Room-Temperature, High-Yield Route to Poly(*n*-alkylmethylsilane)s and Poly(di-*n*-hexylsilane)

S. J. Holder,* M. Achilleos, and R. G. Jones

Functional Materials Group, School of Physical Sciences, University of Kent at Canterbury, Canterbury, Kent, CT2 7NH, U.K.

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ABSTRACT: The synthesis of poly(*n*-hexylmethylsilane) in crude yields from 50 to 83% and poly(di-*n*-hexylsilane) in crude yields from 67 to 82%, was accomplished by performing Wurtz-type reductive-coupling polymerizations of the corresponding dicholorodiorganosilanes in THF at room temperature. After purification, both polymers were obtained in isolated yields of greater than 50%, which are the highest achieved for such polysilanes to date. The general applicability of the synthetic procedure was also demonstrated by syntheses of poly(methyl-*n*-octylsilane) and poly(methyl-*n*-propylsilane) in good yields. The results indicate that the reductive coupling of dichlorodiorganosilanes in THF at room temperature offers not only greatly improved polymer yields but also provides a general route to polydiorganosilanes that is a considerable improvement on Wurtz-type syntheses carried out in toluene at 110 °C

Introduction

The Wurtz-type reductive coupling of dihalodiorganosilanes has been the primary method of synthesis of polysilanes for two decades.[1] Contemporary interest in polysilanes commenced in the late 1970s with the discoveries by Mazjyasni, West, and David and later in the 1980s by Trujillo, Wesson and Williams, and others of the synthesis of tractable polysilanes by the reduction of dichlorodiorganosilanes with molten sodium in toluene.[2] Studies of the reaction under a wide range of different conditions have facilitated an understanding of the mechanism of polymerization. Early studies by Ziegler et al.[3] led to a molecular mechanism first proposed by Gauthier and Worsfold[4] involving anionic, radical-anionic and radical intermediates formed in sequence. This mechanism was later expanded upon by Matyjesewzki[5] and is shown in Figure 1. Since then, our group has confirmed the consistency of the mechanism and provided an explanation for the ubiquitous polymodal molecular weight distributions of polysilanes synthesized using the Wurtz methodology.[6] Typically, three separate fractions are produced during the reaction: (I) a thermodynamically favored cyclic fraction (typically five or six monomer units) produced by end-biting and backbiting reactions of oligo- and polysilanes, respectively; (II) a polymeric fraction with an intermediate molecular weight ($\overline{DP}_n \approx 30-50$) determined by the termination of chain growth by a conformationally induced backbiting reaction; and (III) a kinetically driven polymeric fraction of a high molecular weight ($\overline{DP}_n \approx 1000-10\,000$) formed through uninterrupted chain growth and some subsequent condensation reactions.

Recently, a mathematical model (the kink−diffusion model) based on defect diffusion within a growing polysilane chain has been developed by McLeish et al. which predicts the polymodal distributions that result from the Wurtz-type reductive coupling of dichloromethylphenylsilane.[7] The kink−diffusion mechanism predicts (and it has been experimentally observed) that raising the reaction temperature of any Wurtz reductive-coupling polymerization results in an increase in

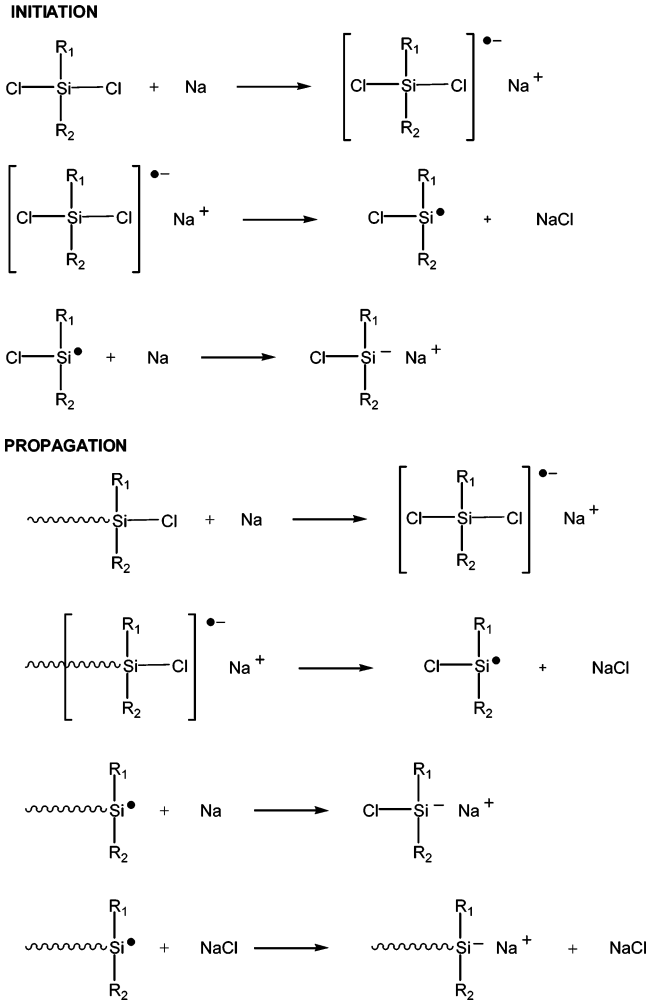

Figure 1. The molecular mechanism of the Wurtz reductive-coupling polymerization of dichlorodiorganosilanes as proposed by Gauthier and Worsfold[4] and expanded upon by Matyjaszewski et al.[5]

* Author to whom correspondence should be addressed. E-mail: S.J.Holder@kent.ac.uk.

