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An oligosilane initiator for the Wurtz-type polymerisation of dichloromethylphenylsilane

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Abstract

1-Chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane was employed as an initiator in the Wurtz-type reductive coupling polymerisations of dichloromethylphenylsilane with sodium in toluene at 65 °C. Yields of polymethylphenylsilane (PMPS) were in the range 32–35% which was almost double that obtained by otherwise identical reactions in the absence of the initiator (16–19%). Furthermore, higher molecular weight parameters were observed for PMPS synthesised with the initiator. This is believed to be a result of the low reduction potential of the oligosilane allowing for it to compete efficiently in the initiation step with the dichloromethylphenylsilane monomer and inhibit end-biting, which usually occurs in conventional syntheses by reaction of the silyl anion with the terminal silicon–chlorine bond in the early stages of the polymerisation. ^{29}Si NMR spectroscopic analysis of an isolated high molecular weight fraction supported the incorporation of the oligosilane in the PMPS chain. In contrast, the use of the initiator in the Wurtz-reductive coupling of dichloromethylphenylsilane in tetrahydrofuran at room temperature led to no increase in molecular weights or yields of PMPS which confirms that the end-biting reaction is not as significant in polymerisations carried out under these conditions.
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1. Introduction

Contemporary interest in polysilanes commenced in the late 1970s with the discovery and development of the synthesis of tractable polysilanes by the reduction of dichlorodiorganosilanes with molten sodium in toluene by Mazjyasni, West and David, and later in the 1980s by Trujillo, and Wesson and Williams, and others [1–8]. This is the Wurtz-type reductive-coupling polymerisation and it remains the most common method of polysilane synthesis (Scheme 1). The synthesis of most polysilanes by this route gives low yields and polymodal molecular weight distributions [9]. In this manuscript we will demonstrate a simple means of improving yields of high molecular weight polymethylphenylsilane (PMPS) by the incorporation of a monochloro-organosilane that the evidence suggest acts as an initiator for the polymerisation. Previous efforts to ameliorate the experimental conditions, increase yields, control the molecular weight parameters as well as remove the polymodality obtained under the standard Wurtz conditions have been described by several groups [10–16]. Increases in yields and the molecular weights of polysilanes have been successfully demonstrated by the incorporation of polar compounds such as diglyme, crown ethers, cryptands and acetates. Such additives usually improve the yields and the molecular weight distributions but unfortunately at the expense of the high molecular weight material [10–12,17–19]. PMPS has been amongst the most studied of the polysilanes in part due to the relative affordability and high reactivity of the monomer (dichloromethylphenylsilane) but also due to the interaction of the aromatic ring with the σ-conjugated backbone giving strong broad absorption in the UV–Vis spectrum around 340 nm [20,21]. When PMPS is synthesised by the Wurtz-reductive coupling polymerisation in refluxing toluene in the presence of sodium
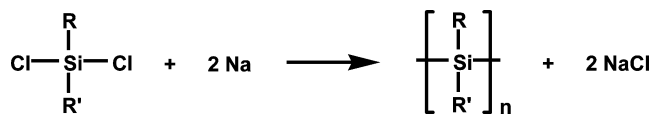
Scheme 1.

metal, yields are typically <40% [22,23] and three separate molecular weight fractions are produced during the reaction (illustrated schematically in Fig. 1): (I) a thermodynamically favored cyclic fraction (typically 5 or 6 monomer units) produced by end-biting and back-biting reactions of oligo- and polysilanes, respectively; (II) a polymeric fraction with an intermediate molecular weight ($\overline{DP}_n \sim 30$–50) determined by the termination of chain growth by a conformationally induced back-biting reaction; (III) a kinetically driven polymeric fraction of a high molecular weight ($\overline{DP}_n \sim 1000$–10 000) formed through uninterrupted chain growth and some subsequent condensation reactions. The polymodality of PMPS synthesised in refluxing toluene was recently explained through a mathe-

matical model called the kink diffusion mechanism developed by McLeish et al. [24]. This mechanism has been described in detail [24] and experimentally demonstrated elsewhere [25]. In the classic Wurtz-type polymerisation conditions using Na in toluene, the limiting factor in giving high yields of the linear polymer are the production of cyclic pentamers due to end-biting in the early stages of chain growth (Scheme 2) [26]. Reducing the temperature of the polymerisation has the effect of reducing the formation of intermediate molecular weight polymer (fraction II) as a result of the reduction in the rate of back-biting. However, the rate of end-biting predominates over the rate of chain propagation and consequently cyclic materials are produced at the expense of linear material [9,22,23].

