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Dehydrocoupling of Phenylsilane Catalyzed by (Dimethylamino)alkyl- or Branched-Alkyl-Substituted Zirconocene Complexes: An Alternative Approach to Longer Chains

Nami Choi, Shun-ya Onozawa, Toshiyasu Sakakura, and Masato Tanaka*

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

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Summary: New zirconocene complexes $Cp^*[Cp(CH_2)_nNMe_2]ZrCl_2$ *(*$n = 2, 3$*) and* $Cp^*[Cp(CH_2)_nCH(CH_3)_2]ZrCl_2$ *(*$n = 1, 2$*) catalyze, in conjunction with 2 equiv of n-BuLi, dehydrocoupling polymerization of phenylsilane to afford high-molecular-weight poly(phenylsilanes) (*$M_w > 10^4$*).* ^{29}*Si NMR reveals that the microstructure of the resulting polymers is predominantly syndiotactic.*

Polysilanes have attracted much attention because of potential applications such as ceramics, electric conductors, photoconductors, photoresists, light-emitting devices, and nonlinear optical materials.[1] The Wurtz type coupling reaction of halosilanes with alkali metals is most widely utilized to synthesize high-molecular-weight polysilanes. Unfortunately, the procedure does not allow stereoselective polymerization or tolerate functional groups.[2] Since its discovery by Harrod and co-workers,[3] dehydrocoupling of primary silanes has been extensively studied as an alternative method, using a wide range of transition-metal catalysts. Group 4 metallocene complex catalysts appear to be more efficient in catalytic performance than the others.[3−5] However, several shortcomings still remain to be overcome. One is the low molecular weight of the product often encountered in the dehydrocoupling; only a few papers have disclosed the synthesis of polysilanes of acceptable molecular weights.[5q] Another aspect to be further scrutinized is the stereoregulation during the polymerization,[5k] which is, as compared with the Wurtz coupling of halosilanes, clearly an advantage of the transition-metal catalysis. Thus, exploration into new metallocene complex catalysts is indispensable to circumvent the shortcomings. With these considerations in mind, we have synthesized (dimethylamino)alkyl-substituted zirconocene derivatives (and their carbon analogues) and found that some of these new complexes, when used as catalysts in combination with *n*-butyllithium or methyllithium, afford respectable molecular weights ($M_w > 1.2 \times 10^4$) and syndioselectivities in the dehydrocoupling polymerization of phenylsilane.

New zirconium complexes were synthesized by the reaction of an appropriately substituted cyclopentadienyllithium with Cp^*ZrCl_3 or $CpZrCl_3$ in THF. For instance, to a THF (10 mL) suspension of Cp^*ZrCl_3 (1.00 g, 3.00 mmol) was added a THF (20 mL) solution of [(2-(dimethylamino)ethyl)cyclopentadienyl]lithium prepared by the reaction of (2-(dimethylamino)ethyl)cyclopentadiene (527 mg, 3.84 mmol) with *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol), and the mixture was stirred overnight. Evaporation of the solvent, addition of ether (40 mL), filtration, and evaporation of the filtrate left a solid material, which was recrystallized from pentane to give analytically pure **2a**[6] in 58% yield (760 mg) as pale yellow crystals. Other zirconium complexes, **1a** through **4b,** were similarly synthesized in 33−59% yields. The dimethylzirconium derivative **2c** or **2d** was generated quantitatively *in situ* from **2a** or **2b** by treatment with 2 equiv of methyllithium. Unlike a zirconium complex that has a (2-(dimethylamino)-1-phenylpropyl)cyclopentadienyl ligand,[7] NMR spectroscopy did not reveal any indication of the dimethylamino groups in these new complexes coordinating to the zirconium center in C_6D_6 at room temperature; ^{1}H NMR of **1a** through **3b** displayed only one singlet (δ 2.07−2.68) due to the NMe moiety. Likewise, only one quartet was found (δ 45.2−45.6) for the NMe group in ^{13}C NMR.