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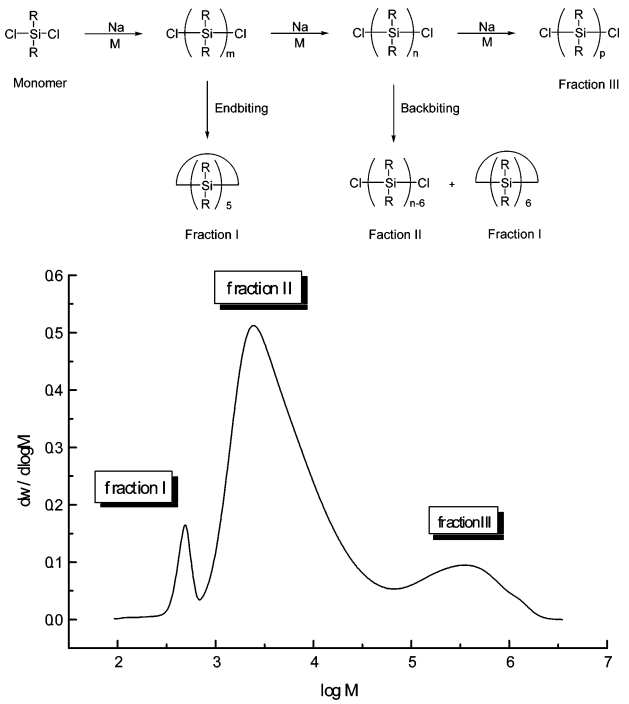

Figure 2. A representation of polymerization by Wurtz-type reductive coupling of dichlorodiorganosilanes illustrating the termination steps and a typical molecular-weight distribution showing the resultant molecular-weight fractions.

termination due to backbiting.[1,8a] This is accompanied by a decrease in termination due to end biting. Consequently, an increase in the intermediate molecular weight fraction (fraction II above) is observed at higher temperatures. In contrast, at lower temperatures, the end-biting reaction predominates, reducing the probability of the growth of the linear chain. However, little intermediate molecular weight polymer is observed as termination by backbiting is suppressed. These effects are easily seen by comparing the reductive coupling of dichloromethylphenylsilane in toluene at various temperatures.[8] A diagrammatic representation of the reactions taking place during the polymerization and a typical molecular weight distribution are shown in Figure 2. The effect of carrying out the reaction in a polar solvent, such as THF or diethyl ether/15-crown-5, at low temperatures promotes a happy medium between the extremes of backbiting and end biting.[6] The silyl anions are stabilized by complexation of the sodium counteranion by the polar solvent, and as a result, the linear chain growth is driven forward to the end product. The growth is promoted due to the reduction in cumulative energy, and consequently time, needed to effect the two-step electron transfer involved in reducing the silicon chloride to the silyl anion.[5b] While this mimics the effect of increasing the reaction temperature of the reaction in a nonpolar solvent, the reduced probability of the end-biting termination reaction is due to the low temperature. The intermediate molecular weight fraction is the major, if not the sole, product. It is a linear product, the formation of which is kinetically driven, and because of a decrease in the rate of propagation relative to initiation, very high molecular weights are not obtained. Thus, increasing the polarity of the solvent facilitates the synthesis of high yields of medium molecular weight polysilanes at room temperature.

As a consequence of this understanding of the Wurtz-type reductive-coupling polymerization, we have demonstrated that polymethylphenylsilane (PMPS) can be synthesized with crude yields as high as 80% at room temperature in THF.[6,8a] Prior to this, typical yields of PMPS obtained from the reaction with molten sodium in toluene under standard Wurtz conditions were less than 50%. PMPS is among the most studied of the polysilanes, which is in part due to the relative cheapness of its precursor, dichloromethylphenylsilane, but it is also due to the reactivity of dichlorodiorganosilanes with aromatic substituents. The aromatic ring stabilizes the silyl anion, thereby lowering the reduction potential of such precursors relative to the reduction potentials of those with nonaromatic substituents.[5b] The reactions are faster, and substantial amounts of polymer (fractions II and III of Figure 2) are formed. However, dichlorodialkylsilanes do not possess aromatic groups, so their anions are not stabilized by an aromatic interaction. As a consequence, the polymerizations are slower, end biting is more probable because of the extended lifetime of Si_5 chains, and most of the product is the thermodynamically favored cyclopentasilane.[9] Under the usual Wurtz-type reductive-coupling conditions in which the reaction is carried out in refluxing toluene, the maximum crude yields of poly(*n*-hexylmethylsilane) (PHMS) and poly(di-*n*-hexylsilane) (PDHS) that have been recorded are 15% and 37%, respectively.[8b] In this paper, we present results showing that high crude yields (>60%) and isolated yields (>50%) of PHMS, PDHS, and other poly(dialkylsilanes) can be obtained from Wurtz-type polymerizations carried out in THF at room temperature.

