

Synthesis of poly(methylphenylsilane) using $[K^+/K^-]$ solutions in THF

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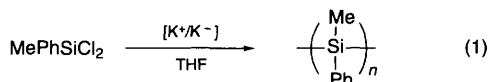
$[K^+/K^-]$ in THF solution allows for the low-temperature (–65 to –75 °C) synthesis of poly(methylphenylsilane) in 35–45% yield from dichloromethylphenylsilane under homogeneous conditions.

Since the discovery of synthetic methods to obtain soluble polysilanes some fifteen years ago,¹ these polymers made from an all-silicon backbone focused considerable interest due mainly to their unusual physico-chemical properties: *e.g.* precursors of β -SiC,² photoresists for microlithography,³ photoconductive potentialities,⁴ photoinitiators for polymerisation of vinyl monomers, *etc.*⁵ From that time, polysilanes were most often synthesized by the Wrutz–Fittig type reductive coupling of dichlorosilanes using molten sodium as reducing agent.⁶ This method remains indeed the only one able to lead easily to high molecular mass polymers. This explains why it continues to be used, despite several major drawbacks such as polymodality of the molecular mass distribution, limited yields and difficult control leading to poor reproducibility. Intense research is being continued in this field and progress towards new synthetic methods is steady: ultrasonically activated coupling,⁷ dehydrogenative coupling,⁸ electrochemical coupling,⁹ ring-opening anionic polymerisation,¹⁰ masked disilenes polymerisation,¹¹ and recently, low-temperature coupling of dichlorosilanes using graphite–potassium intercalation compounds.¹²

The mechanism of polymerisation of dichlorosilanes is still the subject of debate despite the fact that it is now generally accepted that the polymodality results mainly from the heterogeneity of the reaction medium.¹³ Attempts to homogeneously synthesize polysilanes from dichlorosilanes were for a long time considered impossible since Carberry and West obtained only cyclics by using naphthalene–sodium as a homogeneous reducing agent.¹⁴ Also Zeigler did not obtain any polymer using a soluble sodium–biphenyl reagent.¹⁵

Very recently, however, Jones and coworkers succeeded in obtaining poly(methylphenylsilane) under homogeneous conditions using sodium/electron-acceptor systems in THF at –79 °C.¹⁶

In a previous paper,¹⁷ we reported the efficient generation of silyl anions from chlorosilanes using $[K^+/K^-]$ solutions in THF. This method was successfully applied to the synthesis of disilanes from dimethylphenylchlorosilane in high yields. This paper describes the synthesis of polysilanes by means of the same reagent in THF at low temperature [eqn. (1)]. The



$[K^+/K^-]$ solution was prepared under argon in a flamed 250 ml double-necked round-bottomed flask. At –20 °C, a solution of 1321 mg (5 mmol) of 18-crown-6 in 15 ml of THF was slowly added by a syringe to 391 mg (10 mmol) of potassium pearls,¹⁷ and the suspension was stirred for 1 h at –20 °C. This resulted in a blue potassium solution.

Polysilane synthesis: in a typical experiment (Table 1, entry 4) the above $[K^+/K^-]$ solution was cooled to –65 °C and a solution of 955 mg (5 mmol) of dichloromethylphenylsilane in

10 ml of THF was added during 0.1 h through a pressure-equalized funnel. No temperature increase was observed. The reaction mixture was stirred for a further 0.2 h at –65 °C. Thereafter, 2 ml of methanol was added to quench any unreacted potassium. After adding 5 ml of toluene, the mixture was washed with 10 ml of water and concentrated to *ca.* 10 ml. This was added dropwise to 100 ml of methanol and the precipitated polymer was filtered off and dried for 1 h at 60 °C under vacuum. Molecular masses were determined as reported earlier by size exclusion chromatography (SEC) in THF with a polystyrene calibration.¹⁸

Table 1 shows the results obtained under different experimental conditions (temperature, reaction time); it appears clearly that poly(methylphenylsilanes) can be synthesized under homogeneous conditions. However, low temperatures are required to observe higher yields in polymer (entries 4, 9, 10, 13, 14). As the reaction temperature is increased, yields are seen to decrease (entries 2–4), and at 0 °C only oligomeric products could be isolated (entry 1). IR and ²⁹Si NMR spectra are consistent with the poly(methylphenylsilane) structure possessing a high number of Si–H chain ends which certainly argues for a silyl anionic polymerisation mechanism. The Si–O content of the polymers remains also limited. Typical SEC chromatograms reported in Fig. 1 show that the molecular mass distributions are monomodal, except for a small fraction of oligomers.

Although the reproducibility of the results is very good (Table 1, compare entries 5 and 6 or 9 and 10), the molecular masses appear however limited to \bar{M}_w *ca.* 4000. In order to understand the reasons for the limited molecular masses, a few experiments were conducted deliberately using non-stoichiometric ratios of reagents (Table 2).