Therefore, to increase the yields of linear polymer it is necessary to reduce the probability of intramolecular cyclisation due to end-biting in the early stages of growth. Matyjasewski et al. briefly reported the use of a monochloro-oligosilane, Ph(n-hexyl$_2$Si)$_4$I, 'promoter' in the sonochemical synthesis of PMPS in toluene in the context of a larger study [11] and reported some increase in the yield of PMPS produced (from 12% to 19%). Following on from these promising early results in this paper we describe the use of an oligosilane which acts as an initiator in the Wurtz-type reductive coupling polymerisation of dichloromethylphenylsilane and has the effect of reducing the incidence of back-biting. As a consequence, the yields of linear PMPS obtained from the reaction almost double.

2. Experimental

2.1. Materials

Toluene was dried over MgSO$_4$ for at least 24 h and then dried over sodium wire for at least 24 h before distillation over sodium metal under nitrogen atmosphere prior to use. THF was dried over MgSO$_4$ for at least 24 h and then over sodium wire for at least 24 h before distillation
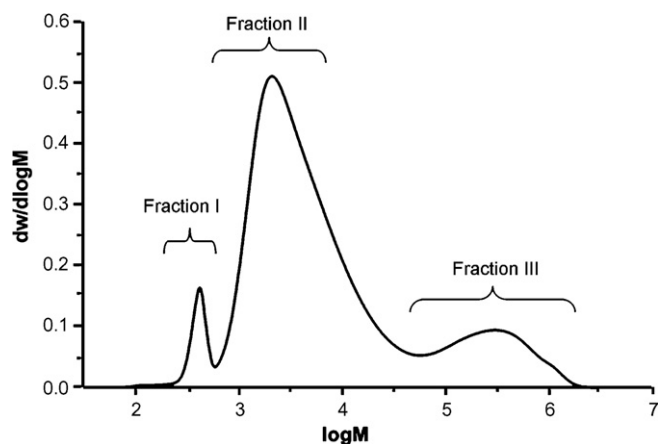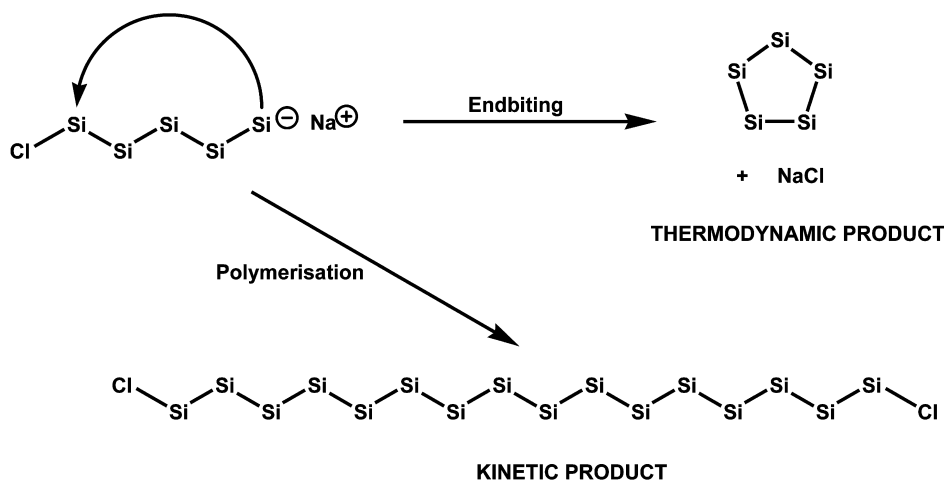

Fig. 1. Size-exclusion chromatogram illustrating the three molecular weight fractions arising from the Wurtz-reductive coupling polymerisation of dichloromethylphenylsilane with sodium in toluene at 110 °C.