Experimental Section

Materials. THF was dried for at least 24 h over anhydrous magnesium sulfate and then for at least 24 h over sodium wire before distillation over sodium wire and benzophenone under nitrogen immediately prior to use. Dichloro-*n*-hexylmethylsilane (Gelest), dichloromethyl-*n*-octylsilane (Gelest), dichlorodi-*n*-hexylsilane (Fluorochem), and dichloromethyl-*n*-propylsilane (Fluorochem) were distilled under reduced pressure and stored at 4 °C under nitrogen. Methanol (99.99% Fisher) was used as received. Sodium (Lancaster, 99%) was stored under paraffin oil and before use was cut and washed under freshly distilled toluene. Sodium dispersions were prepared immediately prior to use by heating the freshly cut metal in distilled toluene under reflux conditions before dispersing it into a fine sand using a homogenizer (Ultra Turax T8, homogenizer, IKA Labortechnik). The toluene was removed under vacuum. All glassware was flamed-dried under vacuum prior to use.

Analyses. NMR spectra were recorded in $CDCl_3$ at 30 °C using a JEOL GX-270 spectrometer. UV−vis spectra were recorded in THF (1.2×10^{-4} mol Si-unit dm^{-3} for PHMS, PMPrS, and PMOS solutions and 9.5×10^{-5} mol Si-unit dm^{-3} for PDHS solutions) using a Helios β Unicam UV spectrometer. IR spectra were recorded from cast thin films on KBr disks using an Avatar 360 FTIR spectrometer. Molecular weights of the polymers were determined at 40 °C as linear polystyrene equivalents in THF solution using size exclusion chromatographic (SEC) equipment supplied by Polymer Laboratories Ltd. consisting of a bank of two 300 mm × 7.5 mm PLgel mixed-C columns, an LC 1120 HPLC pump, and a Shodex RI-101 refractive index detector.

Synthesis of Poly(*n*-hexylmethylsilane) (PHMS) (Reactions 1−5). To a two-necked round-bottom flask (250 mL) equipped with an egg-shaped PTFE stirring bar and a condenser, freshly cut sodium metal (2.4 g, 0.1 mol) was added under a nitrogen atmosphere using Schlenk-line techniques. The sodium was transformed to a fine dispersion as outlined above. THF (60 mL) and dichloro-*n*-hexylmethylsilane (9.93 g, 0.05 mol) were added via a syringe. The reaction mixture

was then stirred rapidly at room temperature for 22 h. Termination was achieved by the slow addition of an excess of methanol to ensure complete quenching (>100 mL). The methanol was removed, and water (100 mL) was added to dissolve all the NaCl coproduct. The polymer was then dissolved in excess toluene (reactions 2−5) or dichloromethane (reaction 1), and after rapid stirring, the mixture was placed in a separating funnel. After rapid shaking with water, the two layers were separated. The solvent layer was kept and the aqueous layer was washed 3−4 times with the organic solvent to dissolve any polymer traces left in the water. The solvent extracts were combined, dried for 2 h over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. Removal of the cyclosilane fraction was achieved through repeated precipitations in which a THF solution of the crude polymer was slowly added slowly dropwise to rapidly stirred propan-2-ol (40 mL × 2). Molecular weight parameters were determined by SEC, and the samples were otherwise characterized by IR, UV−vis, ^{1}H, and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$, ppm) δ: 0.06−0.39 (Si−**CH_3**), 0.60−1.04 (Si−**CH_2**−) and (−CH_2−**CH_3**), 1.09−1.66 (−**CH_2**−**CH_2**−**CH_2**−**CH_2**−CH_3). ^{13}C NMR for PHMS ($CDCl_3$, ppm) δ: −4 (Si−**CH_3**), 14.5 (Si−**CH_2**), 15.5 (−CH_2−**CH_3**), 23 (−**CH_2**−CH_3), 27.3 (Si−CH_2−**CH_2**−), 32 (−**CH_2**−CH_2−CH_3), 34.4 (Si−CH_2−CH_2−**CH_2**−). IR Spectra of PHMS (cm^{-1}): 2963−2846 (C−H stretching), 1468 (C−H bending), 668 (Si−C stretching), 746 (Si−CH stretching). UV−vis: λ_{max} = 305 nm, ϵ_{max} = 12 500 cm^{-1} dm^3 mol^{-1}.

Sampling during PHMS Syntheses (Reactions 6−8). A similar procedure to that outlined above was followed. Samples (2 mL) of the reaction mixture were removed by syringe and added to methanol (8 mL) every 40 min over the first 160 min and then at 20, 22, 24, and 48 h after the addition of the monomer to the sodium dispersion. The methanol was then removed in vacuo, and water (8 mL) was added to remove NaCl. The samples were washed again with methanol (2 × 8 mL) and then dried under vacuum at 40 °C. The isolated samples were weighed and analyzed by SEC.