An excess of dichloromethylphenylsilane does not lead to a dramatic change in the results (except for lower yield and somewhat lower \bar{M}_w : Table 2, entry 4), whereas in the presence of an excess of potassium solution (Table 2, entry 2) only a trace

Table 1 Synthesis of poly(methylphenylsilanes) using $[K^+/K^-]$ in THF

Entry	Conditions		\bar{M}_w	\bar{M}_n	H	Yield (%)
	$T/^\circ\text{C}$, $t_{\text{add}}^a/\text{h}$,	$t_{\text{reac}}^b/\text{h}$				
1	0, 0.1, 1		640	530	1.55	— ^c
2	–20, 0.1, 1		1630	1050	1.55	1.6
3	–40, 0.1, 1		2400	1300	1.8	14.5
4	–65, 0.1, 0.2		3170	1650	1.9	44
5	–65, 0.1, 2.5		3000	2000	1.5	18
6	–65, 0.1, 2.5		2900	2000	1.45	20
7	–65, 0.1, 5		3300	2200	1.5	13
8	–65, 0.3, 0.5		3530	2000	1.8	35
9	–65, 0.3, 1		4350	2330	1.9	45
10	–65, 0.3, 1		3980	2150	1.85	40
11	–65, 0.3, 2.5		3800	2300	1.7	32
12	–75, 0.1, 0.2		2890	2000	1.4	13
13	–75, 0.3, 0.5		3730	1830	2.0	38
14	–75, 0.3, 2.5		3710	2170	1.7	42

^a Addition time. ^b Reaction time. ^c Only a viscous liquid was recovered.

amount of unisolatable polymer precipitate is observed. This behaviour suggests that the $[K^+/K^-]$ complex can degrade the polymer, while, as already observed, dichloromethylphenylsilane does not induce any noticeable degradation. In order to check this assumption, the degradation reaction of poly(methylphenylsilane) synthesized independently (by a classical Wurtz reaction) was performed in a THF solution of $[K^+/K^-]$ for 30 min at -65°C (molar ratio polysilane monomer unit/ K : 1.8). The remaining products were recovered by solvent evaporation. The chromatograms (a) of the original poly(methylphenylsilane) and (b) of the product recovered after the reaction are displayed in Fig. 2. The degradation of the polysilane by $[K^+/K^-]$ is evident.

It thus appears reasonable to attribute, at least in part, the origin of the low molecular masses observed to a relatively unfavourable balance between the competing polymerisation and degradation reactions, this latter being due to the high reactivity of dissolved potassium.

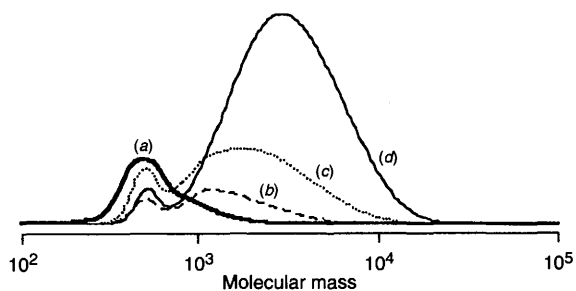


Fig. 1 Molecular mass distributions of poly(methylphenylsilane) obtained using $[K^+/K^-]$ solutions in THF at different temperatures; entry 1(a), 2(b), 3(c) and 11(d)

Table 2 Synthesis of poly(methylphenylsilane) by the $[K^+/K^-]$ method using stoichiometric or non-stoichiometric ratios of reagents

Entry	Conditions ^a		\bar{M}_w	\bar{M}_n	H	Yield (%)
	$t_{\text{react}}^b/\text{h}$	mol ratio ^c				
1	0.5	2 : 1	3530	2000	1.8	35
2	0.5	2.5 : 1	—	—	—	trace
3	1	2 : 1	4350	2330	1.9	45
4	1	1.9 : 1	2950	2060	1.4	20

^a At -65°C and $t_{\text{add}} = 0.3$ h. ^b Reaction time. ^c K :MePhSiCl₂ molar ratio.

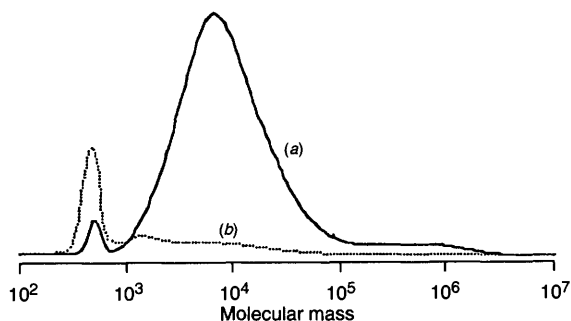


Fig. 2 SEC chromatograms of (a) the original poly(methylphenylsilane) and (b) the same polymer after degradation (see text)

This work demonstrates for the first time that $[K^+/K^-]$ in THF solution allows for the low-temperature synthesis of poly(methylphenylsilane) from dichloromethylphenylsilane under homogeneous conditions. As the $[K^+/K^-]$ complex was previously shown to yield silyl anions, the formation of poly(methylphenylsilane) seems also likely to proceed through the same type of intermediates.

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