Scheme 2.

over sodium wire and benzophenone under nitrogen immediately prior to use. Dichloromethylphenylsilane (Aldrich) was distilled under reduced pressure and stored at 4 °C under nitrogen over magnesium turnings. Sodium (30 wt% dispersion in toluene) (Aldrich), methanol (99.99% Fisher) and 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (Aldrich) were used as received.

NMR spectra were recorded in CDCl$_3$ at 30 °C with a JEOL GX-270 spectrometer. UV–Vis spectra were recorded in THF using a Heλios β Unicam UV Spectrometer. IR spectra were recorded from cast thin films on KBr disks using an Avatar 360 FTIR spectrometer. The molecular weights and polydispersity values were measured using equipment supplied by Polymer Laboratories Ltd. All measurements were carried out at 40 °C using two 300×7.5 mm Plgel µm Mixed-C columns equipped with a LC 1120 HPLC pump and a Shodex RI-101 refractive index detector. The instrumentation was calibrated using polystyrene standards supplied from Polymer Laboratories Ltd.

2.2. Synthesis of polymethylphenylsilane in toluene (Reactions 1a–d)

Sodium (3.2 g, 0.141 moles, in a toluene dispersion) was added using Schlenk-line techniques under a nitrogen atmosphere, to a three-necked round bottom flask (250 mL) equipped with an egg-shaped PTFE stirring bar and a condenser. The toluene was removed under vacuum and then freshly distilled toluene (80 mL) was added via a syringe. The mixture was heated to 65 °C with rapid stirring and dichloromethylphenylsilane (12 g, 0.064 moles) was added dropwise under a nitrogen atmosphere. The mixture was stirred and heated at 65 °C for 1 h. The polymerisation mixture was then cooled to room temperature whereupon methanol (40 mL) was added slowly to terminate the reaction. The precipitate was filtered, rinsed with excess water (to remove NaCl), then methanol and finally dried under vacuum at 40 °C. Molecular weight parameters were determined by SEC.

2.3. Synthesis of polymethylphenylsilane in toluene with 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenylsilane (Reactions 2a–c)

An identical procedure to that for reactions 1a–d was followed employing a mixture of dichloromethylphenylsilane (12.00 g, 0.064 moles) and 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenylsilane (50 mg, 0.064 mmoles) in place of the dichloromethylphenylsilane. Molecular weight parameters were determined by SEC.

2.4. Synthesis of polymethylphenylsilane in THF (Reactions 3a–b)

A pre-formed sodium dispersion in toluene (3.2 g, 0.141 moles) in toluene dispersion was added to a three-necked

round bottom flask (250 mL) equipped with an egg-shaped PTFE stirring bar and a condenser, under a nitrogen atmosphere using Schlenk-line techniques. The toluene was removed under vacuum and then freshly distilled THF (80 mL) was added via a syringe. The mixture was rapidly stirring at room temperature and dichloromethylphenylsilane (12.00 g, 0.064 moles) was added dropwise under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. Methanol (40 mL) was slowly added to terminate the reaction. The precipitate was filtered, rinsed with excess water (to remove NaCl), then methanol and finally dried under vacuum at 40 °C. Molecular weight parameters were determined by SEC.

2.5. Synthesis of polymethylphenylsilane in THF with 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenylsilane (Reaction 4)

An identical procedure to that for reactions 3a–b was followed employing a mixture of dichloromethylphenylsilane (12.00 g, 0.064 moles) and 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenylsilane (50 mg, 0.064 mmoles) in place of the dichloromethylphenylsilane. Molecular weight parameters were determined by SEC.

