

Dehydrocoupling polymerization of arylsilanes with chloro(aryloxy)bis(cyclopentadienyl)zirconium complex catalysts

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Abstract

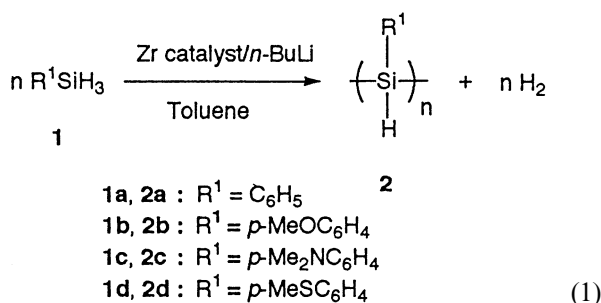
Complexes generated by treating chloro(aryloxy)bis(cyclopentadienyl)zirconium [**3**; aryloxy = 2,6-di-*tert*-butyl-4-methylphenoxy (**3a**), 2,6-diisopropylphenoxy (**3b**), phenoxy (**3c**), 2,3,4,5,6-pentafluorophenoxy (**3d**), and 2,6-dimethoxyphenoxy (**3e**)] with one equivalent of *n*-BuLi catalyze dehydrocoupling polymerization of arylsilanes **1** [aryl = phenyl (**1a**), *p*-methoxyphenyl (**1b**), *p*-dimethylaminophenyl (**1c**), *p*-methylthiophenyl (**1d**)] at room temperature to afford corresponding polysilanes. Their catalytic performance was compared with the conventional system generated from dichlorobis(cyclopentadienyl)zirconium (**4**) and two equivalents of *n*-BuLi. The reaction of **1a** using **3a**/*n*-BuLi, **3b**/*n*-BuLi or **3c**/*n*-BuLi gave high-molecular-weight polysilanes ($M_w = 13.3 \times 10^3$ and $M_n = 5.8 \times 10^3$ with **3a**; $M_w = 10.4 \times 10^3$ and $M_n = 4.2 \times 10^3$ with **3b**; $M_w = 8.8 \times 10^3$ and $M_n = 5.3 \times 10^3$ with **3c**). Formation of the polysilane was fast in comparison with **4**, in particular when the catalyst was ligated by a sterically demanding (**3a**) or electron-withdrawing (**3d**) aryloxy group. The time course of the gel permeation chromatography profiles suggested that complex **3a** showed faster chain growth than **3d**, **3e** and **4**. The extent of the formation of undesired cyclics was relatively small (< 10%) in the sterically demanding **3a**/*n*-BuLi- or **3b**/*n*-BuLi-catalyzed reaction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dehydrocoupling polymerization; Arylsilanes; Aryloxy–zirconocene complex

1. Introduction

Synthesis of polysilanes is experiencing vigorous growth because these polymers have significant potential for electronic, optoelectronic, and ceramic applications [1]. The intriguing electronic properties of polysilanes arise from the delocalized σ -electrons along the backbone [2], and are influenced by the molecular weight [3], polymer conformation [4], and substituents attached to the backbone [5]. The Wurtz-type coupling reaction of halosilanes with alkali metals is the only commercial process and most widely used in the laboratory to synthesize high molecular weight polysilanes [6]. On the other hand, since the discovery of Harrod and co-workers [7], the Group 4 metallocene-catalyzed dehydrocoupling of primary silanes has been intensively studied as an alternate synthetic method [8,9]. However, the molecular weights of the resulting polymers are usually low and undesired cyclic products are also

formed in large quantities. Exceptional cases that afford respectable molecular weights and suppress the formation of cyclics include the use of ‘cation-like’ early transition metal complexes reported by Harrod’s group [9e,i], ethylenebis(indenyl)zirconium complex (**5**) [10] reported by Waymouth and co-workers [9z], and mixed-ring CpCp*Zr-based catalysts reported by Tilley’s group [9j]. In this paper, we wish to report the catalytic performance of a family of chloro(aryloxy)bis(cyclopentadienyl)zirconium complexes (**3**) used in conjunction with one equivalent of *n*-BuLi (Eq. (1)).



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Table 1
Performance of zirconocene complexes in dehydrocoupling of **1a**^a

Entry	Zr	Time (h)	Raw polymer		Fractionation polymer $M_w/10^3$ ^b (M_w/M_n) ^b
			$M_w/10^3$ ^b (M_w/M_n) ^b	Cyclics ^c (%)	
1	3a	120	9.2 (5.0)	8 (6)	11.9 (2.1)
2	3a	168	10.1 (5.5)	7 (10)	13.3 (2.3)
3	3b	120	8.4 (4.9)	8 (9)	10.4 (2.5)
4	3c	120	6.9 (4.8)	17 (21)	8.8 (1.7)
5	3d	96	6.6 (4.9)	19 (23)	9.7 (1.7)
6	3e	120	2.5 (4.2)	nd ^d (13)	3.4 (2.0)
7 ^e	4	120	2.3 (3.8)	36 (40)	3.2 (2.0)
8 ^{e,f}	4	2	1.6 (2.8)	nd ^d	nd ^d
9 ^{e,f}	4	24	2.4 (3.8)	nd ^d (13)	3.7 (2.5)
10 ^{e,f}	4	120	4.3 (4.0)	12 (14)	5.9 (2.2)

^a Reactions were run under conditions I; zirconocene (0.04 mmol), *n*-BuLi (0.04 mmol), **1a** (0.8 ml, 6.4 mmol), and toluene (0.2 ml), room temperature (23°C). Conversion of **1a** was >99%.

^b Determined by GPC using polystyrene standards.

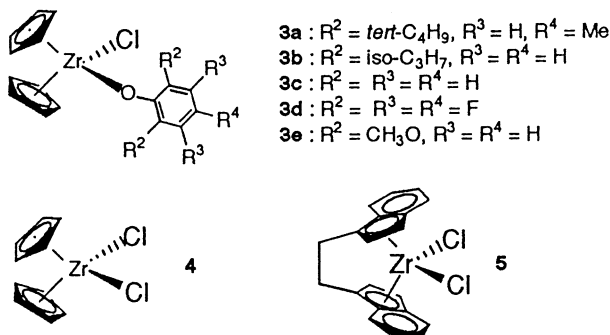
^c Determined by GPC. The numbers in parentheses are determined by ¹H-NMR.

^d Not determined.

^e The quantity of *n*-BuLi was two equivalents relative to the zirconocene complex.

^f B(C₆F₅)₃ (0.04 mmol) was used as cocatalyst.

Some of these zirconium complexes have been tested as catalysts (precursors) for polyolefin synthesis [11]. If the aryloxy ligand is retained throughout the catalysis, the catalyst is envisioned to have only one coordination site for polymerization, which allows better control of dehydrocoupling polymerization of arylsilanes by tuning the steric and electronic nature of the aryloxy ligand. Indeed, some of the family, although very much dependent of the structure, could show respectable performance, e.g. enhanced molecular weight of the resulting polysilanes, suppressed formation of cyclics, higher reaction rate, and applicability to functionalized arylsilane monomers. Corriu and co-workers [9h] reported the performance of diaryloxytitanocene and zirconocene complexes without the use of any external reductants such as *n*-BuLi. We believe the active species generated in their case is different from ours (Chart 1).