In a typical polymerization experiment, a stirred toluene (0.5 mL) solution of zirconium catalyst **2a** (4.5

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(6) **2a**: ^{1}H NMR (C_6D_6) δ 1.79 (s, 15H), 2.10 (s, 6H), 2.43 (t, $J = 7.2$ Hz, 2H), 2.93 (t, $J = 7.2$ Hz, 2H), 5.63 (t, $J = 2.6$ Hz, 2H), 5.84 (t, $J = 2.6$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 12.3 (q), 28.8 (t), 45.5 (q), 60.3 (t), 112.4 (d), 111.7 (d), 123.8 (s), 133.8 (s). Anal. Calcd for $C_{19}H_{29}NCl_2Zr$: C, 52.63; H, 6.73; N, 3.23. Found: C, 52.35; H, 6.91; N, 3.13.

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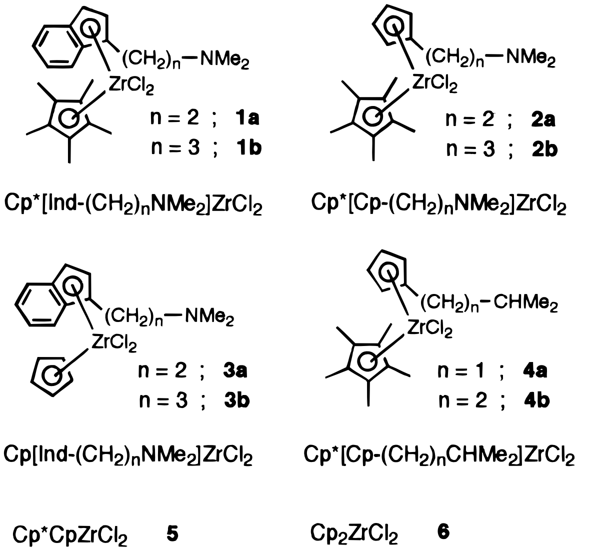
S0276-7333(97)00210-0 CCC: $14.00

Chart 1



mg, 0.010 mmol) was treated at −78 °C with *n*-butyllithium (12.5 μL of a 1.6 M solution in hexane, 0.020 mmol) in an argon-purged Schlenk tube, and the mixture was stirred at −78 °C for 1 h and at 0 °C for 30 min. To the resulting pale yellow solution was slowly added neat phenylsilane (1.0 mL) at 0 °C over 5 min. After vigorous hydrogen evolution ceased (ca. 60 min), the reddish brown mixture was stirred at 30 °C. The molecular weight and its distribution reached an ultimate steady state in 7 days. The resulting mixture was analyzed, after dilution with toluene (ca. 5 mL), by gel permeation chromatography (GPC, polystyrene standards), which showed a bimodal molecular weight distribution comprising linear poly(phenylsilane) of $M_w = 9.9 \times 10^3$ and cyclics. Fractionation by means of preparative GPC (eluent toluene) allowed isolation of the higher molecular weight fraction ($M_w = 1.07 \times 10^4$, $M_w/M_n = 1.8$) as a highly viscous colorless oil.[8,9]

$$n\mathrm{PhSiH_3} \longrightarrow \mathrm{-(SiPhH)_n-} + n\mathrm{H_2} \quad (1)$$

The results of screening reactions using the new (**1a** through **4b**) and conventional ($CpCp^*ZrCl_2$ (**5**), Cp_2ZrCl_2 (**6**)) catalysts are summarized in Table 1. Although introduction of the side arms grossly slows down the chain growth,[10] a great feature that the side arms can induce in most cases lies in their capability to enhance the ultimate molecular weight of the polysilanes as compared with their parent unsubstituted analogues. For instance, the M_w value of the higher molecular weight fraction obtained with the **2a**/*n*-BuLi system was 10.7×10^3 (run 5), while that with **5**/*n*-BuLi was only 1.9×10^3 (run 20). Another example is given in Figure 1, where the time course of the GPC profiles suggests steady chain growth in the **2b**/MeLi-catalyzed reaction (run 16) while the **6**/*n*-BuLi-catalyzed reaction (run 22) experiences the chain growth only in the beginning.[11] The same trends were more or less found with other substituted zirconocene catalysts, with the exceptions of **1a** and **1b**, which were not efficent in the polymerization catalysis presumably because of serious congestion. In general a (dimethylamino)ethyl group was slightly superior to a (dimethylamino)propyl group as the substituent; **2a**, which has (dimethylamino)ethyl, gave a polysilane with $M_w = 10.7 \times 10^3$ ($M_w/M_n = 1.8$) (run 5), and **2b**, which has (dimethylamino)propyl, afforded a polymer with $M_w = 7.06 \times 10^3$ ($M_w/M_n = 1.6$) (run 7) under similar conditions.