3. Results and discussion

3.1. Polymerisation in toluene at 65 °C

To the best of our knowledge no comparison between the reduction potentials of oligosilanes with monosilanes (chlorinated or otherwise) has been performed (e.g. through cyclic voltametry). However electron transmission spectra of a series of permethylated oligosilanes, Me(SiMe$_2$)$_n$Me (with Me=CH$_3$ and $n = 1$–4) have been recorded and interpreted by Modelli et al. [27]. This work demonstrated a significant increase of electron affinity with increasing chain length. Further investigations into electron affinities of chloro-unsaturated and saturated carbon derivatives resulted in the prediction that electron affinities would increase for silane containing chloro-derivatives with increasing Si chain length [28]. Consequently it is not unreasonable to expect that a monochloro-oligosilane would have a higher electron affinity than a dichloromethylphenylsilane monomer and consequently be reduced more readily by the sodium metal [11]. The addition of an oligosilane should effectively eliminate the end-biting of silyl chloride end-groups by the silyl anions (Scheme 2) since the chain is blocked at the chain end with an inactive group (in the present case phenyl and methyl). As noted a previous but limited study indicated that this approach was a promising route to increasing polysilane yields [11]. However, the oligosilane used was not commercially available and the syntheses of monochloro-oligosilanes are far from trivial. Consequently we found another monochloro-oligosilane 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (Fig. 2), that was commercially available which, as a
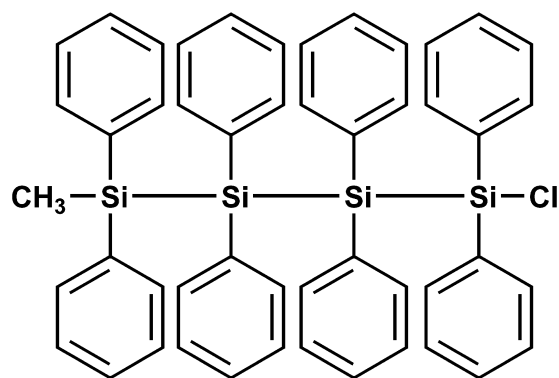
Fig. 2. Structure of 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane.

Table 1
Yields and molecular weight characteristics of the crude PMPS polymers obtained from the Wurtz-reductive coupling polymerisation conducted in toluene at 65 °C at room temperature in the absence and presence of [Cl(Ph$_4$Si)$_4$CH$_3$]; mole ratio of sodium:monomer = 2.2:1.0; mole ratio of dichloromethylphenylsilane:Cl(Ph$_4$Si)$_4$CH$_3$ = 1:1000

Exp. No.	Cl(Ph$_2$ Si)$_4$ CH$_3$	Yield (%)[a]	Fraction III		Fraction I + II		L_p/H_p[b]
			M_n	M_w/M_n	M_n	M_w/M_n	
1a	NO	16	80 900	2.67	495	2.39	65:35
1b	NO	13	84 900	2.62	432	2.65	63:37
1c	NO	13	84 600	2.83	353	3.35	55:45
1d	NO	19	73 800	2.59	475	2.85	60:40
2a	YES	34	393 200	3.99	424	3.32	30:70
2b	YES	32	293 600	2.98	322	2.81	35:65
2c	YES	35	379 600	3.20	445	3.05	33:67

[a] Determined gravimetrically after one precipitation with methanol.
[b] Ratio of fraction I + II (L_p) to fraction III (H_p) determined from SEC UV detector response at 254 nm.

result of the substituent phenyl groups, was expected to have a high electron affinity.

In order to test the use of this initiator in the Wurtz-type polymerisation, reaction conditions needed to be identified that led to only cyclic material and high molecular weight linear polymer (thereby side-stepping the complication of the back-biting process). Miller et al. synthesised PMPS and polyethylphenylsilane (PEPS) in toluene over a range of temperatures [7]. They observed that the ideal temperature range to obtain a monomodal high molecular weight polymer from these polymerisations (after fractionation) was between 50 and 65 °C. At 65 °C, a monomodal PEPS was obtained in 9% yield (after fractionation to remove cyclics) consisting of high molecular weight (M_w of 1.3×10^6). The differences between the polymerisations conducted at 65 °C and at 110 °C in toluene were due to temperature effects. At 110 °C a trimodal distribution is obtained consisting of the three different fractions. As the temperature of the polymerisation decreases, termination due to back-biting decreases and less intermediate molecular weight material is produced [9]. At 65 °C high molecular weight material predominates and the formation of the cyclic fraction is primarily a result of end-biting and it this that keeps the yield of linear polysilane low.