Synthesis of Poly(di-*n*-hexylsilane) (PDHS) (Reactions 9−12). To a two-necked round-bottom flask (50 mL) equipped with an egg-shaped PTFE stirring bar and a condenser, freshly cut sodium metal (0.828 g, 0.036 mol) was added under a nitrogen atmosphere using Schlenk-line techniques. The sodium was transformed to a fine dispersion as outlined above. To the sodium dispersion, THF (20 mL) followed by dichlorodi-*n*-hexylsilane (4.81 g, 0.018 mol) was added via a syringe. The reaction was then stirred rapidly at room temperature for 22 h. Termination was achieved by the slow addition of methanol followed by the addition of excess methanol (>100 mL). The polymer precipitate was filtered, rinsed with water and then methanol, and then dried under vacuum at 40 °C. Removal of the cyclosilane fraction was achieved through repeated precipitations in which a THF solution of the crude polymer was slowly added slowly dropwise to rapidly stirred propan-2-ol (40 mL × 2). Molecular weight parameters were determined by SEC, and the samples were otherwise characterized by IR, UV−vis, ^{1}H, and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$, ppm) δ: 0.69−1.13 (Si−**CH_2**) and (−CH_2−**CH_3**), 1.13−1.68 (−**CH_2**−**CH_2**−**CH_2**−**CH_2**−CH_3). ^{13}C NMR (CDCl3, ppm) δ: 14.5 (Si-**CH_2**), 15.5 (−CH_2−**CH_3**), 23 (−**CH_2**−CH_3), 28 (Si−CH_2−**CH_2**−), 32.3 (−**CH_2**−CH_2−CH_3), 35 (Si−CH_2−CH_2−**CH_2**-). IR (KBr, thin film, cm^{-1}): 2952−2857 (C−H stretching), 1470 (C−H bending), 660 (Si−C stretching), 724 (Si−CH stretching). UV−vis: λ_{max} = 315 nm, ϵ_{max} = 21 000 cm^{-1} dm^3 mol^{-1}.

Synthesis of Poly(methyl-*n*-propylsilane) (PMPrS) (Reactions 13−14). To a two-necked round-bottomed flask (100 mL) equipped with an egg-shaped PTFE stirring bar and a condenser, freshly cut sodium metal (1.48 g, 0.064 mol) was added under nitrogen atmosphere using Schlenk-line techniques. The sodium was transformed into a fine dispersion as outlined above. To the sodium dispersion, THF (40 mL) followed by dichloromethy-*n*-propylsilane (5.1 g, 0.032 mol) was added via a syringe. The reaction was then stirred at room temperature for 22 h. Termination was achieved by the slow addition of methanol followed by the addition of excess methanol (>100 mL). The polymer precipitate was filtered, rinsed with water and then methanol, and then dried under vacuum at 20 °C. Removal of the cyclosilane fraction was achieved through repeated precipitations in which a THF solution of the crude polymer was slowly added dropwise to rapidly stirred ethanol (40 mL × 2). Molecular weight parameters were determined by SEC, and the samples were otherwise characterized by IR, UV−vis, ^{1}H, and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$, ppm) δ: 0.06−0.36 (Si−**CH_3**), 0.65−1.13 (Si−**CH_2**− and −CH_2−**CH_3**), 1.25−1.63 (−**CH_2**−CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: −4 (Si−**CH_3**), 15 (Si−**CH_2**−), 16.5 (−CH_2−**CH_3**), 23 (−**CH_2**−CH_3). IR (KBr, thin film, cm^{-1}): 2950−2862 (C−H stretching), 1455 (C−H bending), 750 (Si−CH stretching), 665 (Si−C stretching). UV−vis: λ_{max} = 306 nm, ϵ = 5242 cm^{-1} dm^3 mol^{-1}

Synthesis of Poly(methyl-*n*-octylsilane) (PMOS) (Reaction 15−16). PMOS was synthesized by an identical procedure to that described for the synthesis of PDHS (reactions 2−5) using freshly cut sodium metal (1 g, 0.042 mol), THF (25 mL), and dichloromethyl-*n*-octylsilane (4.87 g, 0.021 mol). Molecular weight parameters were determined by SEC, and the samples were otherwise characterized by IR, UV−vis, ^{1}H, and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$, ppm) δ: 0.15−0.34 (Si−**CH_3**), 0.73−0.98 (Si−**CH_2**−) and (−CH_2−**CH_3**), 1.14−1.47 (Si−CH_2−**CH_2**−**CH_2**−**CH_2**−**CH_2**−**CH_2**−CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: −4 (Si−**CH_3**), 14.6 (Si−**CH_2**−), 15.6 (−CH_2−**CH_3**), 23.2 (−**CH_2**−CH_3), 27.5 (Si−CH_2−**CH_2**−), 29.9 ((Si−CH_2−CH_2−**CH_2**−), 31.3 (Si−CH_2−CH_2−CH_2−**CH_2**−), 32.4 (−**CH_2**−CH_2−CH_3), 34.7 (−**CH_2**−CH_2−CH_2−CH_3). IR (KBr, thin film, cm^{-1}): 2921−2851 (C−H stretching), 1462 (C−H bending), 747 (Si−CH stretching), 667 (Si−C stretching).). UV−vis: λ_{max} = 304 nm, ϵ = 5658 cm^{-1} dm^3 mol^{-1}

Table 1. Yields and Molecular-Weight Characteristics of the Crude Polymers Obtained from the Wurtz Reductive-Coupling Polymerization of 0.714 mol dm^{-3} DCHMS at 22 °C in THF

reaction	crude yield (%)	M_n	M_w	M_w/M_n
1	50	850	7100	8.5
2	67	1100	5200	4.6
3	83	1650	14 200	8.6
4	60	1450	7900	5.4
5	70	1290	14 000	10.8