(Chart 1)

2. Results and discussion

The reactions catalyzed by **3** were carried out under conditions I in most cases, i.e. at room temperature (r.t.) (23°C) in toluene (0.2 ml) using a 160:1:1 molar ratio of a silane monomer (6.4 mmol), **3** (0.04 mmol), and *n*-BuLi (0.04 mmol) in a closed Schlenk flask. However, in control experiments in which the conventional dichlorobis(cyclopentadienyl)zirconium (**4**) complex was used, we followed Corey's standard procedure [9x,e',h'] in which the **4**/*n*-BuLi molar ratio was set at 1:2 by doubling the quantity of *n*-BuLi. Although the monomer was consumed in the first few hours, the reaction was continued for several days to enhance the molecular weight. The mixtures resulting from the polymerization were analyzed by gel permeation chromatography (GPC) with calibration using polystyrene standards. As has been usually encountered in dehydrocoupling polymerization of primary silanes with conventional catalyst systems, the molecular-weight distributions obtained with the new catalyst systems were also bimodal in most cases, comprising linear polysilane of a higher molecular weight and lower molecular weight (M_w = ~500) cyclics¹. Fractionation by preparative GPC with oxygen-free toluene eluent led to isolation of the linear polysilane as an off-white or colorless sticky liquid,

¹ Regardless of the resolution of linear and cyclic polysilanes in GPC, the M_w and M_n for the raw polymer in Table 1 are given for the entire polymer covering the whole bimodal distribution.

which was soluble in most organic solvents such as benzene and THF and was further analyzed by GPC and by ^{29}Si -NMR spectroscopy (vide infra). Reprecipitation from toluene–petroleum ether according to Harrod's procedure, after filtration of the reaction mixture (entry 1, Table 1) through a Florisil column to remove the catalyst, also led to isolation of the higher-molecular-weight polysilane (in 56% yield), which showed nearly the same spectroscopic data as the higher-molecular-weight fraction obtained by preparative GPC. As the results summarized in Table 1 show, some of the aryloxy–zirconocene complexes **3** display superiority to the conventional complex **4** in three aspects in dehydrocoupling of phenylsilane **1a** and prove to be listed among the best systems known for the dehydrocoupling.

2.1. Molecular weight

First, some of the new zirconocene systems can enhance the ultimate molecular weight of the polysilane as compared with **4**. For example, the M_w value of the higher-molecular-weight fraction obtained with the chloro(2,6-di-*tert*-butyl-4-methylphenoxy)bis(cyclopentadienyl)zirconium (**3a**)/*n*-BuLi system was 11.9×10^3 (entry 1), while the value in the control experiment using the conventional **4**/*n*-BuLi system was only 3.2×10^3 (entry 7). Other new systems substituted by 2,6-diisopropylphenoxy (**3b**, entry 3), phenoxy (**3c**, entry 4), and 2,3,4,5,6-pentafluorophenoxy (**3d**, entry 5) groups performed similarly, although 2,6-dimethoxyphenoxy complex (**3e**, entry 6) did not show the efficacy, presumably due to the electronic nature of the methoxy group.

Fine tuning of the steric and electronic effects of the ligand is crucial for higher molecular weights. Tilley could achieve high molecular weights, e.g. $M_w = 13.9 \times 10^3$ and $M_n = 5.7 \times 10^3$ (after fractionation), by using CpCp*Zr complexes [9j]. Harrod reported that the molecular weight could be even higher, e.g. $M_w = 13.8 \times 10^3$, $M_n = 7.3 \times 10^3$ (after fractionation), when the polymerization was catalyzed by 'cation-like' catalysts such as the one generated from CpCp*ZrCl₂, *n*-BuLi, and B(C₆F₅)₃ [9i]. The highest molecular weights that the new aryloxy complexes could achieve were found with **3a**; $M_w = 13.3 \times 10^3$, $M_n = 5.8 \times 10^3$ (entry 2). These values are not only higher than those for dichloro complex **4**, but are similar or close to the highest values reported by Tilley and Harrod. Thus, our strategy to introduce an aryloxy ligand into the zirconium center proves to be a useful tool to enhance the ultimate molecular weight, although the performance depends on the structure of the aryloxy ligand.

2.2. Formation of cyclics

In experiments to compare the catalyst performance, we determined the percentage of cyclics in the raw

polymer. The data are also listed in Table 1. In most cases where the degree of polymerization is relatively high (M_w of the raw polymer $\geq$ ca. 3000), the GPC profile shows distinct separation between the linear polysilanes and the cyclics, so that the extent of the formation of the cyclics in the raw polymer can be readily determined by GPC. When the profile is not sufficiently resolved because of a low degree of polymerization or because of the cyclics being formed only in a small quantity, the extent of the cyclics formation can be determined by integration of the signals arising from Si–H units in linear (4.3–4.9 ppm) and cyclic (4.9–5.3 ppm) structures in ^1H -NMR spectroscopy. Although the values obtained by GPC and ^1H -NMR spectroscopy appear slightly different from each other, the difference is not serious.

A second feature in the aryloxy–zirconocene complex-catalyzed reactions, as entries 1–3 in Table 1 indicate, lies in the tunability of the aryloxy ligand structure for minimized formation of the cyclics. Thus, the formation of the cyclics in the reactions using **3a** or **3b** was $\leq 10\%$ of the entire raw product, which was smaller than the 36% observed with **4**, and was in the same range as or slightly better than the value obtained using Harrod's 'cation-like' system used under similar conditions (entry 10). The efficacy in this respect decreases in the order **3a** $\geq$ **3b** $>$ **3e** $>$ **3c** $\geq$ **3d**. The trends appear to primarily arise from the steric demand of the *ortho* substituent, and agree with Tilley's argument on the cyclics formation mechanism, which involves highly congested four-center transition state [8b].

2.3. Time course of the dehydrocoupling

Thirdly, monitoring the time course of the reaction by ^1H -NMR spectroscopy revealed the superiority of some of the new catalyst systems in the reaction rate. The reaction to examine this aspect was run under conditions

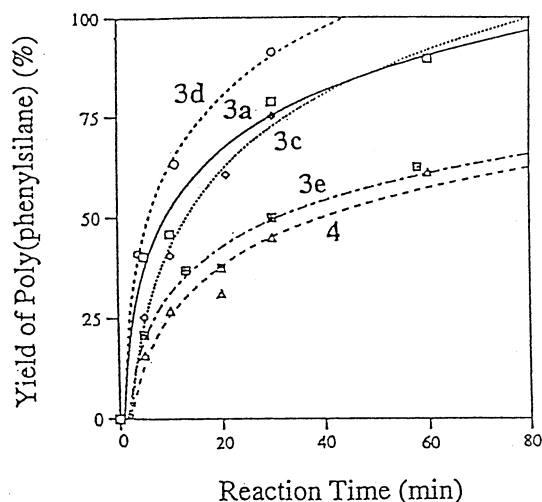


Fig. 1. Progress of the dehydrocoupling of **1a** using zirconocene complex catalysts.

II, i.e. at r.t. in toluene (0.5 ml) and mesitylene (50 μ l, as internal standard for ^1H -NMR spectroscopy) using a 320:1:1 molar ratio of **1a** (6.4 mmol), **3** (0.02 mmol), and *n*-BuLi (0.02 mmol) under constant flow of nitrogen gas. Since the signals assignable to the $-(\text{SiHPh})_n-$ structures (4.3–5.3 ppm) are distinctly separated from the signals due to PhSiH_3 (4.26 ppm) and mesitylene (2.15 ppm), integration readily affords the quantities of the monomer and the product. Fig. 1 shows, for instance, that the use of perfluorophenoxy complex **3d** rapidly promoted the dehydrocoupling as compared with **4**. Complexes **3a** and **3c** behaved similarly but to a modest extent. However, the efficacy of dimethoxyphenoxy complex **3e** was only marginal. The comparison of the performance among complexes **3** concludes that the dehydrocoupling rate is enhanced by the introduction of an electron-withdrawing (such as F) or sterically demanding (such as *tert*-butyl and isopropyl at the *ortho* position) group into the aryloxy ligand.

The time course of the GPC profiles (Fig. 2) indicates that the chain growth was efficiently promoted by the use of **3a** ligated by the sterically demanding aryloxy ligand, while it was slow in the **3e**- or **4**-catalyzed reaction. Complex **3d** displayed intermediate performance in this respect.