Consequently four polymerisations (**1a–d**) of dichloromethylphenylsilane in toluene with sodium at 65 °C were performed following a procedure similar to that reported by Miller et al. [7] using methanol as the precipitating solvent rather than 2-propanol. In all cases a commercial sodium sand was used to ensure a similar total surface area of sodium was present between all reactions. The results obtained from our group were broadly similar to those obtained by Miller. The yields of the crude polymers from the reaction (prior to fractionation) were in the range of 13–19% (Table 1). The molecular weight distributions were bimodal consisting of the low molecular weight material and the high molecular weight polymer (Fig. 3). The principal difference being that since these reactions were terminated by methanol instead of propan-2-ol, the bulk of the cyclics were preserved in the crude product whereas the

yields quoted by Miller et al. (∼9%) were those for purified/fractionated linear polymer free from cyclics.

Three polymerisations (**2a–c**) were conducted in otherwise identical conditions to reactions **1a–d** but including 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane in a molar ratio to DCMPS of 1:1000. The yields obtained from these reactions were 32–35%, almost double those recorded for **1a–d** (Table 1). A typical chromatogram is presented in Fig. 3 overlaid with that of a polymerisation performed without the oligosilane. As this result, and those in Table 1 demonstrate, the relative proportion of high molecular weight linear polysilane to cyclic material increases in all cases, directly corresponding to an increased yield of the linear polymer. Furthermore the high molecular weight fraction III shows an increase in molecular weight parameters. This strongly indicates that the immedi-
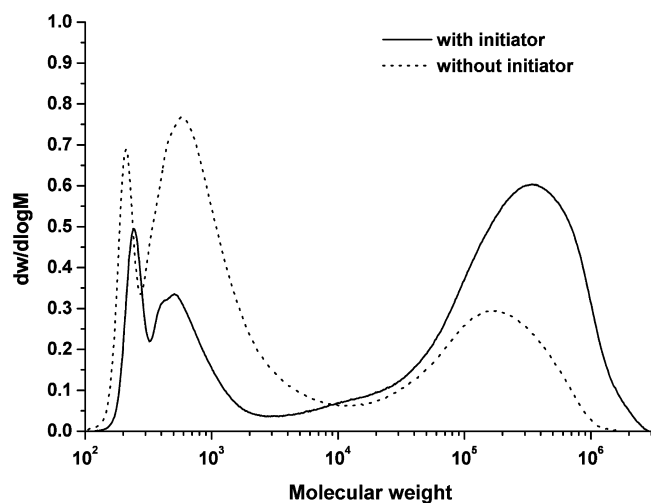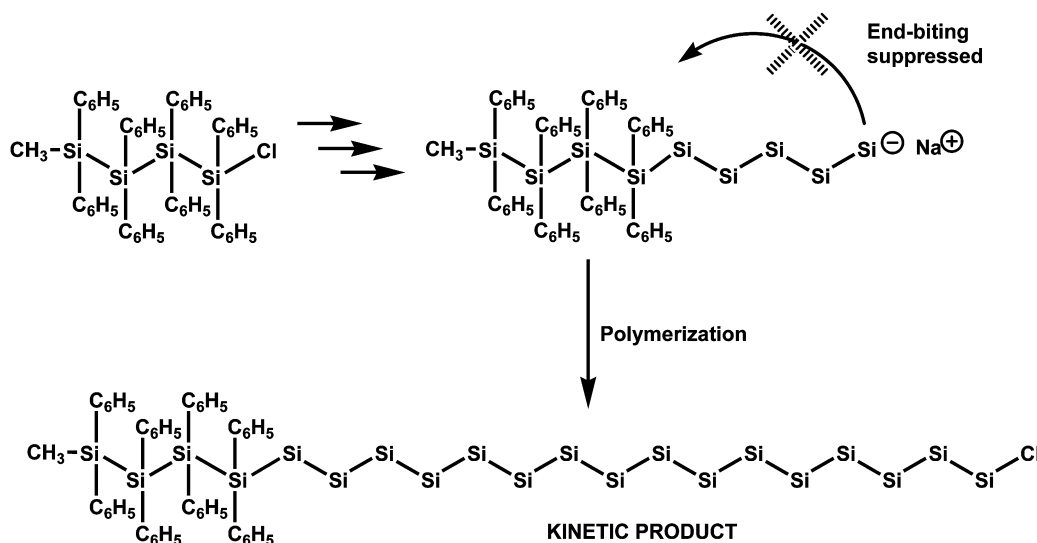

Fig. 3. Molecular weight distributions of PMPS synthesised at 65 °C in toluene with the initiator 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (**1c**) and without (**2c**).

