# Graphite–potassium, a New Reagent for the Synthesis of Polysilanes

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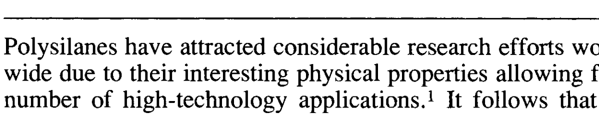
Poly(methylphenyl)silane, $10^3 \leqslant \bar{M}_w \leqslant 10^5$, can be synthesized from methylphenyldichlorosilane using graphite–potassium ($C_8K$) suspended in THF at −20 to 25 °C.

Polysilanes have attracted considerable research efforts worldwide due to their interesting physical properties allowing for a number of high-technology applications.[1] It follows that the chemical synthesis of these materials is being continuously investigated. Despite the recent discovery of several alternative methods,[2] the Wurtz–Fittig type reductive coupling of dichlorosilanes using sodium metal as reducing agent remains the only method leading to high molecular mass polymers. Usually carried out with molten sodium in refluxing toluene, the strict reproducibility of this reaction is difficult to achieve. The resulting polymodal molecular mass distributions together with their possible mechanistic implications have been discussed on several occasions,[3] and various attempts have been made at finding remedies to the major disadvantages of this method. The use of crown ethers or cryptands[3d,4] gave significant results with respect to the molecular mass distributions and/or in achieving milder reaction conditions, whereas the use of yttrium or pyrophoric lead appears less satisfactory because of the slow reactions and low yields observed.[5]

Herein we report preliminary results on the synthesis of poly(methylphenyl)silane from methylphenyldichlorosilane using the graphite–potassium intercalation compound ($C_8K$)[6] as the reducing agent [eqn. (1)].



$$2n\,C_8K + n\,PhMeSiCl_2 \longrightarrow \left(\begin{matrix} Me \\ | \\ -Si- \\ | \\ Ph \end{matrix}\right)_n + 2n\,KCl + \text{graphite} \quad (1)$$

In a typical experiment (Table 1, entry 2), a THF solution (15 ml) of methylphenyldichlorosilane (2.177 g, 11.4 mmol) was added dropwise to a well stirred THF (15 ml) suspension of graphite–potassium [prepared[7] from graphite (2.23 g; Merck-Schuckardt) and potassium (0.891 g, 22.8 mmol)] at 0 °C under argon. After 2.5 h of reaction at this temperature, 2 ml of methanol was added to the mixture to quench any unreacted potassium. The resulting black suspension was filtered, the solids were rinsed with 30 ml THF, and the organic phase was concentrated to about 10 ml and added to 100 ml of methanol. The resulting polymer precipitate (261 mg, 19% yield) was isolated, dried and characterized by IR spectroscopy and size exclusion chromatography (SEC) using linear polystyrene standards[8] (Fig. 1). Results obtained by varying the reaction conditions and the $C_8K$ : monomer ratio are shown in Table 1.

The major point emerging from these results is that the graphite–potassium reagent appears as a suitable reducing system allowing for the synthesis of polysilanes under considerably milder conditions than in the Wurtz–Fittig system. Table 1 shows that poly(methylphenyl)silane can be obtained in yields ranging from 20 to 30% in THF solution at 0 °C (entries 2, 5, 6); polymerization even occurs at lower temperatures (−20 °C, entries 3, 4) without greatly affecting the yield in polysilane. This is most certainly due to the greater reducing power of potassium compared to that of sodium, as well as to the activation of potassium metal arising from its intercalation as separate atoms into graphite sheets.

Size exclusion chromatographic analyses of the isolated crude polymer samples as shown in Fig. 1 indicate that bimodal molecular mass distributions occur in most cases. In entry 2 however, trimodal molecular weight distribution can be clearly observed. These features are quite similar to those observed in Wurtz-type polymerizations, and have been attributed to the heterogeneous nature of the reaction mixture, and/or to the possibility of simultaneous operation of several reaction mechanisms.[3] It appears from Table 1 that the most important factor influencing the molecular masses is the $C_8K$ : monomer ratio. The highest molecular masses were observed using the stoichiometric value of 2 [eqn. (1)], whereas the presence of an excess of $C_8K$ causes quite dramatic decreases in the molecular mass (Table 1, entries 5–7). This can be rationalized in terms of attack of polysilane chains by the excess potassium leading to