2.4. Microstructure of the resulting polysilane

Waymouth and co-workers reservedly proposed a tentative assignment of the microstructure of the

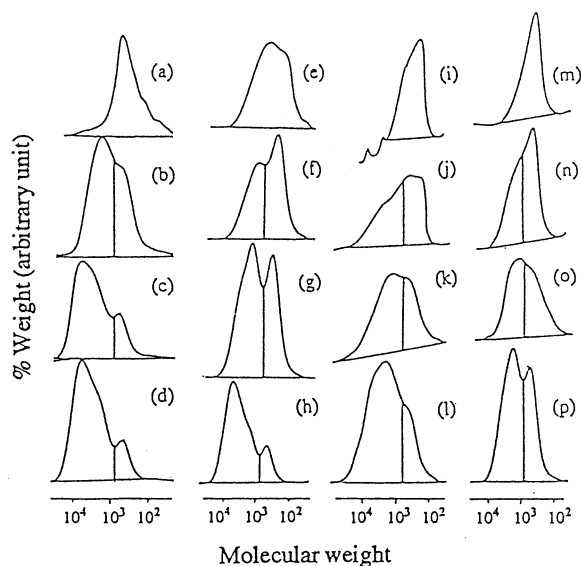


Fig. 2. Time course of GPC profiles in the zirconocene complex-catalyzed dehydrocoupling of phenylsilane: **3a** (a–d), **3d** (e–h), **3e** (i–l), **4** (m–p). Reaction time: (a, e, i, m) 5 min; (b, f, j, n) 20 min; (c, g, k, o) 2 h (d, h, l, p) 5 h.

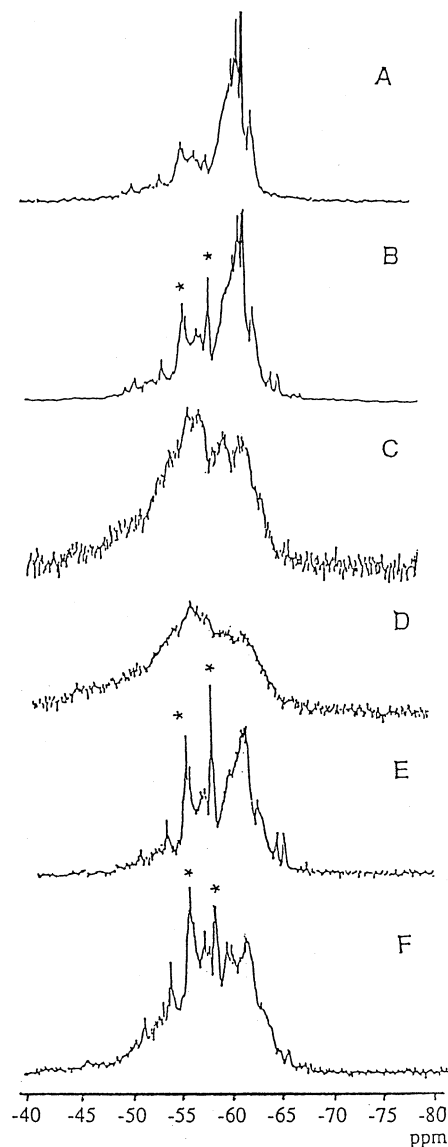


Fig. 3. ^{29}Si -NMR (DEPT) spectra of poly(phenylsilane)s (higher molecular weight fractions) prepared by the use of zirconocene complex catalysts **3a** (A), **3b** (B), **3c** (C), **3d** (D), **3e** (E), and **4** (F). The asterisk denotes SiH_2 signals.

poly(phenylsilane) [9z], which was solely based on the similarity in ^{29}Si -NMR spectroscopy to *trans*-hexaphenylcyclohexasilane [12]. However, the chemical shifts of cyclic silicon compounds can differ from those of linear analogs [13]. Because stereochemistry-defined linear oligosilanes are not available, we have no warrant for any assignment of the microstructure based on the spectroscopic comparison. Indeed, recent publications show the complexity of the microstructure analysis based on the ^{29}Si -NMR spectroscopy [6c,9a]. In this context we simply illustrate in Fig. 3 the spectra of the polymers formed by using the new and conventional systems (for comparison) at r.t. and do not discuss the stereoregularity in detail.

Table 2

Effects of reaction temperature and concentrations of **1a** and **3a** in **3a**/*n*-BuLi-catalyzed dehydrocoupling of **1a**^a

Entry	Temperature (°C)	Solvent	Time (h)	Raw polymer	
				$M_w/10^3$ ^b (M_w/M_n) ^b	Cyclics ^c (%)
11	50	Toluene	2	4.5 (4.0)	17
12	50	Toluene	5	4.9 (4.9)	16
13	50	Toluene	24	5.2 (4.5)	19
14	23	Toluene	2	2.8 (2.8)	nd ^d
15	23	Toluene	5	5.1 (3.9)	9
16	23	Toluene	24	8.6 (4.8)	9
17	0	Toluene	5	0.7 (3.1)	nd ^d
18	0	Toluene	24	0.9 (3.0)	nd ^d
19	0	Toluene	72	1.3 (4.2)	nd ^d
20	0	Toluene	120	1.5 (4.8)	nd ^d
21	23	None	2	3.4 (3.6)	nd ^d
22	23	None	5	5.3 (4.1)	10
23	23	None	24	8.1 (4.5)	7
24 ^c	23	Toluene	24	1.8 (3.9)	51

^a Reactions were run under conditions I [**3a** (0.04 mmol), *n*-BuLi (0.04 mmol), **1a** (0.8 ml, 6.4 mmol), and toluene (0.2 ml for entries 11–20, 3.0 ml for entry 24), room temperature (23°C)] except entries 21–23, where the reaction was run neat without toluene solvent. Conversion of **1a** was >99% unless otherwise noted.

^b Determined by GPC using polystyrene standards.

^c Determined by GPC.

^d Not determined.

^e Conversion of **1a** was 85%.

2.5. Effect of reaction conditions

In addition to the structure of the catalyst, various other factors such as the presence or absence of the solvent, temperature, concentration of the monomer, etc. are reported to influence the dehydrocoupling process [8b,9e]. For instance, reactions in neat phenylsilane at lower temperatures are envisioned, based on the consideration by Tilley, to be favorable for suppression of the cyclics formation [8b]. Waymouth found that polymerization at higher concentrations of Cp₂ZrMe₂ or Cp₂ZrHCl caused a change in the profiles of ²⁹Si-NMR spectra of the resulting polymers [9z]. Harrod reported that the presence of even a small quantity of an aromatic solvent significantly decrease the activity because of competition between the Si–H and aromatic ring for the coordination site [9e]. In this context, we briefly examined the effects of these factors under conditions I using **3a** as catalyst precursor to further clarify the nature of the aryloxy systems (Table 2).

The reaction run at 50°C decreased the ultimate molecular weight and increased the formation of the cyclics as compared with the reaction at r.t. (entry 13 versus entry 16). The ²⁹Si-NMR spectrum of the polymer from entry 13 is illustrated in Fig. 4. The origin of the increased formation of the cyclics at 50°C is ambiguous; it can be due either to more extensive involvement of the higher energy cyclization pathway at the higher temperature as argued by Tilley [8b] and/or to a possible change of the catalyst structure, such that an

aryloxy ligand-free catalyst carries the catalysis (vide infra). On the other hand, the reaction run at 0°C gave only low molecular weight (<2.0 × 10³) oligosilanes (entries 17–20). Since the conversion of the monomer was 100% in each entry, the low molecular weight is presumably because the monomer–chain and chain–chain couplings required for the chain growth are very slow at this temperature.