Table 1. Molecular Weight of Poly(phenylsialnes)[a]

run no.	catalyst	amt of catalyst (mol %)	raw polymer $M_w/10^3$ (M_w/M_n)	raw polymer % cyclics[b]	fractionation polymer $M_w/10^3$ (M_w/M_n)
1	**1a**/2*n*-BuLi	0.1	0.52 (1.1)	20	nd[c]
2	**1a**/2*n*-BuLi	0.5	0.54 (1.2)	55	nd
3	**1b**/2*n*-BuLi	0.1	2.26 (1.4)	40	nd
4	**1b**/2*n*-BuLi	0.5	2.57 (1.7)	48	2.90 (1.6)
5	**2a**/2*n*-BuLi	0.1	9.90 (2.4)	20	10.7 (1.8)
6	**2a**/2*n*-BuLi	0.5	5.89 (2.2)	24	nd
7	**2b**/2*n*-BuLi	0.1	6.90 (2.4)	20	7.06 (1.6)
8	**2b**/2*n*-BuLi	0.5	2.26 (1.4)	54	nd
9	**3a**/2*n*-BuLi	0.1	4.22 (2.0)	20	7.51 (1.6)
10	**3a**/2*n*-BuLi	0.5	3.40 (1.8)	55	nd
11	**3b**/2*n*-BuLi	0.1	2.55 (1.6)	20	4.88 (1.4)
12	**3b**/2*n*-BuLi	0.5	2.22 (1.6)	55	nd
13	**4a**/2*n*-BuLi	0.1	8.93 (2.5)	21	9.04 (2.1)
14	**4b**/2*n*-BuLi	0.1	6.25 (2.4)	30	8.96 (1.6)
15	**2a**/2MeLi	0.5	7.39 (1.6)	32	nd
16	**2b**/2MeLi	0.5	11.4 (2.5)	32	12.6 (1.8)
17	**5**/2*n*-BuLi/ 10EtNMe$_2$	0.1	2.64 (1.7)	27	2.97 (1.5)
18	**5**/2*n*-BuLi/ 10EtNMe$_2$	0.1	1.32 (1.5)	25	nd
19	**5**/2*n*-BuLi[d]	0.1	1.65 (1.6)	13	nd
20	**5**/2*n*-BuLi	0.1	1.75 (1.6)	15	1.90 (1.4)
21	**6**/2*n*-BuLi[d]	0.1	2.63 (1.7)	22	nd
22	**6**/2*n*-BuLi	0.1	3.35 (1.8)	22	4.05 (1.6)
23	**6**/2MeLi[e]	0.1	2.20 (1.6)	23	3.60 (1.5)

[a] Reactions were run at 30 °C for 7 days. Conversion of phenylsilane was always >99%. [b] Determined by ^{1}H NMR and GPC.[5k] [c] Not determined. [d] Reaction time 1 day. [e] Reaction time 5 h.

