

New Directions in Polyphosphazene Chemistry

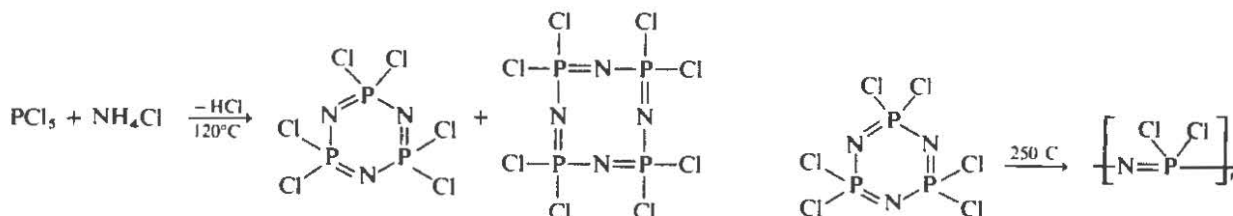
Scott P. Lockledge

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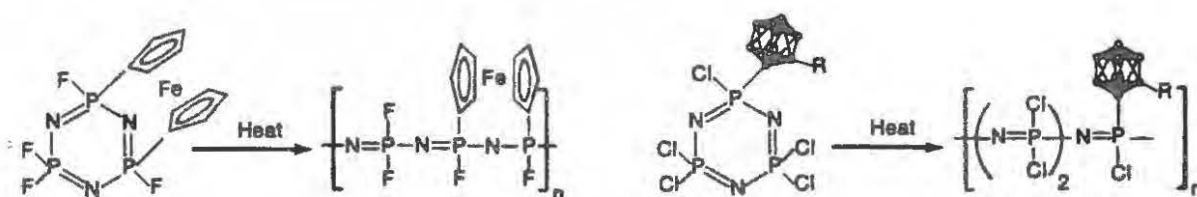
Polyphosphazenes are a broad class of inorganic polymers of the general formula $[-N=P(R)_2-]$ where R is a halogen, pseudohalogen, alkyl, aryl, alkoxy, aryloxy, or an organometallic unit [1]. The halogen derivative was first reported by Stokes in 1897, but was a heavily crosslinked insoluble elastomer which slowly hydrolyzed [2]. It was not until the mid 1960's when Allcock and coworkers synthesized high molecular weight uncrosslinked polymers that the substitution chemistry was examined [3].

Polyphosphazenes are prepared from the trimer $(PNC\ell_2)_3$ which is formed in the reaction of ammonium chloride and phosphorus pentachloride. This trimer polymerizes at 250°C to yield polymers of molecular weight 3 to 4 million atomic mass units [4,5].



Substitution chemistry in the backbone of polyphosphazenes is very versatile and over 300 different species are known. Three basic routes to substitute polyphosphazenes are available. The first is the polymerization of the halogen trimer followed by substitution. The second involves substitution and subsequent polymerization yielding only moderate molecular weight polymers. The third is direct polymerization of silylmonophosphazene, eg. $(CH_3)_3SiN=P(R)-(OCH_2CF_3)R$ [6]. As in classical polymer chemistry, it is these substituents, combined with the inherent flexibility of the polyphosphazene backbone, that give rise to new and unique properties.

Recent efforts have been directed toward synthesis of polyphosphazenes containing transition metals [7]. Strategies for incorporating metals into the



polyphosphazene include: direct coordination of the metal to the backbone nitrogen [8], direct bonding of the metal to the backbone phosphorus [12], and incorporation of the metal into a pendant side group [9-11,13-15]. These polymers have demonstrated catalytic ability, chemotherapeutic effects, semiconductivity and several other interesting properties.

Recent efforts have also been directed toward synthesizing polyphosphazenes with rigid, stackable side groups. These compounds are able to bridge the gap between polymers and 3-dimensional solids by conferring a degree of crystallinity, giving rise to a new set of properties. Several organo-ether complexes displaying liquid crystalline behavior [16] and an entire series with varying glass transition temperatures [17], T_g , have been synthesized. Polyphosphazenes with low glass transition temperatures have also been investigated as potential solid electrolytes since research on polymer-salt complex electrolytes implicates a liquid like mechanism [18,19].

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