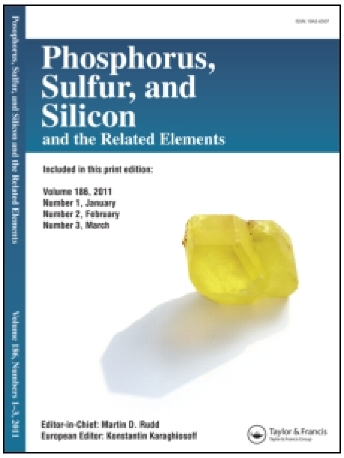

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Silicon-Containing Polymers Derived from Mono and Disubstituted Cyclophosphazenes

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SILICON-CONTAINING POLYMERS DERIVED FROM MONO AND DISUBSTITUTED CYCLOPHOSPHAZENES

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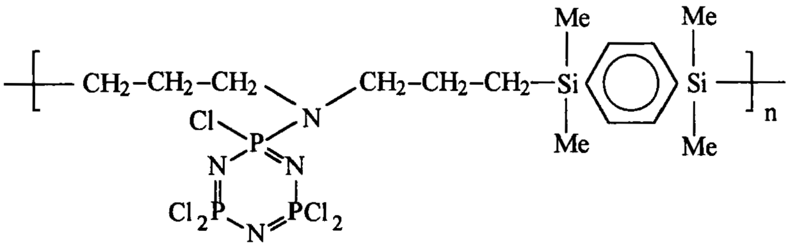
Abstract Two classes of silicon-containing polymers are described, one in which phosphazene rings are part of the polymer backbone, the other where phosphazene rings are present as pendant groups. X-ray structures of some monomeric precursors and reaction products are shown.

INTRODUCTION

In previous papers we reported about the synthesis of phosphazene-substituted siloxanes and silanes by hydrosilylation.[1-2] These studies have now been extended to the preparation of various polymeric systems in which silicon is incorporated in the main chain and phosphazene rings are present either as part of the main chain or as pendant groups. Hydrosilylation and Wurtz coupling were used as synthetic tools.

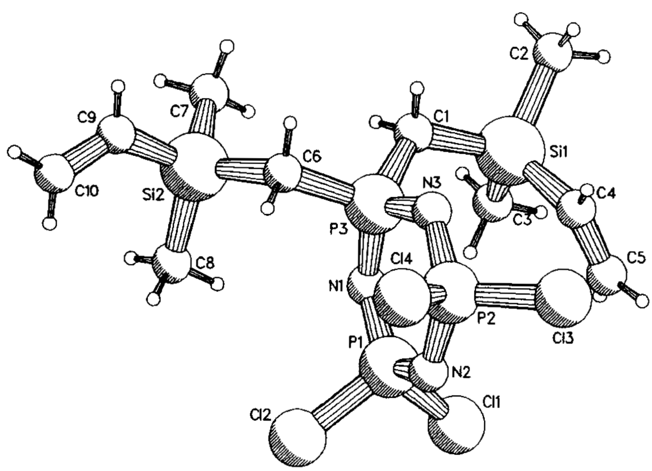
RESULTS AND DISCUSSION

Hydrosilylation of the difunctional cyclophosphazene $(NPCl_2)_2NPClN(CH_2CH{=}CH_2)_2$ (**1**) with $Me_2HSiC_6H_4SiHMe_2$ (**2**) in the presence of Karstedt's catalyst gave product (**3**), of which the structure (only β-addition is concerned) is given below, in high yield (90%). Similar results were obtained for hydrosilylation reactions of compound (**1**) and $Me_2HSiC_6H_4C_6H_4SiHMe_2$ (**4**), or $Me_2HSiC_6H_4OC_6H_4SiHMe_2$ (**5**). Molecular weights up to 14×10^3 were obtained.



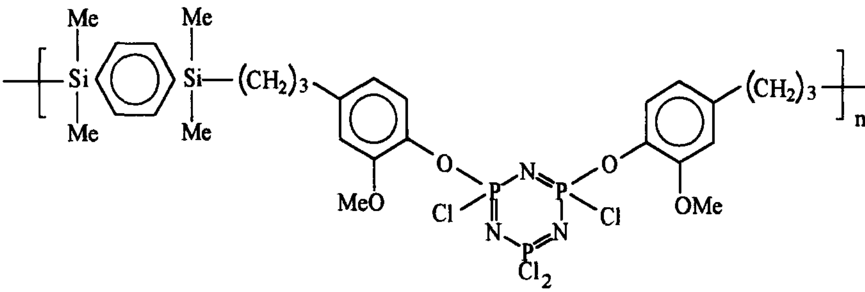
(3)

In addition to aromatic disilanylene derivatives, $Me_2HSiOSiHMe_2$ (**6**) $Me_2HSiCH_2CH_2SiHMe_2$ (**7**) and EtHSiHEt (**8**) were used. For compound (**8**) only the formation of low-molecular weight materials was observed. Probably steric factors retard the condensation process. Glass transition temperatures of the polymers prepared depend on the silicon precursor used and can be explained from the nature of the silicon part, e.g. the highest value was observed for the polymer derived from the biphenyl derivative (**4**), the lowest for the polymer derived from the siloxane derivative (**6**).



