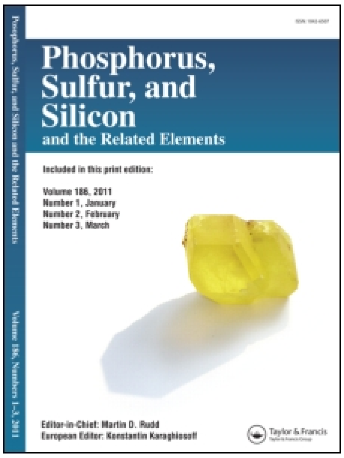

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Bosscher, G. , Hagen, H. , Meetsma, A. , Jekel, A. P. and Van De Grampel, J. C.(1996) 'Novel Alkenyl Substituted Cyclophosphazenes for the Synthesis of Thermally Stable Polymers', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 67 — 70

To link to this Article: DOI: 10.1080/10426509608545092

URL: http://dx.doi.org/10.1080/10426509608545092

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 67–70
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NOVEL ALKENYL SUBSTITUTED CYCLOPHOSPHAZENES FOR THE SYNTHESIS OF THERMALLY STABLE POLYMERS

G. BOSSCHER, H. HAGEN, A. MEETSMA, A. P. JEKEL AND J. C. VAN DE GRAMPEL
Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ABSTRACT. The synthesis of some new alkenyl substituted tetrachlorocyclophosphazenes is discussed. The reaction of acetyl chloride with a hydridocyclophosphazene yielded a vinylacetate derivative or a carbon-bridged bicyclophosphazene. Elimination reactions with $(NPCl_2)_2NP(^iPr)C(CH_3)_2OSO_2CH_3$ yielded a propene derivative and an ANSA compound. X-ray structures of the bicyclophosphazene and ANSA compound are presented. The vinylacetate and propene derivatives did not homopolymerize under radical conditions. Copolymerization with styrene resulted in polymers with a maximum incorporation of 17 mol% for the vinylacetate derivative and 18 mol% for the propene derivative. In TGA studies high char yields up to 64 wt% were observed for the homo- and copolymers of the vinylbenzyl substituted tetrachlorocyclophosphazene. XPS studies showed the residue to contain P, N and C.

INTRODUCTION

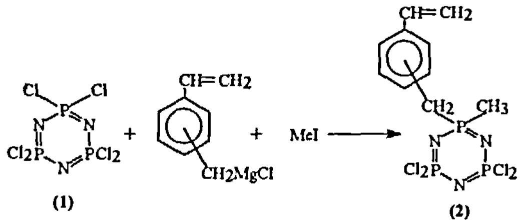
Over the past years a large number of polymerizable cyclophosphazene derivatives have been reported as well as their polymerization behavior[1]. The incorporation of these inorganic compounds in an organic polymer is of interest as it allows for a large variety of substitution reactions. Furthermore these (co)polymers exhibit interesting thermal properties such as flame retardancy[1]. Most of the synthesized cyclophosphazene monomers have the polymerizable group linked to the inorganic ring with a phosphorus-oxygen bond. A disadvantage of the phosphorus-oxygen bond is the possibility of rearrangement reactions resulting in degradation of the polymer[2].

Objective of this research is the synthesis of organic backbone polymers with phosphazene side groups with a direct P-C bond.

RESULTS AND DISCUSSION

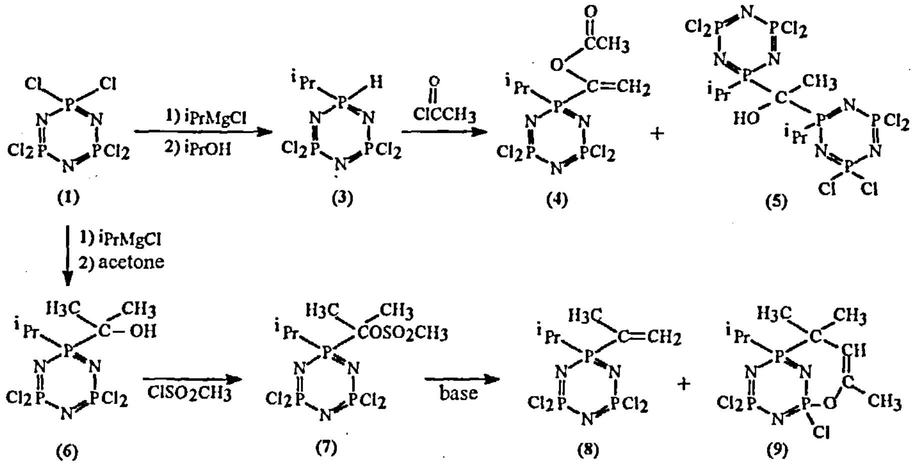
The strong electron-withdrawing nature of the cyclophosphazene necessitates the shielding of the double bond from the inorganic ring. To achieve this two strategies can be followed. The first is the use of a spacer group between the double bond and cyclophosphazene ring. Another approach is to compensate for the electronegative effect of the phosphazene group by an electron-donating substituent.