The chain length of the linear polysilane and the extent of cyclics formation in the reactions using neat phenylsilane (entries 21–23) were very similar to those in corresponding reactions run in the presence of a small quantity of toluene (entries 14–16), which does not agree with Harrod's experience [9i]. When a larger quantity of toluene was used as solvent (entry 24) the cyclics were extensively formed and the molecular weight was much lower than in entry 16, as anticipated from the Tilley's observation and argument based on the unimolecular cyclization mechanism [8b].

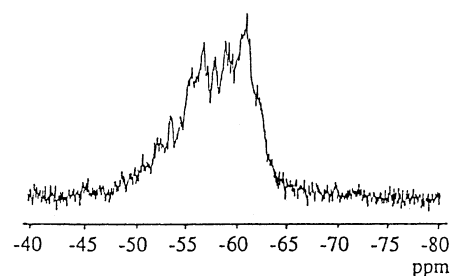


Fig. 4. ²⁹Si-NMR (DEPT) spectrum of poly(phenylsilane) obtained by the use of **3a**/BuLi catalyst at 50°C.

Table 3
Dehydrocoupling of **1a** with preheated **3a**/*n*-BuLi catalyst ^a

Entry	Temperature (°C)	Solvent	Time (h)	Raw polymer			Fractionation polymer $M_w/10^3$ ^b (M_w/M_n) ^b
				$M_w/10^3$ ^b (M_w/M_n) ^b	Cyclics ^c (%)		
25	23	Toluene	2	2.5 (3.3)	nd ^d		nd ^d
26	23	Toluene	5	4.2 (3.9)	nd ^d		nd ^d
27	23	Toluene	24	4.8 (4.1)	9 (11)		6.0 (2.1)

^a Reactions were run under conditions I; **3a** (0.04 mmol), *n*-BuLi (0.04 mmol), **1a** (0.8 ml, 6.4 mmol), and toluene (0.2 ml), room temperature (23°C). Conversion of **1a** was >99%. The catalyst was preheated with 0.05 ml of phenylsilane at 50°C for 30 min before injection of further **1a** (6.4 mmol); see the text.

^b Determined by GPC using polystyrene standards.

^c Determined by GPC. The numbers in parentheses are determined by ¹H-NMR.

^d Not determined.

2.6. Attempted study on the structure of the active species: comparison with Corriu's system

¹H-NMR and GC–MS studies on the reaction of an equimolar mixture of **3b**, *n*-BuLi and **1a** revealed that neither (2,6-diisopropylphenoxy)phenylsilane nor 2,6-diisopropylphenol was formed at r.t. (23°C), suggesting that the Zr–OAr bond remained intact. When the NMR tube was heated at 50°C for 30 min, several very weak signals emerged in the Si–H region (4.3–5.3 ppm). However, none of these agreed in chemical shift with (2,6-diisopropylphenoxy)phenylsilane. Besides these signals the NMR spectrum displayed very weak new signals also in the Cp region (5.8–6.1 ppm), suggesting a structural change having taken place to some extent upon heating, although it was unable to identify what it was. GC–MS analysis did not detect the formation of (2,6-diisopropylphenoxy)phenylsilane nor diisopropylphenol in the reaction mixture, but diphenyldisilane was found to be formed. Accordingly, the weak signals that appeared at 4.3–5.3 ppm are presumably mainly due to diphenyldisilane and other oligosilanes. Corriu and co-workers [9h] examined the catalytic performance of diaryloxytitanium and zirconium complexes without addition of any external reductants like *n*-BuLi. In order to trigger the catalysis at r.t., they normally preheated the reaction mixture for a while to 50°C to activate the catalyst species, such that the starting aryloxy–metal precursors were converted to H–M species with incidental formation of aryloxysilanes by the reaction with the hydrosilane monomer. Accordingly, their resulting polymers showed similar characteristics, independent on the structure of the aryloxy ligand in the precursor complex. We also examined the catalytic performance of **3a** in a procedure similar to Corriu's (Table 3). Thus, a mixture prepared as in entries 14–16 (Table 2), i.e. **3a** (0.04 mmol), *n*-BuLi (0.04 mmol), and toluene (0.2 ml), was preheated for 30 min at 50°C with a small amount (0.4 mmol) of **1a**. After cooling the mixture to r.t., **1a** (6.4 mmol) was further added to the

mixture and the reaction was continued at the same temperature over 24 h. The molecular weight of the polymer after 24 h (entry 27) was lower than that from entry 16, indicative of the active species having at least partly experienced a structural change upon the pre-heating. Neither (2,6-diisopropylphenoxy)phenylsilane nor diisopropylphenol was found by GC–MS to be formed in this mixture. ¹H-NMR spectroscopy of the mixture at 50°C was not informative of the structure of active catalyst species (vide supra) either. However, based on the polymerization characteristics depending on the structure of the catalyst, we can safely presume that, at least at r.t., the aryloxy ligand is bound to zirconium throughout the catalysis.

2.7. Applicability to functionalized monomers

Another feature of the new catalyst systems is their applicability to arylsilanes having 'coordinative' functional groups (Table 4). There have been only a limited number of attempts to polymerize substituted phenylsilanes reported. Waymouth and co-workers reported reactivities of arylsilanes having non-coordinative substituents, such as *meta* and *para* substituted tolylsilanes and (trifluoromethyl)phenylsilanes, relative to that of unsubstituted phenylsilane, using a conventional zirconocene-based catalyst [9m]. We have learned that the conventional zirconocene catalysts do not polymerize arylsilanes such as *p*-methoxyphenylsilane (**1b**) and *p*-dimethylaminophenylsilane (**1c**) that possess coordinative functional groups, presumably due to the catalyst deactivation by coordination of methoxy and dimethylamino groups to the metal center. For example, under conditions I, the reaction of **1b** using the **5/2n**-BuLi catalyst system gave only the corresponding disilane and trisilane [14]. An attempted polymerization of **1c** did not proceed at all in the presence of the same catalyst [14]. In contrast, the **3a/n**-BuLi catalyst system did polymerize **1b**, **1c**, and *p*-methylthiophenylsilane

Table 4
Dehydrocoupling of functionalized silanes with **3a**/*n*-BuLi catalyst ^a

Entry	Silane	Time (h)	Conv. (%) ^b	Raw polymer M_w^c (10^3) (M_w/M_n) ^c	Fractionation polymer M_w^c (10^3) (M_w/M_n) ^c
2	1a	168	>99	10.1 (5.5) ^d	13.3 (2.5)
28	1b	168	68	2.1 (3.9) ^d	2.8 (3.5)
29	1c	72	91	1.0 (2.0)	1.0 (1.7)
30	1d	96	>99	8.6 (3.7) ^d	9.8 (2.2)

^a Reactions were run under conditions I; **3a** (0.04 mmol), *n*-BuLi (0.04 mmol), silane (6.4 mmol), and toluene (0.2 ml), room temperature (23°C).

^b Determined by ¹H-NMR.

^c Determined by GPC using polystyrene standards.

^d The raw polymers contain 7–10% of low molecular weight fraction ($M_w \sim 500$).

(**1d**) to give poly(arylsilane)s (**2b–d**), although the molecular weight was not high in all cases. ²⁹Si-NMR profiles of the resulting polymers are illustrated in Fig. 5 including the one for polyphenylsilane obtained using the same catalyst. The present catalyst system is useful for the synthesis of functionalized oligo- and/or poly(arylsilane)s.

Unlike the substituted phenylsilanes, 2-thienylsilane, a heteroaromatic silane having a coordinative sulfur functionality, did not polymerize; the reaction of 2-thienylsilane using the **3a**/*n*-BuLi system under the conditions I was slow and formed only the corresponding disilane and trisilane (144 h, conversion 59%: disilane 52%, trisilane 7%). As experienced with other catalyst systems, polymerization of alkylsilanes was less efficient than that of phenylsilane; for example, the reaction of *n*-HexSiH₃ by the same procedure as entry 2, Table 1, gave only oligomers ($M_w = 1.0 \times 10^3$).

