enough about polymer chemistry to be able to polymerize small molecules, or even to recognize a polymer if I had made one. Thus, I spent the next two years as a postdoctoral fellow at the Canadian National Research Council in Ottawa, learning about the polymerization of olefins, before moving to a long-range polymer synthesis group at the American Cyanamid Laboratories in Stamford, Connecticut.

There I acquired a detailed familiarity with many aspects of polymer chemistry and eventually found an excuse to begin work again on phosphorus-nitrogen chemistry. It had been five years since I had last worked in this field, and the experience gained in that time made a big difference. Within weeks of beginning the project, my assistant Robert L. Kugel and I had found a way to polymerize hexachloro-cyclotriphosphazene to an organic-solvent-soluble high polymer. And, we used this polymer as a reactive polymeric intermediate to replace the chlorine atoms by organic side groups to obtain stable organophosphazene high polymers. Even then, as we made and purified the first examples of the new polymers, it was clear that we had access to hundreds of new materials, each with its own set of unique and potentially useful properties. We published our findings in a communication to *JACS* and (after being joined by Kent Valan, who helped with the synthesis and characterization of several additional derivatives) assembled the full *Classic* paper.

However, it became apparent that I would not be able to continue to develop the fundamental scientific aspects of this field in an industrial laboratory, and I had been thinking more and more that my future resided in the academic environment. So in 1966, I accepted a position at Pennsylvania State University. Since then, my coworkers and I have been able to develop the chemistry of what has proved to be an even wider and more diverse field than we ever imagined. More than 230 papers on this topic have come from our laboratory, and more than 1,800 papers and patents from other research groups.[1-6]

In retrospect, I see that our ability to initiate and develop this field was a consequence of the breadth and diversity of experience I had gained in organometallic chemistry, organic synthesis, inorganic synthesis, and polymer chemistry, and I try to pass this message along to my students.

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2. **Neilson R H & Wisian-Neilson P.** Poly(alkyl-arylphosphazene) & their precursors. *Chem. Rev.* 88:541-62, 1988.
3. **Allcock H R.** Current status of polyphosphazene chemistry. *Inorganic and organometallic polymers.* (Zeldin M, Wynne K J & Allcock H R, eds.) A.C.S. Symposium Series 360, 1988. p. 250-67.
4. **Manners I, Renner G, Nuyken O & Allcock H R.** Polycarbophosphazenes: a new class of inorganic-organic macromolecules. *J. Amer. Chem. Soc.* 29:5478-80, 1989.
5. **Allcock H R.** Polyphosphazenes as new biomedical and bioactive materials. (Langer R & Chasin M, eds.) *Biodegradable polymers as drug delivery systems.* New York: Marcel Dekker, 1990. p. 163-93.
6. **Mark J E, Allcock H R & West R.** *Inorganic polymers.* Englewood Cliffs, NJ: Prentice Hall, 1992. 272 p.

Received October 5, 1990