Results and Discussion

Synthesis of Poly(*n*-hexylmethylsilane). Kinetic Analysis and Concentration Effects. A number of syntheses of PHMS were performed using different concentrations of dichloro-*n*-hexylmethylsilane (DCHMS). The molecular weight parameters of five crude samples of PHMS synthesized using a DCHMS concentration of 0.714 mol dm^{-3} are given in Table 1. Generally, the reactions were very slow with maximum yields being reached only after 22 h. As with the polymerization of dichloromethylphenylsilane (DCMPS), an induction period of 0.5−2 h was often noticed after which the mixture gradually acquired the deep blue color characteristic of the Wurtz reaction.[10] Unlike the polymerization of DCMPS, however, the mixture did not heat up dramatically and only a slight warming of the mixture and vessel could be detected, almost certainly a consequence of the dramatically reduced rate of propagation

The reactions were terminated by precipitation in methanol and washing with water (to remove NaCl byproduct). After optimization of the purification procedure (reactions 2−4 in Table 1), high yields of crude PHMS (>60%) were obtained for high-concentration (0.714 mol dm^{-3}) reactions, a maximum yield of 83% being recorded in one instance. Such high yields of

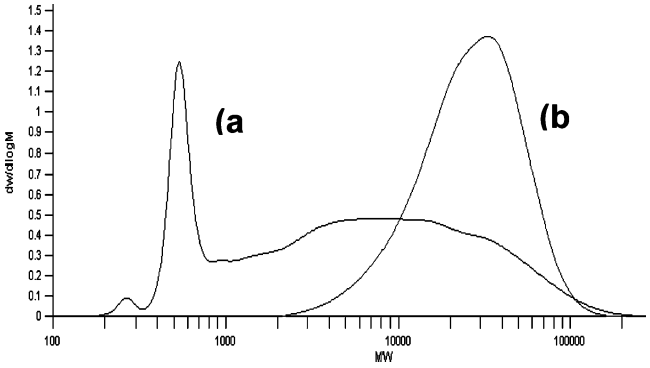

Figure 3. Molecular-weight distributions for the (a) crude and (b) purified products of a Wurtz-type reductive coupling of dichloro-*n*-hexylmethylsilane in THF at 22 °C.

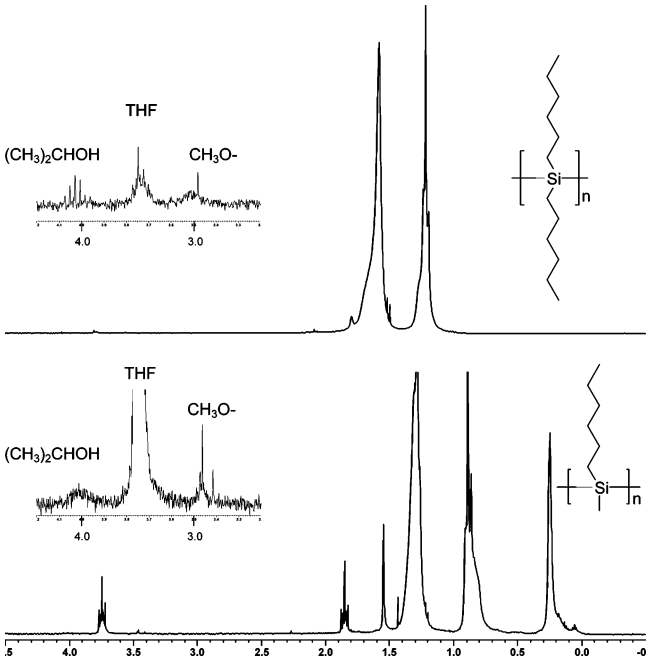

Figure 4. ^{1}H NMR spectra of poly(*n*-hexylmethylsilane) and poly(di-*n*-hexylsilane) synthesized using a sodium dispersion in THF at 22 °C. Spectra recorded at 30 °C in $CDCl_3$.

PHMS, and poly(dialkylsilane)s in general, are exceptional for the Wurtz-type reductive coupling of dihalodiorganosilanes. The crude yields included significant portions of cyclosilanes, which were removed by the repeated precipitations in methanol and 2-propanol. Nevertheless, final yields were still in the range 52−61%. Typical molecular weight distributions of a crude and a purified sample are shown in Figure 3. The structure and purity of the resultant polymers was demonstrated by ^{1}H NMR and ^{13}C NMR spectroscopic analysis (an ^{1}H NMR spectrum is illustrated in Figure 4). UV−vis spectroscopic analysis of PHMS revealed a broad absorption with a λ_{max} of 305 nm, consistent with an uninterrupted Si chain conjugation length greater than 30 Si atoms.[6]

On reducing the concentration of DCHMS from 0.714 to 0.350 mol dm^{-3} in the reaction mixtures, a decrease in crude yield from 60−82% to 55% was observed. Further reducing the concentration to 0.175 mol dm^{-3} led to a maximum crude yield of only 23%. Surprisingly, few, if any, studies appear to have been made of the effect of concentration on Wurtz-type reductive-coupling polymerizations. Matyjaszewski reported relatively little