2.8. Conclusions

The ligand structure is a crucial factor that influences the catalysis. The results herein described indicate that the performance (molecular weight, extent of the formation of the undesired cyclics, reaction rate) of aryloxy–zirconocene-based catalysts can be substantially modified by introducing sterically demanding and electron-withdrawing aryloxy ligands. Furthermore, the present catalyst system is useful for preparation of various functionalized poly(arylsilane)s.

3. Experimental

3.1. General procedures and materials

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual-manifold Schlenk line interfaced to a high-vacuum system, or in an argon-filled glove box with a recirculator (<1 ppm O₂). NMR spectra were measured in C₆D₆ on a Bruker ARX-300 instrument (300 MHz for ¹H; 75.5 MHz for

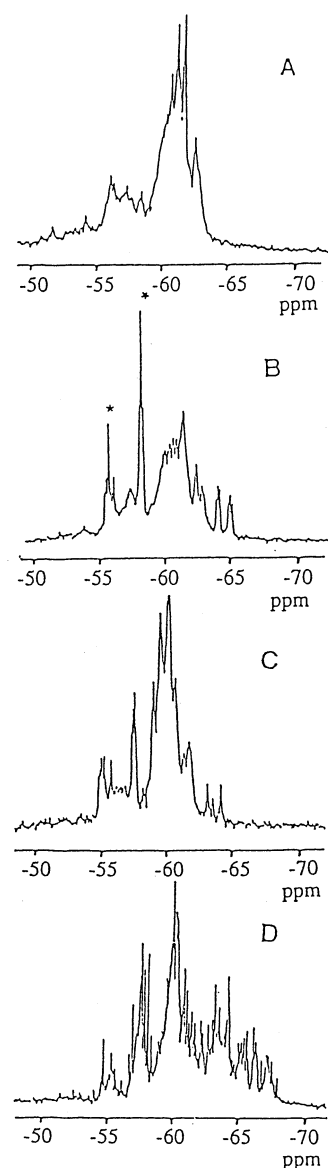


Fig. 5. ²⁹Si-NMR (DEPT) spectra of poly(arylsilane)s **2a** (A), **2b** (B), **2d** (C), and **2c** (D) (higher-molecular-weight fractions) prepared by the use of **3a**/BuLi catalyst. The asterisk denotes SiH₂ signals.

^{13}C ; 59.6 MHz for ^{29}Si). An INEPT technique was used for ^{29}Si -NMR measurements ($\tau = 27$ ms, $\Delta = 12$ ms). The chemical shifts were referenced to Me_4Si (0 ppm) for ^1H -, ^{13}C - and ^{29}Si -NMR. IR spectra were obtained using a Jasco FT/IR-5000 spectrometer. GC–MS analyses were performed with Shimadzu QP-1000 and/or QP-5000 spectrometers (EI, 70 eV). GC–(HR)MS analyses (EI, 70 eV) were performed on a Jeol DX-303 spectrometer. Molecular weights of polymers were measured with a GPC system equipped with a Shimadzu LC-6A high-pressure pump, Shodex KF-80M (pore size: 6 mm), KF-802 (pore size: 6 mm), and KF-801 (pore size: 6 mm) columns, and Shimadzu RID-2A, Shodex SE-61 (RI) and/or Shimadzu SPD-M1A (UV) detectors using THF eluent and polystyrene standards. Preparative-scale GPC was carried out with a Japan Analytical Industry Co. Ltd. LC-908-G30 system equipped with Jaigel-1H (i.d. 20×600 mm, pore size: 10 mm) and Jaigel-2H (i.d. 20×600 mm, pore size: 10 mm) columns. Elemental analyses were performed by the Analysis Center, National Institute of Materials and Chemical Research. $\text{C}_6\text{H}_5\text{SiH}_3$ and $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ were obtained from the Chisso Corporation and distilled from LiAlH_4 before use. Other liquid materials and solvents were dried over appropriate agents (4 Å molecular sieves, sodium, CaH_2 and LiAlH_4) and distilled in vacuo or under nitrogen. ZrCl_4 (Aldrich), **5** (Aldrich), and Cp_2ZrCl_2 (Strem) were commercial products and used as received. Compounds **3a** [15], **3b** [11], $\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}$ [16], $\text{B}(\text{C}_6\text{F}_5)_3$ [17] and 2-thienylsilane [18] were synthesized according to the literature methods. $p\text{-CH}_3\text{C}_6\text{H}_4\text{SiH}_3$ was obtained by reduction of $p\text{-CH}_3\text{C}_6\text{H}_4\text{SiCl}_3$ (Chisso Corp.) with lithium aluminum hydride according to the procedure given for **1d** (vide infra).

3.2. *p*-Methylthiophenylsilane (**1d**)

3.2.1. Generation of *p*-methylthiophenylmagnesium bromide

A 300 ml round-bottom flask equipped with a reflux condenser and a pressure-equalizing dropping funnel was charged with 2.99 g (123 mmol) of Mg and 100 ml of Et_2O . The magnesium turnings were activated by the addition of a few drops of 1,2-dibromoethane and a solution of *p*-bromothioanisole (25 g, 123 mmol) dissolved in 50 ml of Et_2O was slowly added at a rate to maintain a gentle reflux. After the addition the solution was further stirred at r.t. for 12 h.

3.2.2. Generation of (*p*-methylthiophenyl)trichlorosilane

In a 500 ml round-bottom flask equipped with a reflux condenser and pressure-equalizing dropping funnel were placed 200 ml of Et_2O and 50.0 g of SiCl_4 (198 mmol). The foregoing solution of the Grignard reagent was slowly added through the funnel to the $\text{SiCl}_4\text{--Et}_2\text{O}$

solution at r.t. over a period of 2 h. After addition of the Grignard reagent, the solution was refluxed for 24 h. The reaction mixture was cooled and filtered to remove the salt to give a yellow solution.

3.2.3. Reduction with LiAlH_4

To a mixture of 3.50 g (92.3 mmol) of LiAlH_4 and 250 ml of Et_2O placed in a 500 ml round-bottom flask equipped with a reflux condenser and pressure-equalizing dropping funnel was slowly added the foregoing yellow solution containing *p*- $\text{MeSC}_6\text{H}_4\text{SiCl}_3$ over a period of 3 h. Gentle reflux was maintained during the addition. After completion of the addition, the mixture was further refluxed for 48 h, cooled and was quenched by a slow addition of water. The ether layer was separated, washed with water, dried over magnesium sulfate, and was filtered. The filtrate was concentrated and the residue was fractionally distilled to give 8.77 g (46% overall yield based on the starting bromide) of **1d**. B.p. $45^\circ\text{C}/0.4$ mmHg. ^1H -NMR: δ 1.93 (s, 3H), 4.22 (s, 3H), 6.90 (d, 2H), 7.23 (d, 2H). ^{13}C -NMR: δ 14.57, 125.87, 126.79, 129.02, 136.41. ^{29}Si -NMR (DEPT): δ –59.92. IR (neat): 3066, 2988, 2922, 2158, 1582, 1541, 1485, 1437, 1383, 1321, 1255, 1131, 1083, 917, 870, 806, 741, 727, 690, 642, 518, 474 cm^{-1} . MS (relative intensity): m/z 155 [$\text{M}^+ + 1$, 12], 154 [M^+ , 74], 152 (23), 139 (38), 138 (88), 137 (28), 124 (12), 109 (11), 107 (24), 106 (14), 105 (29), 103 (14), 91 (31), 80 (7), 79 (87), 78 (47), 77 (100), 76 (72), 69 (8), 66 (10), 65 (16), 63 (8), 61 (28), 60 (13), 55 (13), 54 (10), 53 (59), 52 (10), 51 (31), 50 (18), 45 (19). HRMS: Calc. for $\text{C}_7\text{H}_{10}\text{SSi}$ [M^+] 154.0272. Found 154.0256. Anal. Calc. for $\text{C}_7\text{H}_{10}\text{SSi}$: C, 54.49; H, 6.53. Found: C, 54.62; H, 6.03%.

