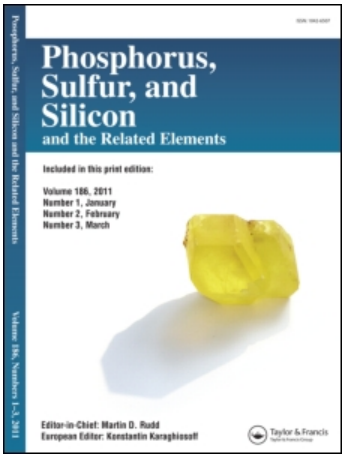

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Phosphazene Containing Macromolecules from Novel Monomers

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To cite this Article Bosscher, Gerard , De Vries, Gerard P. and Van De Grampel, Johan C.(1994) 'Synthesis of Phosphazene Containing Macromolecules from Novel Monomers', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 419 — 420
To link to this Article: DOI: 10.1080/10426509408021883
URL: http://dx.doi.org/10.1080/10426509408021883

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 419-420
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SYNTHESIS OF PHOSPHAZENE CONTAINING MACROMOLECULES FROM NOVEL MONOMERS

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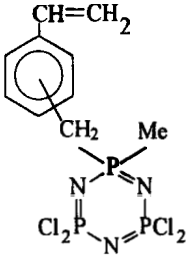
Phosphazene rings substituted with polymerizable groups have been the subject of extensive research for many years. Polymerization reactions with these monomers result in hybrid inorganic-organic polymers, which demonstrate an enhanced flame retardancy. Furthermore the remaining PCl_2-groups offer the possibility of further derivatization of the polymer. Most of the monomers synthesized have the double bond separated from the strong electron-withdrawing phosphazene ring by an insulating spacer.[1] Another class of monomers consists of olefins with both phosphazene and electron-donating substituents directly attached to the double bond.[2] In this paper some new examples of both classes are presented below:



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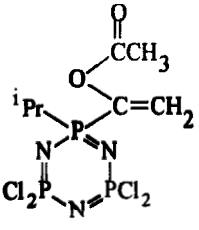

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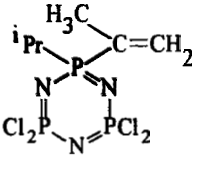

3

From the results of radical homo- and copolymerization of **1** and MMA it follows that the benzylic group acts as an efficient insulating spacer.[3] This is also demonstrated by the comparison of the ^{13}C δ (=CH_2) values of styrene and **1** (Table I).

For the derivatives **2** and **3** the electron-withdrawing effect of the phosphazene ring on the double bond is counterbalanced by the acetyl and methyl group, respectively. The

greater electron-donating capacity of the acetyl group is reflected by the smaller chemical shift of the vinyl ß-carbon atom compared with that of **3** (Table I). Radical homopolymerization reactions of **2** and **3** were unsuccesful, probably due to steric hindrance caused by the substituents on the double bond.

TABLE I. ^{13}C NMR data for some olefins

compound	^{13}C δ (=CH_2) (ppm)
vinylacetate	96.4
styrene	113.7
1	114.3
2	119.2
3	129.6

TABLE II. Selected data for the copolymer system: **2**/styrene, 1 mol% AIBN, 50 °C

2 in feed (mol %)	**2** in copol. (mol %)	reaction time (h)	yield (%)	$\overline{M}_n$ ($\times 10^{-3}$)	T_g (°C)
5.2	2.1	40	44	65	107
10.2	6.5	45	26	60	95
20.3	8.7	50	—	45	115
30.2	15.7	70	14	25	130
40.0	—	50	0	—	—

However for the system **2**/styrene, copolymers were obtained with reasonable amounts of **2** incorporated (Table II). A higher amount of **2** in the feed results in a rapid decrease of conversion and molecular weight of the copolymer until with 40 mol% and higher no polymer was obtained. This phenomenon can be ascribed to the fact that the phosphazene monomer acts as a chain transfer or terminating agent.[2,4] It is however not clear whether the organic part of the monomer or the presence of PCl bonds is responsible for this behavior. To investigate the susceptibility of the PCl_2 groups to radical species, styrene was radical polymerized in the presence and absence of $(NPCl_2)_3$. In the presence of $(NPCl_2)_3$ a lower yield of polymer was obtained with a lower molecular weight and a broader molecular weight distribution.

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