Scheme 3.

ate effect of the presence of a monochloro-oligosilane was to inhibit end-biting as illustrated in Scheme 3.

We have chosen the word initiator for the behaviour of the oligosilane carefully. Were the 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane simply acting as an end-capping agent in a chain growth polymerisation then we would expect the molecular weight distributions and parameters to be substantially different from those observed. A likely result would be a broad continuous distribution of molecular weights from low to high molecular weights (albeit with noticeable peak ascribable to cyclic material still). This has been observed for numerous anionic chain growth polymerisation processes [29] and this is not the case here. Though this is a simplistic expectation in some ways (since it does not take into account back-biting), were the compound acting as an end-capping agent significant differences would certainly be expected in the THF reaction (Section 3.2). Crucially the increased yields in polymeric product from reactions **1a**–**1d** would not be expected from an end-capping action on the part of the oligosilane. Consequently we prefer to use the term initiator rather than additive (which is used to represent other agents in the Wurtz-type polymerisation such as crown ethers and ethyl acetate [10–12,17–19]) or promoter (as used by Matyjaszewski et al. [11]). Admittedly the silane has not been conclusively demonstrated to form the starting end of the polymer chains and future studies will endeavour to prove that this is so.

A sample of the crude PMPS prepared with the initiator was fractionated by repeated precipitation into methanol, hexane and then acetonitrile from THF to remove cyclic material and isolate the high molecular weight fraction exclusively (the molecular weight distribution and molecular weight parameters of the resultant polymer are given in Fig. 4a). ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy were performed on the resulting polymer in an attempt to identify

the presence of the oligomer in the linear PMPS. Analysis of the ^{1}H and ^{13}C NMR spectra showed no significant differences from spectra obtained for normal samples of PMPS. This was not unexpected given that the peaks from the 1-chloro-4-methyloctaphenyltetrasilane all coincide with the broad peaks arising from the methyl and aryl groups of the PMPS (^{1}H and ^{13}C NMR of the oligosilane and the PMPS are given in supporting information). The ^{29}Si spectrum of 1-chloro-4-methyloctaphenyltetrasilane is given in Fig. 4b along with assignments. For the PMPS synthesised using the oligosilane initiator the peak in the ^{29}Si NMR arising from the –SiPh$_2$Cl (at 2.47 ppm) was no longer evident and new peaks were observed at −20.95 ppm, −27.24 ppm and −30.92 ppm (Fig. 4c). The signal at −20.95 ppm most likely corresponds to the –SiPh$_2$CH$_3$ end-group, however given that this is also the region where −[PhMeSiO]– resonances occur this assignment is tentative. The signals at −27.24 ppm and −30.92 ppm are tentatively assigned to –SiPh$_2$ resonances. They occur in the region where signals have been previously reported for the Si resonances of polydiarylsilanes (−28.9 ppm to −34.4 ppm) and polydiphenysilane copolymers (−29.03 ppm to −36.78 ppm) [30,31]. However, they are significantly shifted from the signals observed in the spectrum of the oligosilane. Such signals are not observed in standard PMPS ^{29}Si NMR spectra however [32]. This is strong supporting evidence for the incorporation of the methyloctaphenyltetrasilane in the PMPS (presumably at the end of the polymer chain). The ^{29}Si NMR spectrum for the samples is shown in Fig. 4c (^{1}H NMR and ^{13}CNMR spectra are included in the Supporting Information).