3.3. *p*-Methoxyphenylsilane (**1b**)

B.p. $75^\circ\text{C}/10$ mmHg (lit. [19] $180^\circ\text{C}/740$ mmHg). ^1H -NMR: δ 3.33 (s, 3H), 4.28 (s, 3H), 6.71 (d, 2H), 7.33 (d, 2H). ^{29}Si -NMR: δ –60.26. IR (neat): 3008, 2960, 2838, 2532, 2156, 1897, 1599, 1566, 1504, 1464, 1441, 1400, 1311, 1282, 1251, 1183, 1118, 1035, 922, 874, 826, 795, 754, 731, 646, 627, 509, 487 cm^{-1} . MS (relative intensity): m/z 138 [M^+ , 29], 137 (15), 122, (7), 121 (13), 108 (8), 107 (17), 91 (20), 79 (13), 78 (21), 77 (29), 67 (10), 66 (15), 65 (19), 61 (13), 60 (26), 59 (100), 55 (9), 53 (24), 51 (12), 50 (9), 43 (10). HRMS: Calc. for $\text{C}_7\text{H}_{10}\text{OSi}$ [M^+] 138.0500. Found 138.0515. Anal. Calc. for $\text{C}_7\text{H}_{10}\text{OSi}$: C, 60.82; H, 7.29. Found: C, 60.64; H, 8.05%.

3.4. *p*-Dimethylaminophenylsilane (**1c**)

M.p. $43\text{--}45^\circ\text{C}$ (lit. [20] $49\text{--}50^\circ\text{C}$). ^1H -NMR: δ 2.42 (s, 3H), 4.46 (s, 3H), 6.51 (d, 2H), 7.46 (d, 2H). ^{29}Si -NMR (DEPT): δ –60.86. IR (C_6H_6): 3092, 3074, 3038, 2328, 2152, 1961, 1816, 1601, 1516, 1481, 1357,

1178, 1118, 1036, 922, 851, 810, 675 cm^{-1} . MS (relative intensity): m/z 152 [$\text{M}^+ + 1$, 11], 151 [M^+ , 69], 150 (52), 148 (17), 134 (7), 121 (74), 120 (100), 119 (12), 107 (16), 106 (7), 105 (20), 104 (10), 103 (13), 93 (7), 91 (9), 79 (11), 78 (8), 76 (24), 74 (21), 73 (21), 72 (10), 67 (9), 66 (11), 65 (7), 56 (8), 55 (10), 54 (8), 53 (34), 44 (17), 43 (8), 42 (21). HRMS: Calc. for $\text{C}_8\text{H}_{13}\text{NSi}$ [M^+] 151.0817. Found 151.0801. Anal. Calc. for $\text{C}_8\text{H}_{13}\text{NSi}$: C, 63.52; H, 8.66. Found: C, 63.18; H, 8.71%.

3.5. Chloro(phenoxy)bis(cyclopentadienyl)zirconium (**3c**)

To a mixture of $\text{Cp}_2\text{ZrCl}(\text{Me})$ (300 mg, 1.10 mmol) and toluene (20 ml) placed in a 30 ml Schlenk flask was slowly added a solution of phenol (103 mg, 1.10 mmol) in toluene (10 ml) over a period of 20 min. The mixture was further stirred for 20 h at r.t., evaporated in vacuo, and the residue was extracted with 50 ml of hexane. After evaporation of the hexane solution to ca. 10 ml, the residual solution was cooled to -78°C to give 142 mg (37%) of a white solid. M.p. $217\text{--}219^\circ\text{C}$ dec. ^1H -NMR: δ 5.92 (s, 10H), 6.67–7.20 (m, 5H). ^{13}C -NMR: δ 114.33, 115.60, 118.04, 120.57, 129.79. MS (relative intensity): m/z 348 [M^+ , 14], 331 (20), 283 (13), 269 (18), 255 (23), 243 (40), 231 (48), 219 (45), 205 (20), 193 (33), 181 (100), 169 (100), 162 (35), 124 (13), 100 (88). HRMS: Calc. for $\text{C}_{16}\text{H}_{15}\text{ClOZr}$ 347.9858. Found 347.9874. Anal. Calc. for $\text{C}_{16}\text{H}_{15}\text{ClOZr}$: C, 54.91; H, 4.32. Found: C, 55.06; H, 4.27%.

3.6. Chloro(2,3,4,5,6-pentafluorophenoxy)bis-(cyclopentadienyl)zirconium (**3d**)

A procedure similar to that for **3c**, using 2,3,4,5,6-pentafluorophenol (202 mg, 1.10 mmol), gave 77 mg (16% yield) of the title compound as a white solid. M.p. $150\text{--}152^\circ\text{C}$. ^1H -NMR: δ 5.89 (s, 10H). MS (relative intensity): m/z 438 [M^+ , 62], 404 (16), 337 (15), 294 (38), 292 (57), 291 (17), 290 (58), 274 (17), 261 (21), 259 (71), 258 (18), 257 (100), 256 (40), 213 (17), 229 (52), 228 (16), 227 (78), 226 (18), 225 (86), 213 (30), 211 (54), 210 (19), 209 (69). HRMS: Calc. for $\text{C}_{16}\text{H}_{10}\text{ClF}_5\text{OZr}$ 437.9387. Found 437.9434. Anal. Calc. for $\text{C}_{16}\text{H}_{10}\text{ClF}_5\text{OZr}$: C, 43.68; H, 2.29. Found: C, 43.27; H, 2.17%.

3.7. Chloro(2,6-dimethoxyphenoxy)bis(cyclopentadienyl)zirconium (**3e**)

A procedure similar to that for **3c**, starting with 200 mg of $\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}$ (0.74 mmol) and 115 mg of 2,6-dimethoxyphenol (0.74 mmol), gave 48 mg (16%) of the title compound as a yellow waxy solid. ^1H -NMR: δ 3.45 (s, 6H), 6.11 (s, 10H), 6.44–6.76 (m, 3H). ^{13}C -NMR: δ 56.14, 106.61, 114.20, 114.80, 115.83, 118.98.

MS (relative intensity): m/z 408 [M^+ , 13], 393 (25), 381 (36), 355 (12), 347 (13), 345 (21), 343 (51), 331 (38), 330 (18), 328 (18), 319 (18), 305 (18), 293 (75), 292 (19), 290 (19), 281 (70), 269 (45), 267 (20), 255 (30), 243 (83), 231 (100), 229 (20), 227 (34), 225 (36), 219 (90), 217 (19), 212 (20), 205 (37). HRMS: Calc. for $\text{C}_{18}\text{H}_{19}\text{ClO}_3\text{Zr}$ 408.0069. Found 408.0072. Anal. Calc. for $\text{C}_{18}\text{H}_{19}\text{ClO}_3\text{Zr}$: C, 52.73; H, 4.67. Found: C, 52.52; H, 4.71%.

3.8. Dehydrogenative coupling of silanes with chloro(aryloxy)zirconocene complex catalysts

A typical reaction procedure (entry 1): A 30 ml J. Young-valve-equipped Schlenk flask was loaded in a glove box with **3a** (20 mg, 0.04 mmol) and toluene (0.2 ml). One equivalent of *n*-BuLi (28 ml, 1.6 M solution in hexane) was added to the flask at -78°C and the temperature was raised to 0°C . After the mixture was stirred for 30 min at 0°C , phenylsilane (0.8 ml, 6.4 mmol) was added, and the mixture was set at r.t. (23°C). Intense evolution of H_2 gas was immediately observed. After the reaction over 120 h, a small amount of THF (0.2 ml) was added to deactivate the catalyst and an aliquot of the mixture was analyzed by GPC with oxygen-free toluene eluent. The remainder of the solution was evaporated in vacuo ($23^\circ\text{C}/0.1$ mmHg) to give a viscous polymeric material (660 mg inclusive of the catalyst residue, ca. 94% based on phenylsilane charged), which was fractionated by preparative GPC with oxygen-free toluene eluent to give a higher molecular weight fraction of poly(phenylsilane) (380 mg, 56%).