The favorable effect of the side arms is not peculiar to the (dimethylamino)alkyl structures. In practice, their carbon analogues such as 2-methylpropyl and 3-methylbutyl groups, when introduced onto the cyclopentadienyl ligand, also exerted similar influence. Thus, the molecular weight achieved by the use of **4a** or **4b** was not very different from that obtained under the same conditions using **2a** or **2b**, respectively (runs 5, 7, 13, and 14). Accordingly, the increases in molecular weights caused by the side arms is presumably due not to the coordinative interaction of the amino groups but rather simply to the steric influence boosted by the side arms. In agreement with this, an addition of $EtNMe_2$ (10 equiv relative to Zr; run 18) to the **5**/*n*-BuLi catalyst system did not exhibit any favorable effect as compared with the parent system (run 19). The lack of possible nitrogen coordination to the zirconium center in the starting complex (*vide supra*) is also in agreement with this statement. The favorable effect of the side arms is likely to stem from the induced modest steric demand that effectively prevents the formation of hydride-

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(8) Very recently Jutzi and co-workers reported dehydrogenative coupling of phenylsilanes with a diisopropylamino-bearing zirconocene catalyst, which provided atactic oligosilanes.[5v]

(9) Polyphenylsilanes obtained in our experiments were usually very viscous oils, as was reported by Waymouth and co-workers.[5k]

(10) Application of a dynamic vacuum[4b] facilitated the chain growth. A separate experiment of the same procedure except for the concentration of **2a** (1.0 mol %) and the pressure of the reaction system (ca. 10 Torr) gave a high-molecular-weight fraction of $M_w = 9.8 \times 10^3$ ($M_w/M_n = 2.28$) in only 5 h.

(11) As evidenced by Figure 1, the content of the low-molecular-weight fraction (cyclics) was almost steady during the polymerization process.

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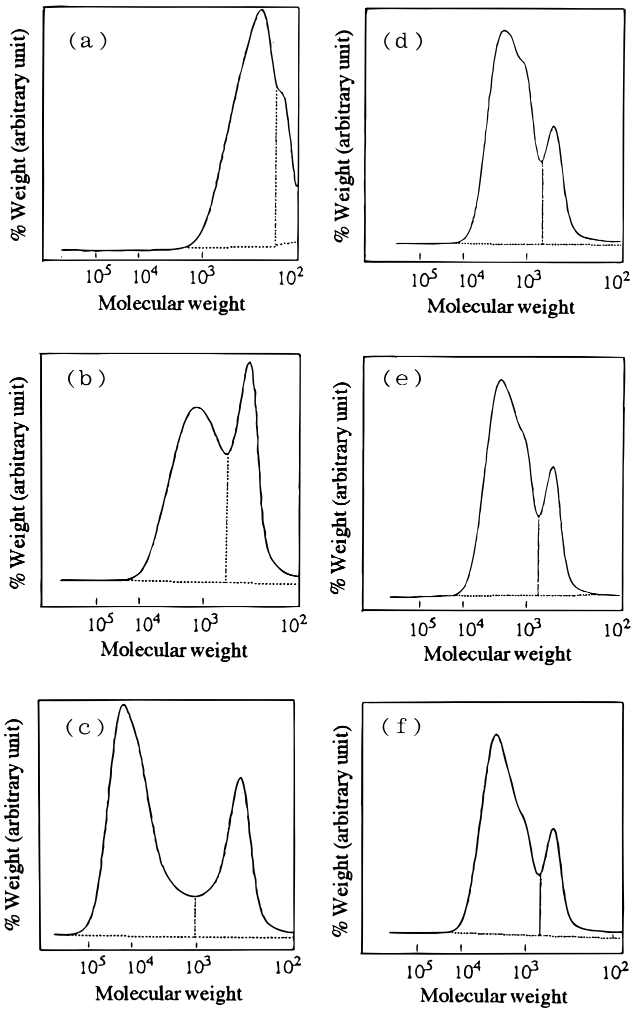

Figure 1. Time course of GPC profiles in runs 16 (left) and 22 (right). Reaction time: (a, d) 5 h; (b, e) 1 day; (c, f) 7 days.

bridged inactive dimer[12] without prohibiting the four-centered transition state of a lower activation energy pathway.[4b]

