Poly(methylphenylsilane) with an Enhanced Isotactic Content prepared using the Graphite Intercalation Compound, C_8K

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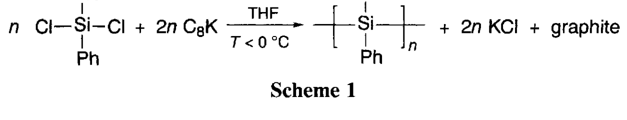
Poly(methylphenylsilane) of $\bar{M}_w$ approaching 10^5, formed in association with the solid phase in the reaction of the potassium–graphite intercalation compound, C_8K, with dichloromethylphenylsilane in THF at low temperatures has a significantly higher isotactic content than that formed using the conventional alkali metal reductive-coupling reaction.

The very high silicon content of polysilanes and their interesting electronic, photophysical and photochemical properties have led to the identification of a considerable number of applications in recent years.[1–3] However, the realisation of their full industrial potential is inhibited for want of a ready synthesis of high molecular mass polymers of narrow distribution. The alkali metal reductive-coupling of dichloroorganosilanes in a boiling solvent, usually an aromatic hydrocarbon, remains the sole method for readily achieving high molecular masses but in any of its modifications that have been reported to date only polysilanes with broad, polymodal distributions are formed. The mechanistic reasons for this have been the subject of several publications[4–12] but the problem persists. In addition, the products of the reaction are essentially atactic as the metal surface (on which the polymer grows and near which the alkali metal halide co-product crystallizes) offers no steric control to the propagation reaction. Though several alternative synthetic methods have been described[13–18] none are finding general application as each has its drawbacks. However, they include the anionic ring-opening polymerisation recently reported by Fossum and Matyjaszewski[17,18] which has been invaluable in characterising the ^{29}Si NMR resonances of the stereogenic centres within poly(methylphenylsilane), PMPS.[19]

Within the last year there have been several reports[20–23] of a new modification of the alkali metal reductive-coupling reaction in which a graphite intercalation compound, C_8K dispersed in THF, is used to form PMPS from dichloromethylphenylsilane, DCMPS, at temperatures as low as −79 °C in accordance with Scheme 1. In this paper we report the ready isolation of a high molecular mass, essentially monomodal fraction of the product of this reaction and its characterisation as a PMPS with an isotactic content of 50%.

All reactions were carried out under an argon atmosphere using both glassware and graphite that had been flame dried under vacuum immediately prior to use. C_8K intercalates were prepared in accordance with a method described in a recent review.[24] The requisite volumes of THF were then added and the temperature reduced to that chosen for the reaction (−79, −50, −30, −17 or 0 °C) before the addition of a stoichiometric amount of DCMPS. Mixtures were stirred vigorously for the duration of the reaction, after which sufficient methanol was added to quench the unreacted potassium. For reactions conducted at all of the temperatures specified above, two polymer fractions were isolated as follows. The solution and graphite phases were separated by filtration and the solid residue washed with small aliquots of cold THF. The potassium salts were removed from the graphite residues by successive Soxhlet extractions with methanol, water and methanol. Again using the Soxhlet method, polymer was extracted from the graphite phase using either THF or toluene. It was then isolated by precipitation in methanol from (*a*) the solution phase of the product mixtures and (*b*) the graphite THF–toluene extracts. Oligosilanes were removed by extraction with hexane. For a reaction carried out at −79 °C for 1 h, the polymer yields from the solution and graphite phase were 23 and 15%, respectively. The molecular mass distributions were narrow and virtually monomodal as is shown in Fig. 1.



$$n\ \mathrm{Cl{-}\underset{Ph}{\overset{Me}{Si}}{-}Cl} + 2n\ \mathrm{C_8K} \xrightarrow[T<0\ °\mathrm{C}]{\mathrm{THF}} \left[\underset{Ph}{\overset{Me}{\mathrm{Si}}}\right]_n + 2n\ \mathrm{KCl} + \mathrm{graphite}$$

Scheme 1

In some experiments the effectiveness of the extractive procedure was checked by using hexane, THF, toluene and carbon disulfide (an excellent solvent of PMPS) in sequence. At the end of these procedures the dried graphite still had an excess mass which was comparable to the amount of high polymer removed in the sequential extractions so it is concluded that not all of the polymer can be removed using standard laboratory work-up procedures.

