

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

Polymerization of Organo-Substituted Silanes by Hydrosilylation

Rächel H. J. Hendriks^a; Robert Puyenbroek^a; Erwin G. M. Veldman^a; Bea M. W. Voss^a; Andries P. Jekel^a; Johan C. Van De Grampel^a

^a Department of Polymer Chemistry, University of Groningen, AG Groningen, The Netherlands

To cite this Article Hendriks, Rächel H. J. , Puyenbroek, Robert , Veldman, Erwin G. M. , Voss, Bea M. W. , Jekel, Andries P. and Van De Grampel, Johan C.(1994) 'Polymerization of Organo-Substituted Silanes by Hydrosilylation', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 93: 1, 363 – 364

To link to this Article: DOI: 10.1080/10426509408021858

URL: <http://dx.doi.org/10.1080/10426509408021858>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYMERIZATION OF ORGANO-SUBSTITUTED SILANES BY HYDROSILYLATION

RÄCHEL H.J. HENDRIKS, ROBERT PUYENBROEK, ERWIN G.M. VELDMAN, BEA M.W. VOSS, ANDRIES P. JEKEL AND JOHAN C. VAN DE GRAMPPEL

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

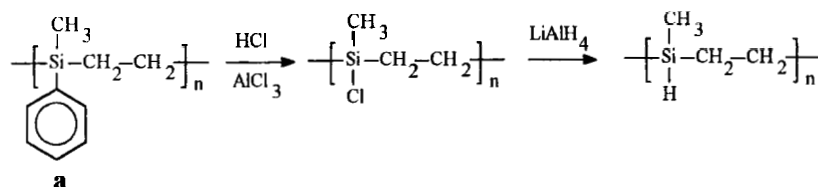
Abstract Polymerization of unsaturated organo-substituted silanes by catalytic hydrosilylation leads to both polymeric and cyclic carbosilanes.

Catalytic hydrosilylation of unsaturated organo-substituted silanes is a well known reaction to synthesize polycarbosilanes¹

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.

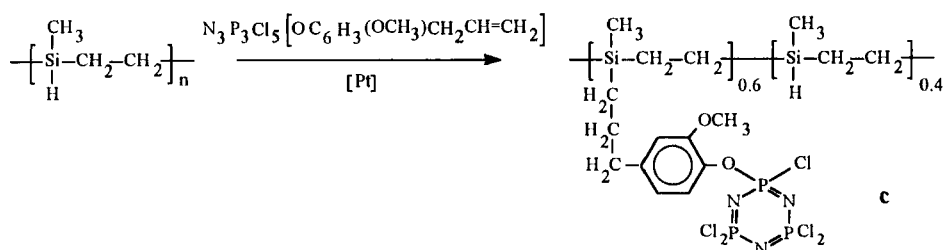
NMR spectroscopy showed polymerization of monomer **1** to occur via α - and β -addition (30:70), resulting in a polymeric structure with SiMePh-CH-(CH₃) and SiMePh-CH₂-CH₂ units (polymer **a**). For the polymerization of monomer **2** only β -addition was observed (polymer **b**).

The silicon-bonded phenyl groups in polymer **a** were replaced by chlorine atoms by treatment with a HCl/AlCl₃ mixture². Subsequent reaction of the SiCl groups with LiAlH₄ led to a polymer which possesses SiH groups³ (Scheme 1, for β -addition only).



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 ^1H -, ^{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 ($^{\circ}\text{C}$)
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).