To characterize the microstructures of the poly(phenylsilanes), crude polymerization mixtures were separated by preparative GPC (eluent toluene) to isolate higher molecular weight fractions. ^{29}Si NMR of a poly(phenylsilane) isolated from run 23 (**6**/2*n*-BuLi) displayed broad signals in the region δ −48 to −65 (Figure 2a), indicative of an atactic structure. A sample obtained from run 19 (**5**/2*n*-BuLi) also displayed a slightly less broad signal within a narrower range (δ −55 to −65), suggesting that the polymer structure was essentially the same (Figure 2b). In sharp contrast, polymer samples isolated from the reaction mixtures of runs 5 (**2a**/2*n*-BuLi, 0.1 mol %) and 16 (**2b**/2MeLi, 0.5 mol %) displayed relatively sharp multiplets in a much narrower range (δ −59.5 to −62.5) (Figure 2c,d) as was observed with the [ethylenebis(indenyl)]zirconium catalyst.[5k] On the basis of Waymouth's argument, we conclude that the polysilane obtained by the use of **2a**/2*n*-BuLi (run 5) or **2b**/2MeLi (run 16) is highly syndiotactic. Similar ^{29}Si NMR studies of the poly(phenylsilanes) have revealed the following decreasing order of stereoregularity (syndiotacticity): (**1a**, **1b**) **2a**, **2b**, **4a**, **4b** ≫ **5** > **3a**, **3b**, **6**. This trend clearly suggests that only those complexes that have both Cp (inclusive of a indenyl ligand) and Cp* derivatives as ligands bound to zirconium can be more or less syndioselective (**1a**, **1b**, **2a**, **2b**, **4a**, **4b**, **5**).[13]

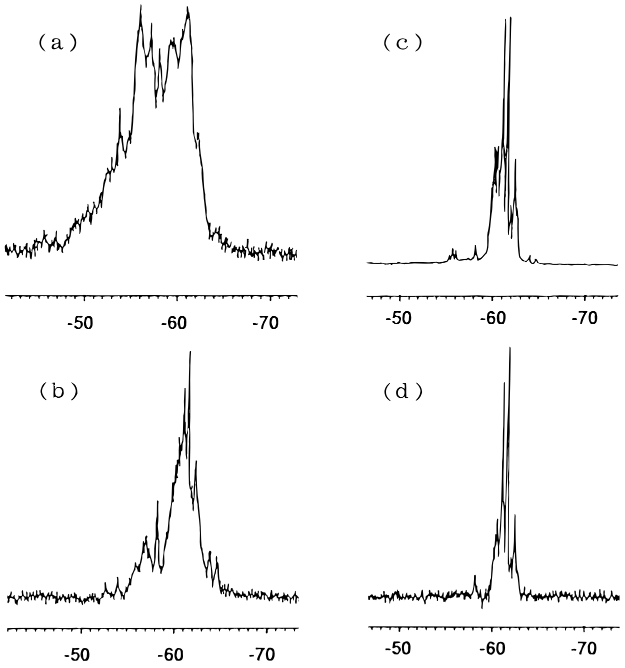

Figure 2. ^{29}Si NMR spectra of poly(phenylsilanes) (higher molecular weight fractions) obtained from (a) run 23, (b) run 19, (c) run 5, and (d) run 16.

These results, in conjunction with the arguments in the previous section, prompt us to conclude that only those catalysts that have a modestly congested reaction site can (1) sustain the chain growth, albeit sluggishly, to ultimately achieve high molecular weights and (2) exert stereoregulation during the chain growth. In this respect, **1a** and **1b**, although they prefer syndiotacticity, are too congested to achieve high molecular weights and, in contrast, **3a** and **3b** are not sufficiently congested to effectively control the stereodifferentiation. The key role played by the (dimethylamino)alkyl (and branched alkyl) groups introduced to the Cp ring is steric: the modest congestion reduces the catalytic activity and prevents possible back-biting but safely retains the active site to elongate the polymer chain and thus enables the eventual achievement of higher molecular weights. In addition the congestion is obviously beneficial in controlling the stereodifferentiation involved in the chain growth.

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Supporting Information Available: Text describing experimental details and spectral and/or analytical data for zirconocene complexes (**1a** thourgh **4b**) and polyphenylsilane (5 pages). Ordering information is given on any current masthead page.

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[13] Waymouth and co-workers reported that polymerization of phenylsilane at a high concentration using **6** or Cp_2ZrHCl resulted in syndiotactic polysilane formation.[5k]