Low-temperature Syntheses of Polysilanes and Polygermanes in Diethyl Ether

R. Harry Cragg, Richard G. Jones,* Anthony C. Swain, and Samantha J. Webb

Centre for Materials Research, Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, UK

Both soluble and insoluble polysilanes and an insoluble polygermane have been prepared in high yield and at moderate temperatures from the interactions of alkylaryl-, diaryl-, and dialkyl-dichlorosilanes and diphenyldichlorogermane with sodium sand in the presence of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) in refluxing diethyl ether.

In recent years there has been considerable interest in the synthesis and characterisation of soluble polysilanes[1,2] following from the recognition of their potential application as precursors of carbosilanes[3] and as resists for microlithiography.[4] Polysilanes are most commonly prepared by the Wurtz-type coupling of an organodichlorosilane using molten sodium in refluxing toluene in accordance with Scheme 1.

The product polymers usually have bimodal, if not polymodal, molecular weight distributions and the parallel formation of low molecular weight cyclic products is inevitable. As a

Table 1. Reaction conditions, conversions, and product molecular weights for the polymerization of selected organodichlorosilanes ($R^1R^2SiCl_2$).

Polysilane[a] R^1, R^2	Solvent	Crown ether	Conversion (%)	M_w
Me, Ph	Toluene	No	11	9690
Me, Ph	Toluene	Yes	26	9510
Me, Ph	Ether	No	8	3700
Me, Ph	Ether	Yes	99 (55[b])	65950
Ph, Ph	Toluene	No	36	
Ph, Ph	Ether	Yes	81	
Ph, *p*-Tol	Ether	Yes	40	
Me, *p*-Tol	Toluene	Yes	8	4340
Me, *p*-Tol	Ether	No	1	3400
Me, *p*-Tol	Ether	Yes	66 (25[b])	7030
n-Hex n-Hex	Ether	Yes	22 (9[b])	23800

[a] *p*-Tol = *p*-MeC_6H_4; n-Hex = n-hexyl. [b] Yield taken from reference 1 for syntheses in toluene without any additive.

$$n\,R^1R^2SiCl_2 + 2n\,Na \xrightarrow[\text{reflux}]{\text{toluene}} [-SiR^1R^2-]_n + 2n\,NaCl$$

Scheme 1

consequence the yields of desired polymer are usually only in the region of 9—55%[1] and are difficult to reproduce. Recently it has been shown[5,6] that in the presence of catalytic amounts of a crown ether, better reproducibility of polymer yields can be achieved with molecular weight distributions tending to the monomodal. Furthermore, for the polymerisation of dichloro-di-n-heptylsilane in toluene the polymer yield was higher when 15-crown-5 rather than heptane or diglyme was added to the reaction mixture. However, in the case of the polymerization of dichloromethylphenylsilane,[5] the presence of the crown ether did not alter the proportion of cyclic to polymeric product, even though the yield of the latter was increased to about 60%.

The polymerisations of methylphenyl-, methyltolyl-, diphenyl-, phenyltolyl-, and di-n-hexyl-silane and of diphenylgermane have been investigated to establish the optimum reaction conditions for the formation of high yields of high molecular weight products. The results are given in Table 1. Molecular weights were determined as polystyrene equivalents in tetrahydrofuran (THF) solution using size exclusion chromatography. In the case of the otherwise intractable polydiarylsilanes and polydiphenylgermane, slight solubility for this purpose was achieved in boiling THF but the resultant data are considered to be unreliable and so are not quoted.

The reactions of dichloromethylphenylsilane with sodium sand in refluxing toluene, in refluxing toluene in the presence of 15-crown-5, and in refluxing diethyl ether all gave low yields of a low molecular weight polymer. On the other hand the reaction using diethyl ether as the reflux medium in the presence of 15-crown-5 resulted in an almost quantitative yield of product consisting of 12% of cyclic material (removed by extraction in hexane) and 88% of high molecular weight polymer which was readily soluble in THF. Similar trends are observable for the other polymerizations including those of the dichlorodiarylsilanes.

The results suggest that high yields of polysilanes can better be achieved from the interaction of a dichlorosilane and sodium sand in the presence of 15-crown-5 at the low refluxing temperature attainable using diethyl ether. Polydiphenylgermane was obtained in 74% yield under these conditions.

Received, 25th April 1990; Com. 0/01841D

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