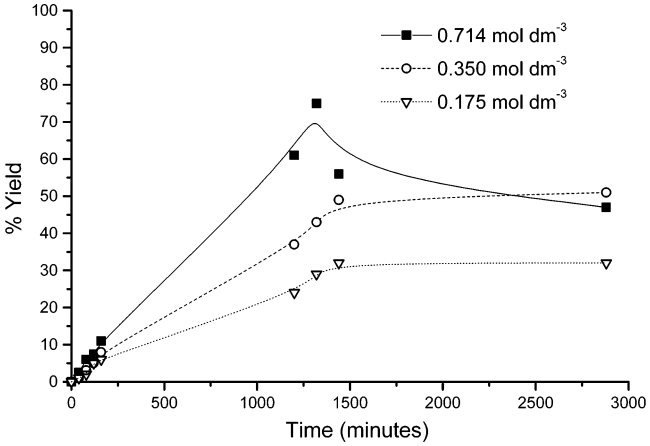

Figure 5. Plots of the variation with time of the crude yields of poly(*n*-hexylmethylsilane) synthesized using a sodium dispersion in THF at 22 °C at three different monomer concentrations.

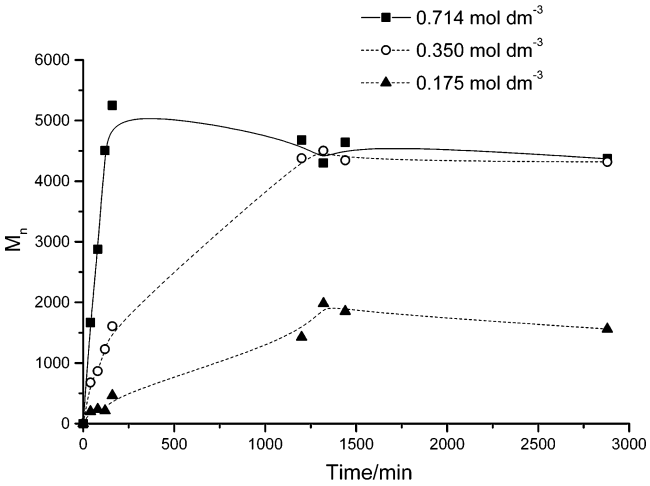

Figure 6. Plots of the variations with time of the number-average molecular weight of poly(*n*-hexylmethylsilane)s synthesized using a sodium dispersion in THF at 22 °C at three different monomer concentrations.

effect upon molecular weight parameters or yields upon reducing the monomer concentration when conducting Wurtz reductive-coupling polymerizations in the presence of ultrasound,[5b] but full data supporting these observations was not supplied. Generally, the reduced monomer concentration will reduce the propagation rate ($R_p \propto [M]$) and the competitive end-biting reaction will increasingly dominate [The probability of end biting remains constant at given temperature (it is independent of concentration), whereas the propagation rate decreases with concentration.] (see Figure 2), leading to an increased proportion of cyclosilanes in the crude product.

Sampling of the PHMS syntheses was performed at various times for reactions at various concentrations, and the plots of the variation of yield and molecular weight parameters ($\overline{M}_n$ and $\overline{M}_w$) with time for the product samples (molecular weights > 1000)[10] are shown in Figures 5, 6, and 7, respectively. It is apparent that yields and molecular weights increase with time in the early stages of the reaction, as would be expected for a predominantly chain-growth polymerization. Figure 8 shows an expansion of the low-conversion regions of the plots of $\overline{M}_n$ vs time shown in Figure 6, and the

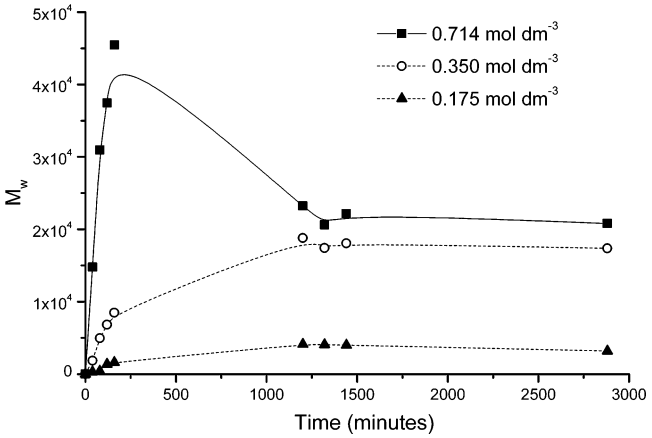

Figure 7. Plots of the variations with time of the weight-average molecular weight of poly(*n*-hexylmethylsilane)s synthesized using a sodium dispersion in THF at 22 °C at three different monomer concentrations.

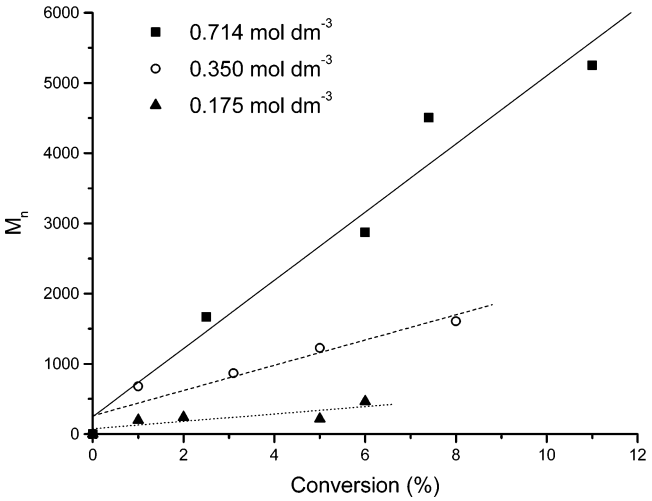

Figure 8. Plots of the variation in the number-average molecular weight with conversion for the synthesis of poly(*n*-hexylmethylsilane) using sodium dispersion in THF at 22 °C at three different monomer concentrations

linearity is remarkable. Linear increases of $\overline{M}_n$, $\overline{M}_w$, and yield with time had previously been observed for the synthesis of PMPS in THF at room temperature.[6]