Polymers were characterised as PMPS using IR spectroscopy and ^1H, ^{13}C and ^{29}Si NMR spectroscopy. In order to obtain well resolved peaks in the ^{29}Si spectra, $Cr(acac)_3$ was added as a spin relaxation agent. Molecular masses of PMPS were measured as linear polystyrene equivalents in THF solution using size exclusion chromatography.

A typical ^{29}Si NMR spectrum of a PMPS formed in diethyl ether using the conventional Wurtz-coupling reaction is shown in Fig. 2(*a*). There are three main resonances (externally

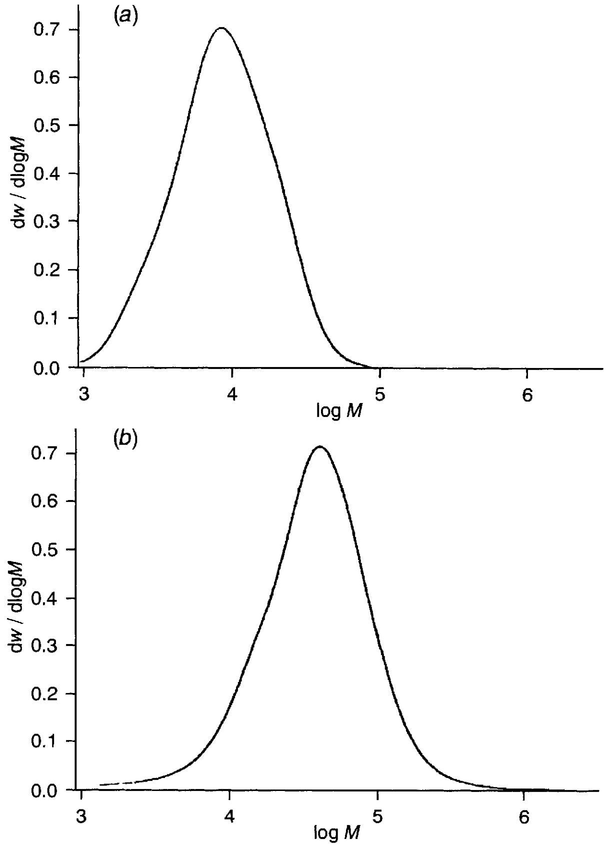


Fig. 1 Molecular mass (*M*) distributions of PMPS isolated from (*a*) the solution phase (M_n = 5650, M_w = 10 100, polydispersity = 1.8), and (*b*) the graphite phase (M_n = 21 800, M_w = 64 000, polydispersity = 1.8) of the C_8K-mediated reductive-coupling of DCMPS in THF

referenced) at δ −39.2, −39.9 and −41.2, each showing some evidence of further splitting. The spectrum and the ratio of the resonance integrals, 3 : 3 : 4 with no more than a 5% variation, are identical to those reported by West and coworkers[25] for the formation of a PMPS using the same reaction in toluene solution. Using statistical reasoning, these researchers assigned the resonances to silicon atoms centred in isotactic triads, syndiotactic triads and heterotactic triads, respectively. They also made the observation that in the absence of any stereochemical control the ratio would be expected to be 1 : 1 : 2 and that the polymer therefore seems to display a partial tacticity which was not observed in the unsymmetrically substituted poly(alkylmethylsilane)s.[26,27] However, on the basis of studies of the ring-opening polymerisations of methylphenyl substituted cyclotetrasilanes, the three resonances have been reassigned by Matyjaszewski and Fossum[19] to heterotactic (δ −39.2), syndiotactic (δ −39.9) and isotactic (δ −41.2) triads. The polymer as conventionally prepared is therefore of a higher isotactic content than had previously been recognised.