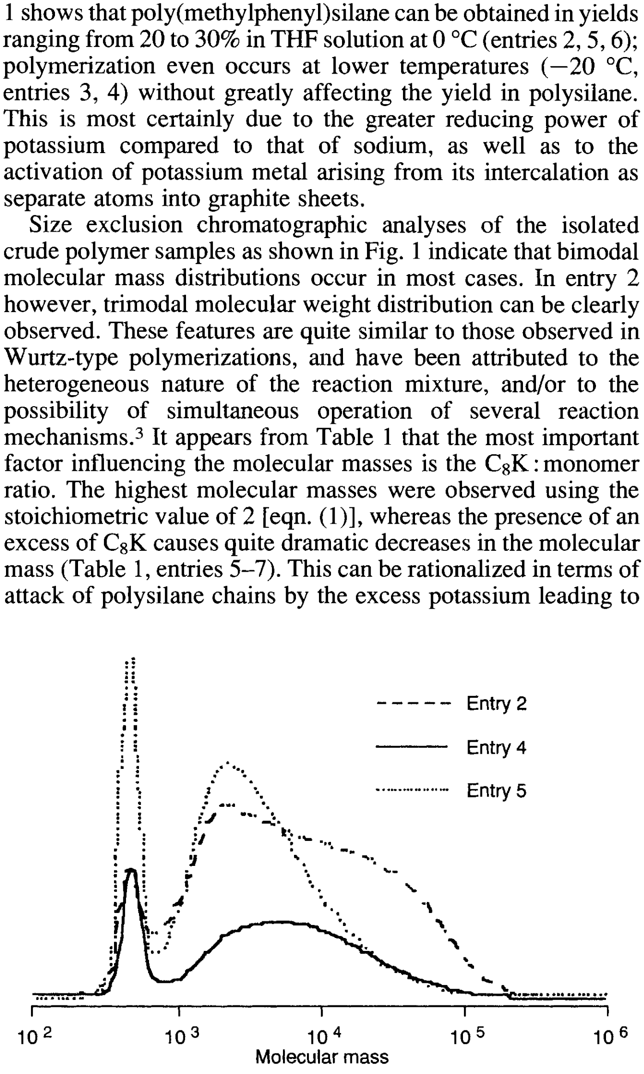


Fig. 1

Table 1 Synthesis of poly(methylphenyl)silanes using $C_8K$ in THF

| Entry | Conditions | $C_8K/MePhSiCl_2$ | $\bar{M}_w$ | $\bar{M}_n$ | $H^a$ | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 0 °C, 0.5 h then 25 °C, 2 h | 2.0 | 7430 | 2135 | 3.48 | 29 |
| 2 | 0 °C, 2.5 h | 2.0 | 16580 | 2490 | 6.66 | 19 |
| 3 | −20 °C, 2.5 h | 2.0 | 8240 | 1555 | 5.30 | 24 |
| 4 | −20 °C, 5 h | 2.0 | 10440 | 1860 | 5.61 | 26 |
| 5 | 0 °C, 2.5 h | 2.2 | 5940 | 1495 | 3.97 | 25 |
| 6 | 0 °C, 2.5 h | 2.5 | 5230 | 1470 | 3.56 | 19 |
| 7 | 0 °C, 1 h | 3.3 | 541 | 530 | 1.02 | 8 |

[a] Polydispersity, $H = \bar{M}_w/\bar{M}_n$.

their cleavage with the formation of shorter chains ended by a silyl anion and capable of undergoing backbiting.[3d] The ultimate result of such processes can be the complete degradation of the polymers (Table 1, entry 7).

Entries 1–4 (Table 1) suggest the effect of reaction temperature and/or duration on the polymerization; a higher temperature (25 °C) leads to a lower molecular mass product, probably due to degradation, (compare entries 1 and 2), and at low temperature (−20 °C) a shorter reaction time again results in shorter polymer chains (entries 3 and 4), presumably this is due to the lowering of the rate of polymerization.

In conclusion, we have shown that graphite–potassium is a valuable reagent for the synthesis of polysilanes, although under the conditions of our preliminary experiments we have not reached very high molecular masses. Nevertheless, from a practical point of view, the reaction system has significant advantages such as (i) easy preparation of $C_8K$, (ii) comparatively low reaction temperatures and short reaction times, (iii) simple work-up by filtration.

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