It is noticeable that, despite the differences in concentration and, consequently, in the relative rates of the reactions, the polymer yields and molecular weights have all reached their maximum values after about 20 h, after which they either level off or decrease. Figure 9 depicts the variations of $\overline{M}_n$ and crude yield with time for the polymerization at the highest concentration of dichloro-*n*-hexylmethylsilane. $\overline{M}_n$ attains a maximum value even while the crude yield continues to increase. This is consistent with the probability of termination by backbiting being the limiting factor of chain-growth in all Wurtz-type reductive-coupling polymerizations as required by the 'kink−diffusion' model of McLeish et al.[7] It should be noted that the purification procedures followed for the isolation of the crude products from the 'synthetic reactions' (reactions 1−5) differed from those of the 'sampling reactions' (reactions 6−8). After precipitation from methanol and washing with water (to remove NaCl), the samples were washed twice more with methanol. This resulted in the further fractionation of the samples and the removal of an

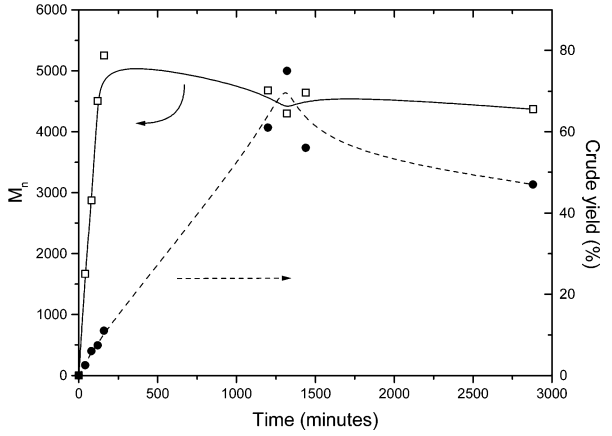

Figure 9. Plot of M_n and crude yield with time for the reductive coupling of dichloro-*n*-hexylmethylsilane with a sodium dispersion in THF at 22 °C.

increased fraction of the cyclics. Consequently, the $\overline{M}_n$ and $\overline{M}_w$values for the crude polymers (Tables 1 and 2) and those from the kinetic analyses (Figures 6−9) differ. In contrast to the sampled reactions, for which the linear portion was of primary interest, the molecular weight parameters reported for the crude polymers include a larger proportion of Fraction I (predominantly cyclic) material which leads to the low $\overline{M}_n$ values observed. The limiting value of $\overline{M}_n \approx 4000-5000$ corresponding to a $\overline{DP}_n \approx 31-39$ is within the range of 30−40 units observed for the average conjugation length of many polysilanes.[12a] This has been proposed as the average separation length of the helix reversals that constitute the 'kinks' of the model. It is the diffusion of the first of these to the alkali metal surface that leads to disengagement of the growing chain and the conformation favorable for backbiting, i.e., termination of growth. However, this limiting value of ~4000−5000 is based on molecular-weight measurements and calculations that include the cyclic fraction (<1000). It is therefore highly qualitative, and a more exact limiting value for the polymer chains remains elusive. For instance, when molecular-weight parameters are calculated setting 1000 as the lower molecular weight limit (thereby excluding the cyclic fractions), the limiting $\overline{M}_n$ value is ~8000 (an example of the plots of $\overline{M}_n$with time for such analyses are given in Figure A in the Supporting Information).

Contrasting with only a slight decrease in $\overline{M}_n$ after it has attained its maximum value, there is a significant decrease in $\overline{M}_w$, as evidenced in Figure 7. A small but significant portion amount of relatively high-molecular-weight material is formed in the very early stages of the polymerization conducted with the highest concentration of DCHMS (0.714 mol dm^{-3}) (see Figure B in the Supporting Information for a representative overlay of the molecular-weight distribution curves). The yield, and consequently monomer conversion, corresponding to this material is less than 10% of the theoretical yield (Figure 5). The decrease in the $\overline{M}_w$ values over the subsequent time period is therefore most likely a statistical side-effect of the subsequent growth of the majority of chains (whose size is limited by kink−diffusion termination). Essentially, this small high-molecular-weight fraction is subsumed in the bulk of material of a lower molecular weight and the $\overline{M}_w$