In a repeated experiment, the product was fractionated according to Harrod's procedure as follows. First, the reaction mixture diluted with toluene was filtered through a Florisil column to remove the catalyst. Evaporation of the filtrate gave 620 mg (91%) of a raw polymer, GPC analysis of which showed $M_w = 9.9 \times 10^3$ and $M_n = 2.3 \times 10^3$. Then the raw polymer was dissolved in 2 ml of toluene and the mixture was poured into 4 ml of petroleum ether to precipitate a linear fraction (360 mg, 53%) of $M_w = 13.9 \times 10^3$ and $M_n = 4.3 \times 10^3$. The structure was confirmed by spectral comparison with the literature data [9j].

3.9. Time course monitoring of the dehydrogenative coupling of phenylsilane (Fig. 1)

3.9.1. A typical reaction procedure

A 30 ml J. Young-valve-equipped Schlenk flask was loaded in a glove box with **3a** (10 mg, 0.02 mmol), toluene- d_8 (0.5 ml) and mesitylene (50 μl , an internal standard for ^1H -NMR spectroscopy). One equivalent of

n-BuLi (14 μ l, 1.6 M solution in hexane) was added to the flask at -78°C and the temperature was raised to 0°C . After the mixture was stirred for 30 min at 0°C , the system was opened to the constant flow of nitrogen gas, the purity of which was $>99.9995\%$. Then the flask was warmed to r.t. by external heating with a water bath, and stirred for 5 min at r.t. Phenylsilane (0.8 ml, 6.4 mmol) was injected to the flask. A 20 μ l portion of the mixture was taken by a micro syringe and was immediately added to ~ 5 ml of THF placed in an NMR tube to deactivate the catalyst. An NMR sample was prepared by adding C_6D_6 (0.5 μ l) to this mixture. The formation of poly(phenylsilane) and consumption of the monomer were easily monitored by ^1H -NMR spectroscopy with probes of the SiH signals at 4.3–5.3 ppm for poly(phenylsilane) and 4.26 ppm for PhSiH_3 , relative to the signal due to mesitylene at 2.15 ppm.

A solution for GPC analysis was similarly prepared.

3.10. Poly(*p*-methoxyphenylsilane) (**2b**)

Sticky semi-solid, yield 32% (after fractionation), $M_w = 2806$, $M_n = 793$, which corresponds to a 5.8-mer. ^1H -NMR: δ 3.25 (br, s, 3H), 4.35–5.05 (br, s, Si–H), 5.05–5.40 (br, s, Si–H in small cyclics), 6.40–7.70 (m, 4H). ^{13}C -NMR: δ 54.41, 114.14, 122.18, 138.62, 160.77. IR (C_6H_6): 3008, 2934, 2838, 2690, 2526, 2460, 2384, 2292, 2098, 1978, 1893, 1804, 1773, 1593, 1564, 1499, 1462, 1398, 1311, 1247, 1181, 1100, 1031, 959, 915, 743, 696, 600, 518, 493, 466 cm^{-1} . UV (GPC): λ_{max} 314 nm. Anal. Calc. for $(\text{C}_7\text{H}_8\text{OSi})_{5.8}\text{H}_2$, a 5.8-mer: C, 61.56; H, 6.16. Found: C, 61.54; H, 5.72%.

3.11. Oligo(*p*-dimethylaminophenylsilane) (**2c**)

Sticky oil, yield 39% (after fractionation), $M_w = 971$, $M_n = 564$, which corresponds to a 3.7-mer. ^1H -NMR: δ 2.45 (br, s, 6H), 4.80–5.42 (br, s, Si–H), 6.32–6.60 (m, 2H), 7.39–7.95 (m, 2H). ^{13}C -NMR: δ 39.74, 112.74, 116.94, 137.96, 151.08. IR (C_6H_6): 3088, 2888, 2814, 2148, 1885, 1601, 1543, 1516, 1481, 1446, 1359, 1325, 1284, 1230, 1207, 1118, 1064, 1006, 922, 808, 731, 677, 648, 629, 512, 474 cm^{-1} . UV (GPC): λ_{max} 326 nm. Anal. Calc. for $(\text{C}_8\text{H}_{11}\text{NSi})_{3.7}\text{H}_2$, a 3.7-mer: C, 64.14; H, 7.76. Found: C, 63.91; H, 7.34%.

3.12. Higher-molecular-weight fraction of poly(*p*-methylthiophenylsilane) (**2d**)

Sticky solid, yield 62% (after fractionation). ^1H -NMR: δ 1.96 (br, s, 3H), 4.38–4.81 (br, s, Si–H), 4.90–5.15 (br, s, Si–H in small cyclics), 6.65–7.65 (m, 4H). IR (C_6H_6): 3064, 3028, 3004, 2922, 2364, 2344, 2106, 1901, 1578, 1539, 1495, 1483, 1437, 1383, 1321, 1253, 1197, 1081, 1015, 957, 913, 803, 748, 731, 694, 650, 605, 520, 489, 464. UV (GPC): λ_{max} 314 nm. Anal.

Calc. for $\text{C}_7\text{H}_8\text{SSi}$: C, 55.21; H, 5.29. Found: C, 54.80; H, 5.16%.

