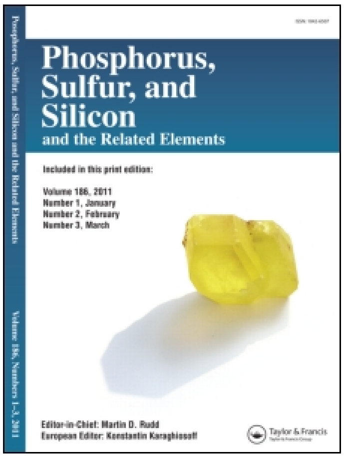

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POLYMERIZATION OF ORGANO-SUBSTITUTED SILANES BY HYDROSILYLATION

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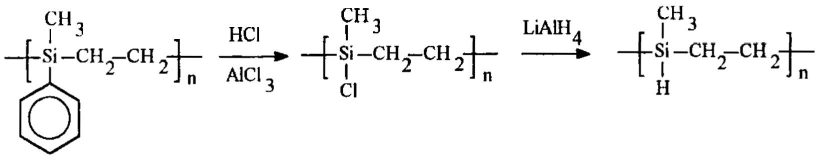
Abstract Polymerization of unsaturated organo-substituted silanes by catalytic hydrosilylation leads to both polymeric and cyclic carbosilanes.

Catalytic hydrosilylation of unsaturated organo-substituted silanes is a well known reaction to synthesize polycarbosilanes[1]

Hydrosilylation of methylphenylvinylsilane (**1**) and dimethylethynylsilane (**2**) was carried out in refluxing pentane in the presence of a platinum(II)-catalyst, leading to both polymeric and cyclic carbosilanes.

NMR spectroscopy showed polymerization of monomer **1** to occur via α- and β-addition (30:70), resulting in a polymeric structure with SiMePh-CH-(CH_3) and SiMePh-CH_2-CH_2 units (polymer **a**). For the polymerization of monomer **2** only β-addition was observed (polymer **b**).

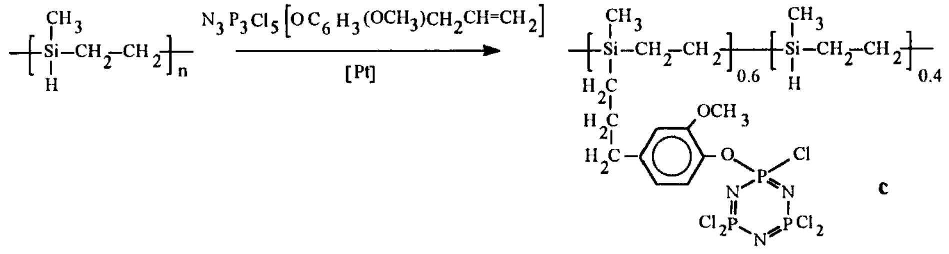
The silicon-bonded phenyl groups in polymer **a** were replaced by chlorine atoms by treatment with a HCl/$AlCl_3$ mixture[2]. Subsequent reaction of the SiCl groups with $LiAlH_4$ led to a polymer which possesses SiH groups[3] (Scheme 1, for β-addition only).



a

SCHEME 1 Functionalization of polymer **a**.

The polymer obtained appeared to be a versatile compound which offers a facile entrance to novel polycarbosilane derivatives, as exemplified in Scheme 2 for the preparation of polymer **c**.



SCHEME 2 Derivatization of the SiH group possessing polymer.

The synthesized polycarbosilanes were characterized by ^{1}H-, ^{13}C-, ^{29}Si- and ^{31}P NMR spectroscopy, GPC and DSC (Table I).

TABLE I Characterization of the synthesized polycarbosilanes.

Polymer	Yield (%)	% cyclic oligomers	M_n	D	T_g (°C)
a	92	32	6100	3.0	22.7
b	60	16	4200	2.8	-23.6
c	--	--	29000	1.4	2.9

Polymer **a** and **c** were also investigated with thermogravimetric analysis to study their thermal stability. Polymer **a** appeared to be stable up to 500°C followed by a rapid decomposition between 500 and 550°C yielding 1.5% of a black residue. For polymer **c** a small decrease in weight of 5% was observed up to 400°C. Further heating to 700°C led to a 59.1% of a black residue.

REFERENCES

1. W.P. Weber, Trends Polym. Sci., 1, 356 (1993).
2. R. West, J. Organometallic Chem., 300, 327 (1986).
3. E. Bacgué, J.P. Pillot, M. Birot and J. Dunoguès, Macromolecules, 21, 34 (1988).