The ^{29}Si NMR spectrum of PMPS isolated from the solution phase of the C$_8$K-mediated reaction is identical to that shown in Fig. 2(*a*). In marked contrast is the typical spectrum of the polymer isolated from the graphite phase which is shown in Fig. 2(*b*). On the basis of the assignments of Matyjaszewski and Fossum this reveals a significantly higher isotactic content of 50%, the integrals of the resonances being almost in the ratio 1 : 1 : 2. Within experimental error the same 1 : 1 : 2 ratio is observed for polymer extracted from the graphite phase using THF, toluene and CS$_2$. We believe that this difference between the polymer from the graphite phase and that formed in the conventional Wurtz reaction arises as a consequence of some steric constraint over the propagation reaction being exercised by the lamellar structure of the graphite lattice, either within the bulk or at the surface. We have thus shown that it is not only possible to synthesise poly(methylphenylsilane) using a graphite intercalation compound as the reducing agent in a reductive-coupling reaction,[23] but that the product is found in the solid as well as the solution phase, and that the fraction from the solid phase has a higher isotactic content than the same polymer formed using the conventional Wurtz-type coupling reaction. To the best of our knowledge this is the first report of a modification of the tacticity of any polysilane formed through an alkali metal mediated reductive-coupling reaction.

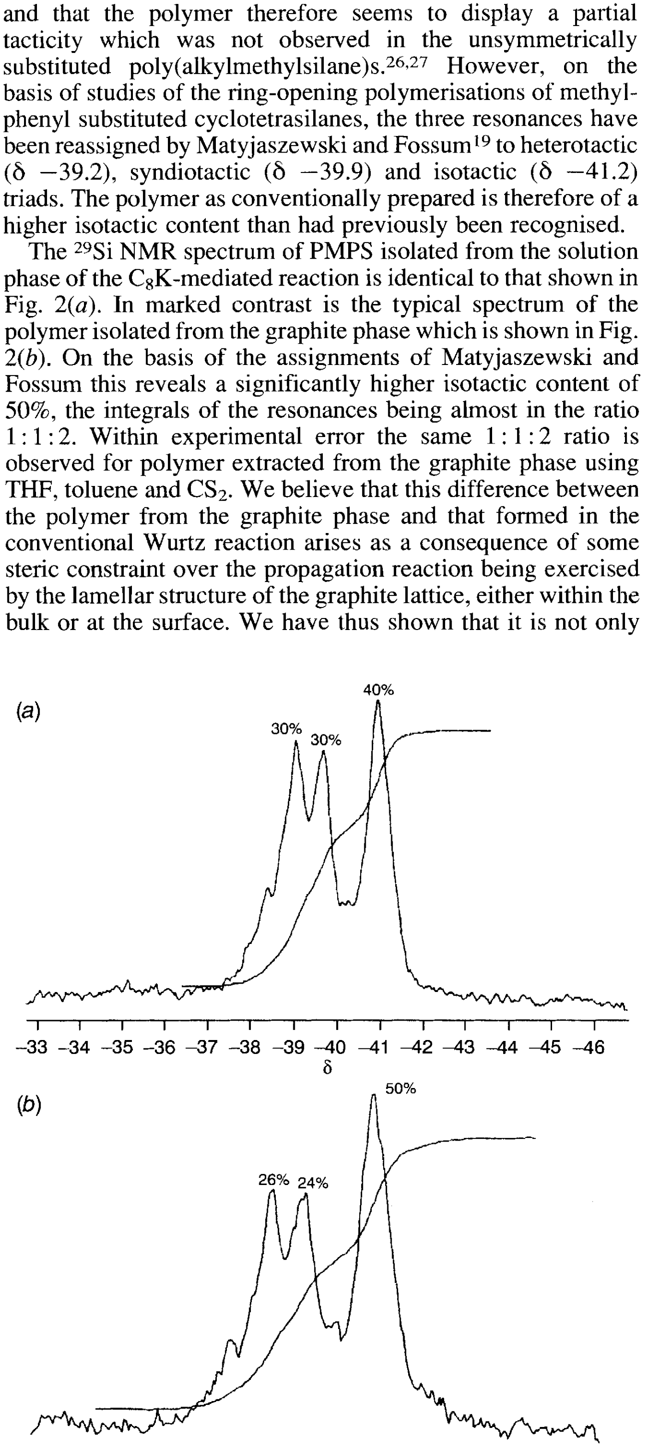


Fig. 2 53.54 MHz ^{29}Si NMR spectra of PMPS isolated from (*a*) a standard Wurtz reductive-coupling reaction using sodium in boiling diethyl ether, and (*b*) the graphite phase of a C$_8$K-mediated reductive-coupling of DCMPS in THF

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