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References

- [1] (a) M. Zeldin, K.J. Wynne, H.R. Allcock, Inorganic and Organometallic Polymers, ACS Symposium Series 360, American Chemical Society, Washington, DC, 1988. (b) J.M. Zeigler, F.W.G. Fearon, Silicon-Based Polymer Science: A Comprehensive Resources, Advances in Chemistry Series 224, American Chemical Society, Washington, DC, 1990.
- [2] (a) J. Maxka, F. Mitter, D. Powell, R. West, Organometallics 10 (1991) 660. (b) A.R. Wolff, I. Nozue, J. Maxka, R. West, J. Polym. Sci. Part A: Polym. Chem. 26 (1988) 701. (c) J. Michl, J.W. Dowing, T. Karatsu, A.J. McKinley, G. Poggi, G.M. Wallraff, R. Sooriyakumaran, R.D. Miller, Pure Appl. Chem. 60 (1988) 939.
- [3] (a) Y.P. Sun, G.M. Wallraff, R.D. Miller, J. Michl, J. Photochem. Photobiol. A: Chem. 62 (1992) 333. (b) Y.P. Sun, J. Michl, J. Am. Chem. Soc. 114 (1992) 8186. (c) Y.P. Sun, Y. Hamada, L.M. Huang, J. Maxka, J.S. Hsiao, R. West, J. Michl, J. Am. Chem. Soc. 114 (1992) 6301.
- [4] (a) P. Trefonas III, J.R. Damewood Jr., R. West, R.D. Miller, Organometallics 4 (1985) 1318. (b) Y.-P. Sun, R.D. Miller, R. Sooriyakumaran, J. Michl, J. Inorg. Organomet. Polym. 1 (1991) 3. (c) H.S. Plitt, J. Michl, Chem. Phys. Lett. 198 (1992) 430. (d) R. Imhof, D. Antic, D.E. David, J. Michl, J. Phys. Chem. A 101 (1997) 4579. (e) E.K. Karikari, A.J. Greso, B.L. Famer, R.D. Miller, J.F. Rabolt, Macromolecules 26 (1993) 3937. (f) S. Mazières, M.K. Raymond, G. Raabe, A. Prodi, J. Michl, J. Am. Chem. Soc. 119 (1997) 6682. (g) R. Imhof, H. Teramae, J. Michl, Chem. Phys. Lett. 270 (1997) 500.
- [5] (a) R.D. Miller, R. Sooriyakumaran, Macromolecules 21 (1988) 3120. (b) K. Pannell, J.M. Rozell, J.M. Zeigler, Macromolecules 21 (1988) 276.
- [6] (a) R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359. (b) R.D. Miller, D. Thompson, R. Sooriyakumaran, G.N. Fickes, J. Polym. Sci. Part A: Polym. Chem. 29 (1991) 813. (c) R.G. Jones, R.E. Benfield, P.J. Evans, S.J. Holder, J.A.M. Locke, J. Organomet. Chem. 521 (1996) 171, and references cited therein.
- [7] C. Aitken, J.F. Harrod, E. Samuel, J. Organomet. Chem. 269 (1985) C11.
- [8] For reviews see: (a) J.F. Harrod, in: K.J. Smith, E.C. Sanford (Eds.), Progress in Catalysis, Elsevier, Amsterdam, 1992, p. 147. (b) T.D. Tilley, Acc. Chem. Res. 26 (1993) 22, and references cited therein. (c) Y. Mu, J.F. Harrod, in: J.F. Harrod, R.M. Laine (Eds.), Inorganic and Organometallic Polymers and Oligomers, Kluwer, Dordrecht, the Netherlands, 1991, p. 23. (d) J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175.
- [9] (a) B.J. Grimmond, J.Y. Corey, Organometallics 18 (1999) 2223. (b) J.L. Huhmann, J.Y. Corey, N.P. Rath, J. Organomet. Chem. 533 (1997) 61. (c) G.L. Casty, C.G. Lugmair, N.S. Radu, T.D. Tilley, J.F. Walzer, D. Zargarian, Organometallics 16 (1997) 8. (d) N. Choi, S. Onozawa, T. Sakakura, M. Tanaka, Organometallics 16 (1997) 2765. (e) V.K. Dioumaev, J.F. Har-

- rod, J. *Organomet. Chem.* 521 (1996) 133. (f) V.K. Dioumaev, J.F. Harrod, *Organometallics* 15 (1996) 3859. (g) R.M. Shaltout, J.Y. Corey, *Tetrahedron* 51 (1995) 4309. (h) S. Bourg, R.J.P. Corriu, M. Enders, J.J.E. Moreau, *Organometallics* 14 (1995) 564. (i) V.K. Dioumaev, J.F. Harrod, *Organometallics* 13 (1994) 1548. (j) T. Imori, T.D. Tilley, *Polyhedron* 13 (1994) 2231. (k) H. Li, F. Gauvin, J.F. Harrod, *Organometallics* 12 (1993) 575. (l) J.Y. Corey, J.L. Huhmann, X.-H. Zhu, *Organometallics* 12 (1993) 1121. (m) J.P. Banovetz, H. Suzuki, R.M. Waymouth, *Organometallics* 12 (1993) 4700. (n) E. Hengge, M. Weinberger, *J. Organomet. Chem.* 443 (1993) 167. (o) T. Kobayashi, T. Sakakura, T. Hayashi, M. Yumura, M. Tanaka, *Chem. Lett.* 7 (1992) 1157. (p) J.Y. Corey, X.-H. Zhu, *J. Organomet. Chem.* 439 (1992) 1. (q) E. Hengge, M. Weinberger, *J. Organomet. Chem.* 441 (1992) 397. (r) J.F. Harrod, Y. Mu, E. Samuel, *Can. J. Chem.* 70 (1992) 2980. (s) H.-G. Woo, R.H. Heyn, T.D. Tilley, *J. Am. Chem. Soc.* 114 (1992) 5698. (t) H.-G. Woo, J.F. Walzer, T.D. Tilley, *J. Am. Chem. Soc.* 114 (1992) 7047. (u) J.F. Harrod, Y. Mu, E. Samuel, *Polyhedron* 10 (1991) 1239. (v) J.E. Durham, J.Y. Corey, W.J. Welsh, *Macromolecules* 24 (1991) 4823. (w) H.-G. Woo, J.F. Walzer, T.D. Tilley, *Macromolecules* 24 (1991) 6863. (x) J.Y. Corey, X.-H. Zhu, T.C. Bedard, L.D. Lange, *Organometallics* 10 (1991) 924. (y) C.M. Forsyth, S.P. Nolan, T.J. Marks, *Organometallics* 10 (1991) 2543. (z) J.P. Banovetz, K.M. Stein, R.M. Waymouth, *Organometallics* 10 (1991) 3430. (a') T. Sakakura, H.J. Lautenschlager, M. Nakajima, M. Tanaka, *Chem. Lett.* 6 (1991) 913. (b') F. Gauvin, J.F. Harrod, *Can. J. Chem.* 18 (1990) 638. (c') J.F. Harrod, T. Ziegler, V. Tschinke, *Organometallics* 9 (1990) 897. (d') C. Aitken, J.P. Barry, F. Gauvin, J.F. Harrod, A. Malek, D. Rousseau, *Organometallics* 8 (1989) 1732. (e') L.S. Chang, J.Y. Corey, *Organometallics* 8 (1989) 1885. (f') W.H. Campbell, T.K. Hilty, L. Yurga, *Organometallics* 8 (1989) 2615. (g') T. Nakano, H. Nakamura, Y. Nagai, *Chem. Lett.* 1 (1989) 83. (h') J.Y. Corey, L.S. Chang, E.R. Corey, *Organometallics* 6 (1987) 1595. (i') J.F. Harrod, S.S. Yun, *Organometallics* 6 (1987) 1381. (j') C. Aitken, J.F. Harrod, U.S. Gill, *Can. J. Chem.* 65 (1987) 1804.
- [10] (a) J.A. Ewen, *J. Am. Chem. Soc.* 106 (1984) 6355. (b) W. Kaminsky, K. Kulper, H. Brintzinger, F.R.W.P. Wild, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 507.
- [11] T. Repo, G. Jany, M. Salo, M. Palomo, M. Leskela, *J. Organomet. Chem.* 541 (1997) 363.
- [12] (a) E. Hengge, *J. Organomet. Chem. Libr.* 9 (1980) 261. (b) E. Hengge, D. Kovar, H.P. Sölldadl, *Monatsch. Chem.* 110 (1979) 805.
- [13] D.A. Stanislawski, R. West, *J. Organomet. Chem.* 204 (1981) 295.
- [14] Y. Obora, M. Tanaka, manuscript in preparation.
- [15] A. Antiñolo, G.S. Bristow, G.K. Campbell, A.W. Duff, P.B. Hitchcock, R.A. Kamarudin, M.F. Lappert, R.J. Norton, N. Sarjudeen, D.J.W. Winterborn, J.L. Atwood, W.E. Hunter, H. Zheng, *Polyhedron* 8 (1989) 1601.
- [16] (a) P.C. Wailes, H. Weigold, *J. Organomet. Chem.* 24 (1970) 405. (b) P.C. Wailes, H. Weigold, A.P. Bell, *J. Organomet. Chem.* 33 (1971) 181.
- [17] A.G. Massey, A.J. Park, *J. Organomet. Chem.* 2 (1964) 245.
- [18] S. Rozite, I. Mazeika, A. Gaukman, N. Erchak, E. Lukevics, *J. Organomet. Chem.* 348 (1988) 169.
- [19] S.D. Rosenberg, J.J. Walburn, H.E. Ramsden, *J. Org. Chem.* 21 (1957) 1606.
- [20] Y. Nagai, M. Ohtsuki, T. Nakano, H. Watanabe, *J. Organomet. Chem.* 35 (1972) 81.