Table 2. Yields and Molecular-Weight Characteristics of Crude and Isolated Polymers Obtained from the Wurtz Reductive-Coupling Polymerization of 0.714 mol dm^{-3} Dichloro-*n*-hexylmethylsilane (DCHMS), Dichloro-di-*n*-hexylsilane (DCDHS), Dichloromethyl-*n*-propylsilane (DCMPrS), and Dichloromethyl-*n*-octylsilane (DCMOS) at 22 °C in THF

reaction	monomer	crude yield (%)[a]	M_n[a]	M_w[a]	M_w/M_n[a]	isolated yield (%)[b]	M_n[b]	M_w	M_w/M_n
2	DCHMS	67	1100	5200	4.6	52	8700	17 700	2.0
3	DCHMS	82	1650	14 200	8.6	61	20 000	31 500	1.6
9	DCDHS	84	9250	29 500	3.2	58	44 900	60 500	1.4
10	DCDHS	65	2400	3150	1.3	53	17 200	42 800	2.5
13	DCMPrS	55	7950	20 600	2.6	40	13 700	33 900	2.5
14	DCMPrS	50	8450	29 350	3.5	38	9300	20 900	2.3
15	DCMOS	71	2400	27 250	11.3	54	11 550	41 200	3.6
16	DCMOS	86	1850	32 000	17.3	58	11 440	49 300	4.3

values are reduced accordingly. There is no evidence of degradation of the polymer chains during this time, though the possibility cannot be discounted entirely. [Chain scission and narrowing of the molecular-weight distribution has been observed for Wurtz-type syntheses of PMPS in diethyl ether containing 15-crown-5, and was attributed to solvated Na^+, Na^-/crown complex attacking preformed polymer chains.[1,8a] Degradation of the polymer chains has furthermore been observed for the reaction conducted in THF with an excess of sodium (a molar ratio of 3.5:1 Na to dichloro-*n*-hexylmethylsilane) over prolonged periods (in excess of 24 h). However, in these circumstances, degradation was accompanied by decreases in yield and $\overline{M}_n$.] The exact reason for this rapid growth of a high-molecular-weight fraction from polymerizations with high monomer concentrations is unclear at present. It may be that at the early stages of the polymerization the high concentration leads to a rate of polymerization substantially higher than the termination rate (which is determined by the rate of diffusion of the kink along the polymer chain). The matter is currently under further investigation.

Synthesis of Poly(di-*n*-hexylsilane). To further test the general applicability of this variation of the Wurtz reductive-coupling polymerization in the synthesis of polysilanes, a number of reactions were performed using dichlorodi-*n*-hexylsilane. PDHS has been one of the most investigated of the polysilanes due to its' thermochromic behavior.[11] However, yields of PDHS from the Wurtz polymerization have been notoriously low.[8b,12] The experimental conditions and results from a number of polymerizations of dichlorodi-*n*-hexylsilane in THF at room temperature are given in Table 2.

In all cases, the crude yields were 50% or higher and reach 84% in one instance. The variations in crude yield and molecular-weight parameters for apparently identical reactions are attributable to differences in the surface areas of the sodium dispersions. The preparations of the sodium 'sands' used in these polymerizations were in accordance with a set procedure and were only qualitatively controlled (i.e., no attempts were made to measure particle size or degree of coagulation). Worsfold has previously reported the effect of sodium surface areas on the induction times, rates of reaction, and molecular weights of PHMS synthesized in toluene at reflux.[13] When smaller surface area sodium dispersions were employed, the rate of monomer consumption and the yield of linear polymer both decreased. It is thus likely that the relatively 'low' yields observed for some of the reactions of the present work can be attributed to relatively poor sodium dispersions. Further experiments are underway utilizing commercially available dispersions to ensure a degree of reproducibility. Irrespective, it is apparent that this reaction can give very high yields of PDHS, as well as PHMS. Upon repeated precipitation from propan-2-ol to remove the cyclic fraction, the yields of isolated linear PDHS were as high as 58%. Recently the application of the room-temperature reaction in THF under the application of ultrasound has been reported to us indicating that these yields can be further optimized.[14]

Synthesis of Poly(*n*-alkylmethylsilane)s. The procedure was also applied to the synthesis of poly(methyl-*n*-propylsilane) (PMPrS) for which crude yields of 50 and 55% were obtained (40 and 38% isolated yields of isolated polymers were obtained after fractional precipitation). These are greater than yields reported in the literature for PMPrS,[12d,e] with only the use of 18-crown-6 in toluene at reflux providing comparable yields.[12f] However, more generally, it has been observed that the yields of short-alkyl-chain polysilanes are significantly lower than those for with longer alkyl chains. Consistent with these observations, the synthesis of poly(methyl-*n*-octylsilane) in THF at room temperature gave high crude (71 and 86%) and isolated (54 and 58%) yields.[15] The results for all polysilanes synthesized are summarized in Table 2.

Conclusions

The synthesis of poly(*n*-hexylmethylsilane) in crude yields from 50 to 83% was accomplished by performing a Wurtz-type reductive-coupling polymerization in THF at room temperature. Optimization of the reaction and the purification procedure allowed for its ready synthesis in isolated yields as high as 61%. Rate studies demonstrated a linear chain growth for low conversions and a limiting number-average molecular weight corresponding to the chain length at which the maximum probability of termination by backbiting occurs.

Under identical reaction conditions, poly(di-*n*-hexylsilane) was synthesized in crude yields from 65 to 84% and isolated yields up to 58%. High yields of poly(methyl-*n*-propylsilane) and poly(methyl-*n*-octylsilane) were also obtained. The synthesis of polysilanes has now been demonstrated for both dialkyl- and alkylphenyl-substituted systems at room temperature in THF, indicating that this is a general method for the synthesis of polysilanes in high yield under considerably more amenable reaction conditions than those reported to date.

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Supporting Information Available: Plots of number-average molecular weight and overlay of molecular-weight distribution curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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