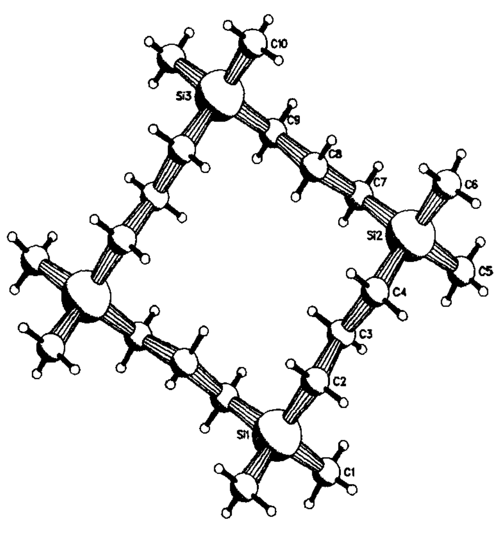
(9)

Low yields (30%) were obtained when using $(NPCl_2)_2NP(CH_2SiMe_2CH{=}CH_2)_2$ (**9**) where the double bond is adjacent to silicon. The lowering of the yield may be caused by the reactivity of the unsaturated organic part, as the *cis*-bis(eugenol) derivative $NPCl_2[NPClOC_6H_3(o\text{-}OMe)(p\text{-}CH_2CH{=}CH_2)]_2$ (**10**) provides yields (70%) comparable to those obtained for (**1**). Polymers derived from (**9**) or (**10**) possess phosphazene rings in the main chain as exemplified by polymer (**11**) formed by hydrosilylation of (**2**) and (**10**).



(**11**)

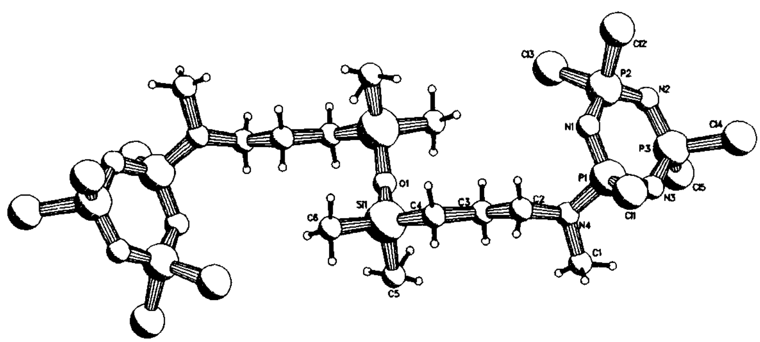
Carbosilane copolymers with formula $[SiMe_2(CH_2)_3]_x[SiMePh(CH_2)_2]_y$ (**12**) can be obtained by hydrosilylation of mixtures of CH_2=CHPhMeSiH (**13**) and CH_2=$CHCH_2Me_2SiH$ (**14**). Incorporation of $CH_2CH_2CH_2Me_2Si$ units appears to be higher than that of $CH_2CH_2PhMeSi$ units, pointing to a higher reactivity of (**14**). This is in line with the ^{13}C chemical shifts of the =CH_2 group; as lower the chemical shift as higher the electron density of the carbon-carbon double bond. In addition to copolymers appreciable amounts of low-molecular species were obtained.



(**15**)

Most likely, cyclic structures are involved. This is supported by the isolation of $[Me_2Si(CH_2)_3]_4$ (**15**) from the reaction mixture formed by hydrosilylation of (**14**).

According to the so-called "small molecule approach" Wurtz coupling with cyclophosphazene derivatives of silanes was studied on mono-chloro compounds, *e.g.* $(NPCl_2)_2NPClOC_6H_3$(*o*-OMe)[*p*-$(CH_2)_3SiMe_2Cl$] (**16**) or the corresponding methylallyl-amino derivative $(NPCl_2)_2NPClN(Me)(CH_2)_3SiMe_2Cl$ (**17**). Neither compound gave rise to the formation of disilanes. Wurtz coupling with the more reactive dichloro species led to vigorous decomposition reactions. It could be proven that only combination of PCl_2 groups with dichlorosilanes in the presence of sodium is responsible for this behavior.



(**18**)

Compounds (**16**) and (**17**) as well as their dichloro analogues could be used as precursors in acid hydrolysis for the formation of disiloxanes and polysiloxanes. Compound $[(NPCl_2)_2NPClN(Me)(CH_2)_3SiMe_2]_2O$ (**18**) derived from (**17**) may serve as an example.

ACKNOWLEDGEMENT

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