

Nickel indenyl complexes as precatalysts for dehydropolymerization of phenylsilane

Frédéric-Georges Fontaine, Talin Kadkhodazadeh and Davit Zargarian*

Département de Chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

The complex (1-MeInd)Ni(PPh₃)Cl reacts with AgBF₄, AlCl₃, methylaluminoxane, or LiAlH₄ to produce intermediates which catalyze the dehydropolymerization of PhSiH₃.

Polysilanes have attracted a great deal of interest in recent years primarily because of their potential applications in optoelectric devices and as precursors to silicon carbide ceramics.¹ The initial discovery of transition metal-catalyzed dehydropolymerization of silanes² and the subsequent development of a class of efficient catalysts for this reaction³ have shown that this approach holds great promise as a viable method for preparing high molecular mass polysilanes. Some of the best systems reported to date are derivatives of group 4 metallocenes which polymerize primary aromatic silanes to yield linear polysilanes with M_n on the order of 7000 (about 100 monomers), in addition to cyclic oligomers.⁴ Most late metal complexes, on the other hand, redistribute silanes or couple them to give oligomers only (dimers, trimers, etc.);⁵ notable exceptions are some complexes of platinum metals which polymerize aliphatic silanes⁶ and cyclic silanes such as silicon-bridged ferrocenophanes⁷ and silafluorene.⁶ In the course of our studies on the complexes (Ind)Ni(PPh₃)X (Ind = indenyl, 1-methylindenyl; X = Cl, Br, Me)⁸ and [(Ind)Ni(PPh₃)L']⁺ (L' = PPh₃, PMe₃, MeCN)⁹ we have found the first example of a late metal compound capable of catalysing the polymerization of PhSiH₃ to linear chains containing about 30–80 monomeric units, as described below.

Although PhSiH₃ does not react with (1-MeInd)Ni(PPh₃)Cl, **1**, addition of AgBF₄ to their mixture caused an immediate colour change (wine-red to black) and a vigorous evolution of gas (presumably H₂). The work-up† of the reaction mixture after 24 h gave an oily white solid which showed a ¹H NMR spectrum typical§ of poly(phenylsilylene); GPC¶ analysis showed that this material contained (PhHSi)_n with $M_w = 2017$ and $M_n = 1469$ (Table 1, run 1). Using AlCl₃ as initiator gave shorter oligomers|| (run 2) while methylaluminoxane (MAO) gave comparable results to AgBF₄ (run 3). The higher solubility of MAO allows the reactions to be carried out at lower

temperatures or in toluene, both of which give improved results (runs 4 and 5).

The formation of Si–Si bonds is rapid at the outset of the reaction but slows down considerably after about 30 min, such that the build-up of higher chains (M_n ca. 2000–3000) takes several hours. Extending the reaction time to 7 days results in significantly higher molecular mass polyphenylsilanes for reactions carried out in CH₂Cl₂ (run 3 vs. run 6), but is not advantageous for reactions carried out in toluene (run 5 vs. run 7). This difference may be related to the higher solubility and/or stability of the catalytically active species (presumably a cation) in CH₂Cl₂ as compared to toluene.** This feature differentiates the present nickel complexes from some of the group 4 metallocene-based catalysts which decompose in chlorinated solvents.^{4b}

The amount of solvent is also an important factor in the dehydropolymerization of silanes: the best results are normally obtained with very little or no solvent at all, which favours linear chain growth over the formation of cyclic oligomers.^{3b,4a} We found, however, that very concentrated solutions (about 4 M in silane) result in the formation of intractable polymers, implying perhaps a significant degree of cross-linking caused by the coupling of backbone Si–H groups. It appears, therefore, that dilute conditions are better for obtaining polysilanes in this Ni system.

The most likely candidates for the catalytically active species in our system are cationic Ni–H or Ni–SiR₃ species, but we have not succeeded in detecting or isolating any such intermediates. We have found, however, that complex **1** reacts with LiAlH₄ to give an intermediate (presumably a neutral Ni–H species)†† which can polymerize PhSiH₃ (run 8). These reactions are very sensitive to solvent polarity (run 9), temperature (run 10), and reaction time (run 11), probably reflecting the limited solubility of LiAlH₄. Since LiAlH₄ can initiate the polymerization of PhSiH₃ and is also used in its preparation from PhSiCl₃,¹⁰ we decided to explore the possibility of conducting these two steps consecutively in one pot. Thus, reacting PhSiCl₃ with an excess of LiAlH₄ and adding this mixture to a dilute Et₂O solution of