3.2. Polymerisation in THF at room temperature

We have previously demonstrated that Wurtz-type polymerisations of DCMPS conducted in THF at room
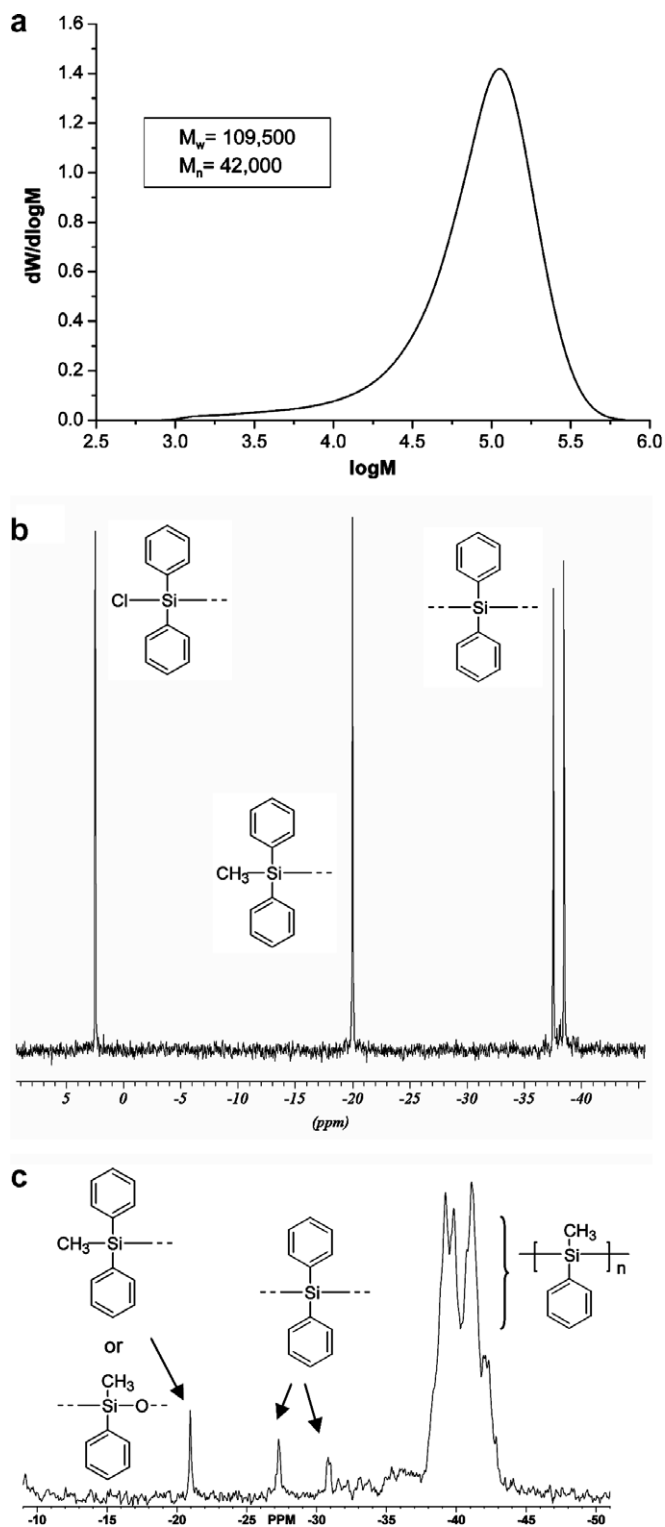
Fig. 4. (a) Molecular weight distribution of fractionated sample of PMPS synthesised at 65 °C in toluene with the initiator 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane. (b) ^{29}Si NMR spectrum of 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane. (c) ^{29}Si NMR spectrum of fractionated sample of PMPS synthesised at 65 °C in toluene with the initiator 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane.

Table 2
Yields and molecular weight characteristics of the crude PMPS polymers obtained from the Wurtz-reductive coupling polymerisation conducted in THF at room temperature in the absence and presence of [Cl(Ph$_4$Si)$_4$CH$_3$]; mole ratio of sodium:monomer = 2.2:1.0; mole ratio of dichloromethyl-phenylsilane:Cl(Ph$_4$Si)$_4$CH$_3$ = 1:1000

Exp. No.	Solvent	Cl(Ph$_4$Si)$_4$ CH$_3$	Yield (%)[a]	M_w	M_n	M_w/M_n
3a	THF	NO	50	28 800	3700	7.6
3b	THF	NO	49	30 500	4250	7.1
4	THF	YES	50	32 000	5240	6.1

[a] Determined gravimetrically after one precipitation with methanol.