An example of a monomer with a spacer group is given below[3].



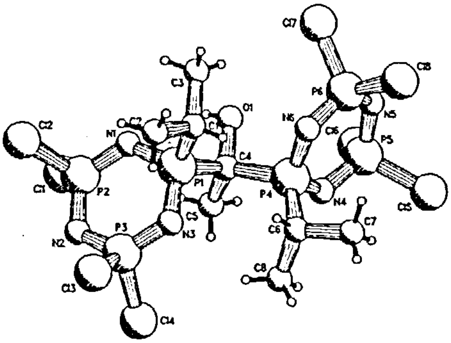
The obtained reactivity ratios from radical copolymerization reactions of methyl methacrylate (MMA) and the vinylbenzyl substituted cyclophosphazene (**2**) showed that the polymerization behavior of (**2**) resembles that of styrene[3].

Examples of the second class of monomers are the vinylacetate (**4**) and the propene derivative (**8**). Reaction schemes for their preparation are given below.

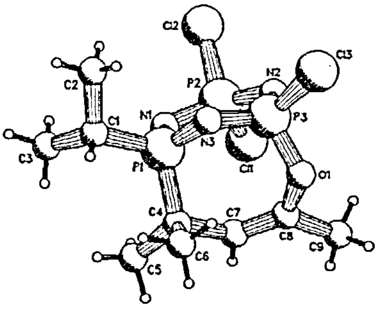


By using different ratios of acetyl chloride to (3), either the vinylacetate derivative (4) or a carbon-bridged bicyclophosphazene (5) was obtained. The structure of (5), which is given below, was confirmed by a single-crystal X-ray structure determination.

The synthesis of (8) involves multiple steps. Although (8) can be obtained from (6) by dehydration, yields are low for this direct procedure. Therefore the hydroxyl group in (6) was transformed in OSO_2CH_3 being a better leaving group. The elimination of the sulphonium group with a base proceeds smoothly and gives (8) in good yields. However apart from the expected product (8) a small quantity of another compound (9) was present in the reaction mixture. This compound was found to be an ANSA derivative of which the X-ray structure is presented below.



(5)



(9)

From the ^{13}C NMR data of (4) and (8) it follows that the electron-withdrawing effect of the phosphazene ring on the double bond is indeed weakened by the acetyl and methyl groups. The larger electron-donating capacity of the acetyl group is reflected by the smaller chemical shift of the vinyl ß-carbon atom compared with that of (8)[4].

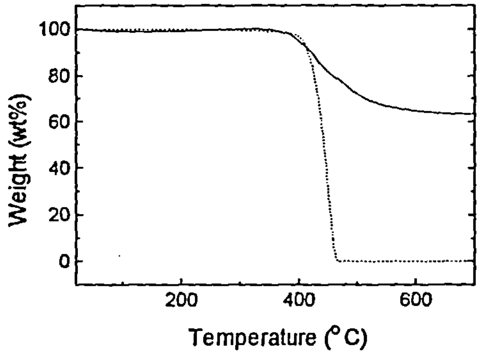
In contrast to the styrene derivative (2), homopolymers of (4) and (8) could not be obtained under radical conditions. This is most probably due to the fact that two steric demanding groups are present at the double bond. For the same reason polymers obtained from the copolymerization of (4) and (8) with MMA consist mainly of MMA. In a copolymerization experiment with MMA and 5 mol% of (4) in the feed, the incorporation of the phosphazene monomer in the polymer amounted only to 0.3

mol%. With the propene derivative (8) a similar result was obtained.

Copolymerizations of (4) and (8) with styrene resulted in much higher incorporation to a maximum of 17 and 18 mol%, respectively. The molecular weights of these polymers decreased with increasing phosphazene content. With feed contents of (4) of 40 mol% or higher (60 mol% for (8)) no polymer was formed. This phenomenon can be explained from steric reasons rather than from the phosphazene ring acting as a transfer or terminating agent.

All polymers derived from styrene and the phosphazene monomers presented here are *self-extinguishing and do not liquefy when placed into a flame. Upon heating,* a black brittle material remained which can be heated until glowing without any visible change. In particular the homopolymer of (2) is of interest. The polymer is stable up to 410 °C. At higher temperature decomposition takes place in one step with a loss of weight of 36 wt% (see TGA-plot). XPS spectra of the polymer before and after heating to 900 °C under N_2 flow indicate that weight loss is due to the evolution of HCl. The remaining residue is composed of P, N and C. The polymers described here may possess interesting flame retardant properties.

TGA-plot of the homopolymer of (2) (-) and styrene (...)



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