Table 1 Dehydropolymerization of PhSiH₃ with (1-MeInd)Ni(PPh₃)Cl^a

Run	Initiator	Solvent	[Ni]:init.:Si	t/d	10 ⁻³ M _w	10 ⁻³ M _n	M _w /M _n
1	AgBF ₄	CH ₂ Cl ₂	1:10:90	1	2.0	1.5	1.37
2	AlCl ₃	CH ₂ Cl ₂	1:9:90	1	1.3	0.6	2.13
3	MAO	CH ₂ Cl ₂	1:9:100	1	1.8	1.1	1.69
4	MAO	CH ₂ Cl ₂ (–40 °C)	1:9:100	1	4.4	2.5	1.80
5	MAO	Toluene	1:9:100	1	4.8	2.9	1.64
6	MAO	CH ₂ Cl ₂	1:9:100	7	7.1	5.9	1.20
7	MAO	Toluene	1:9:100	7	5.0	3.2	1.57
8	LiAlH ₄	CH ₂ Cl ₂	1:4:94	1	2.0	1.6	1.21
9	LiAlH ₄	Toluene	1:3:100	1	0.6	0.5	1.24
10	LiAlH ₄	CH ₂ Cl ₂ (–40 °C)	1:3:100	1	0.7	0.5	1.58
11	LiAlH ₄	CH ₂ Cl ₂	1:4:94	7	3.6	1.6	2.27

^a The initial concentration of PhSiH₃ was 0.15 M in all experiments; the yields were >90% in all cases except run 9 for which the yield was 35%.

1 produced the usual colour change accompanied by vigorous evolution of gas.†† The mixture of (PhHSi)_n obtained from this reaction was shown to have $M_w = 7565$ and $M_n = 1541$ ($M_w/M_n = 4.9$).

In conclusion, complex **1** reacts with cationic initiators or LiAlH₄ to form species which catalyze the dehydropolymerization of (PhSiH)_n with molecular masses and polydispersities comparable to those obtained from the best early metal systems.^{3,4} Some interesting features of this nickel system include no introduction period, good activity at ambient or lower temperatures, tolerance of chlorinated solvents, and relatively narrow polydispersities (e.g., run 6). Studies aimed at elucidating the mechanism of this reaction are in progress.

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Notes and References

† E-mail: zargarian.davit@umontreal.ca

‡ The work-up procedure consisted of passing a toluene solution of the reaction mixture, with or without pre-treatment with methanol, through a short column of Celite, followed by evaporation and analysis by ¹H NMR and GPC.

§ ¹H NMR spectra of (PhSiH)_n (CDCl₃, 300 MHz) contain Si–H resonances at δ ca. 3.7 for cyclic oligomers and broad signals centred around δ 5 for the linear polysilanes. These resonances appear ca. 1 ppm more downfield in C₆D₆.¹¹

¶ The molecular masses were determined with a Waters Associates 600E Chromatograph equipped with a refractive index detector (Waters 410 differential refractometer) and Styragel HR 0.5, HR 2, and HR 4 columns in THF calibrated against a polystyrene standard. The manipulation of the peaks was done using the Waters Millennium Chromatography Manager 2010 v2.15 software.

|| We speculate that the lower molecular masses obtained from the AlCl₃-initiated reactions may be caused by secondary reactions promoted by AlCl₃ (e.g., silane redistribution or Cl transfer to silane chains).

** A reviewer has suggested that higher molecular mass values in run 6 may arise instead from the conversion of some of the Si–H bonds in the polysilane to Si–Cl as a result of being in contact with CH₂Cl₂ for a few days; the Si–Cl bonds would then be converted to siloxanes during the work-up. Although free radical halogenation of (PhSiH)_n has been observed¹² to occur in CCl₄ and CBr₄, it seems to us that such reactions should be less likely in CH₂Cl₂. Nevertheless, this possibility can not be ruled out, and we caution the reader that the polysilanes obtained in runs 6 may not be pure (PhSiH)_n.

†† In our attempts to isolate Ni–H species, we have noted that reacting complex **1** with H[–] sources produces a black compound which shows a

fleeting signal at δ ca. –24 in its ¹H NMR spectrum; the isolation of this compound, however, has eluded us so far.

‡‡ The ratio of PhSiCl₃:LiAlH₄ was ca. 1:1.3, the reaction was run for four days, and the yield was 80%.

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