decrease in end-biting and almost complete cessation of back-biting in comparison to propagation. To ascertain the effect of the initiator on this method, two polymerisations were conducted in THF at room temperature in the absence of initiator (**3a**, **3b**) and one polymerisation in the presence of initiator (**4**). For the two polymerisations without initiator the expected bimodal molecular weight distributions were obtained consisting only of the intermediate molecular weight material and the low molecular weight oligomers (Table 2 and Fig. 5). Yields were ∼50% and no high molecular weight polymer was obtained as expected (due to the increase in initiation rate compared to the propagation). The cyclic oligomers obtained in this polymerisation are due to the end-biting, since the back-biting reaction is temperature dependent and it has been demonstrated that it does not occur to any significant degree in the THF systems [26]. The yields of the PMPS in these reactions are lower than those previously observed for polymerisations in THF under similar conditions [22,23]. This is most likely due to the large surface area:volume ratio of the sodium employed. In the previous reports sodium dispersions made in the laboratory were used which had substantially larger particle sizes (determined by simple visual inspection) and hence lower surface area:volume ratios, than the fine commercial dispersions
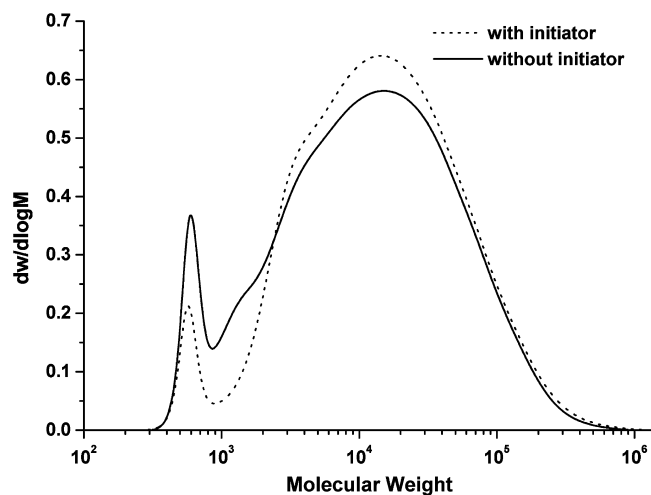

Fig. 5. Molecular weight distributions of PMPS synthesised at room temperature in tetrahydrofuran with the initiator 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane (**4**) and without (**3b**).

temperature give very high yields of PMPS (up to 80%) [22,23]. These high yields were attributable to a dramatic

employed in this study. Profound effects of sodium surface areas on Wurtz-type polymerisations have previously been observed by Worsfold and Trefonas et al. [33,34] and this current observation suggests that increased surface areas can have a detrimental effect on the yields from Wurtz-type polymerisations conducted at ambient temperatures in THF. When the polymerisation was conducted in THF in the presence of the initiator (**4**) almost identical results in terms of yield and molecular weight parameters (Table 2 and Fig. 4) were obtained to the reactions without initiator (**3a**, **3b**). This clearly indicates that the oligosilane is having no significant effect on the outcome of the polymerisation process in THF. This observation agrees with the proposed reaction model which has no significant role for end-biting termination processes in the Wurtz-type polymerisation of dichloromethylphenylsilane at room temperature in THF [9,22,23].

4. Conclusions

The use of 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane as an initiator in the Wurtz-type reductive coupling polymerisations of dichloromethylphenylsilane with sodium in toluene at 65 °C results in yields of almost double those obtained by otherwise identical reactions in the absence of the initiator. This is believed to be a result of the lower reduction potential of the oligosilane allowing it to compete efficiently in the initiation step with the dichloromethylphenylsilane monomer. Consequently a significant number of PMPS chains possess chain ends with no terminal chlorine and end-biting by the reaction of the silyl anion with the silicon–chloride in the early stages of the polymerisation is not possible. Even though no efforts were made to optimise the reaction conditions to maximise the effect of the initiator, clear and immediate benefits were immediately obvious from the incorporation of the initiator. The results of this study (in conjunction with an earlier observation by Matyjaszeski et al.) demonstrates that the use of monohalo-oligosilanes as initiators provides a promising route to increasing the yields of polysilanes under standard Wurtz-type polymerisation conditions at reduced temperatures. Whilst the previously commercially available 1-chloro-4-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane used in this study has unfortunately been discontinued, the use of other low reduction potential molecular species as initiators may have similar beneficial effects. A programme of research to investigate the use of simpler commercially available halo-silanes is planned.

Appendix A. Supplementary material

The ^{13}C and ^1H NMR spectra of the fractionated PMPS sample and 1-chloro-4-methyloctaphenyltetrasilane are available as supporting information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.022.

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