Rapid, Highly Linear-Selective Dehydrocoupling of Phenylsilane with New Group 4 Metallocene-Based Combination Catalysts

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The dehydrocoupling of phenylsilane with Cp'_2MCl_2/Red-Al (Cp' = C_5H_5 or C_5Me_5; M = Ti, Zr, Hf; Red-Al = $Na[H_2Al(OCH_2CH_2OMe)_2]$) combination catalysts rapidly produces linear polyphenylsilanes, and the linear selectivity drastically decreases in the order of $Cp(C_5Me_5)Hf > Cp_2Hf > Cp(C_5Me_5)Zr > Cp_2Zr > Cp_2Ti$; in the presence of solvent (neat > toluene > THF) and 4 Å molecular sieve; with heating.

Polysilanes are an interesting class of inorganic polymers and can be used in the versatile applications such as silicon ceramics, photoelectric conductors, photoresists, and nonlinear optics.[1-3] As an alternative to the conventional Wurtz-type reductive coupling of halosilanes using alkali metal dispersion, the group 4 metallocene-catalyzed dehydrocoupling of hydrosilanes was discovered by Harrod and has been intensively studied by many researchers.[4-6] However, the dehydrocoupling of hydrosilanes generally produces a mixture of linear polymers and cyclic oligomers, leading to decline in molecular weight of the resulting polymers. Therefore, the careful design of new group 4 metallocene catalytic system for producing linear polymer selectively is important. Tilley[5] and Waymouth[7] synthesized the high-molecular-weight polyphenylsilanes with number-average molecular weight (M_n) of *ca.* 5300 and 4700, respectively, by carefully controlling dehydrocoupling reaction conditions of phenylsilane using zirconocene catalysts. Tanaka[8] and Harrod[9] also successfully prepared polyphenylsilanes with M_n of *ca.* 4600 and 7300, respectively, from the dehydrocoupling of phenylsilane by using the $[Me_2N(CH_2)_3\text{-}H_4C_5](Me_5C_5)ZrCl_2/2MeLi$ and $Cp(Me_5C_5)ZrCl_2/2BuLi/(C_6F_5)_3B$ combination catalysts, respectively. Here we report the rapid, highly linear-selective dehydrocoupling of phenylsilane by the new type of $Cp'MCl_2$/Red-Al (Cp' = C_5H_5 or C_5Me_5; M = Ti, Zr, Hf) combination catalyst, *in situ*-generated group 4 metallocene.

In a typical dehydrocoupling experiment, $PhSiH_3$ (1.0 mL, 8.1 mmol) was slowly added at 25 ℃ to a Schlenk flask containing Cp_2ZrCl_2 (23.4 mg, 0.08 mmol) and Red-Al (24 μL, 0.08 mmol; 3.4 M solution in toluene). The reaction mixture immediately turned light yellow, and the reaction medium became rapidly viscous with vigorous evolution of hydrogen gas. The ^1H NMR spectrum of the reaction mixture showed that phenylsilane was completely converted to polyphenylsilane within 1 h. However, the mixture was stirred under a stream of nitrogen for 24 h to reach the steady state of polymer molecular weight distribution. The catalyst was allowed to oxidize by exposure to the air, and the solution was then passed rapidly through a Florisil column (100-200 mesh, 20 cm x 2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded clear tacky product (eq 1).

$$nPhSiH_3 \xrightarrow[Cp_2ZrCl_2/Red\text{-}Al]{-H_2} -\!\!\left(SiPhH \right)_n\!\!- \qquad (1)$$

The product was analyzed by gel permeation chromatography (GPC) and ^1H NMR analytical techniques. The molecular weight distribution obtained by the GPC trace was bimodal, containing high-molecular-weight linear polysilane and low-molecular-weight cyclic oligosilane (M_w = ~500). The peaks corresponding to SiH in the ^1H NMR

Table 1. Results for the dehydropolymerization of phenylsilane with group 4 metallocene-based combination catalysts[a]

Catalyst	M_w	M_w/M_n[b]	%Cyclics[c]
Cp_2TiCl_2/Red-Al	1870	1.30	36
Cp_2TiCl_2/Red-Al/MS4A[d]	710	1.15	62
Cp_2ZrCl_2/Red-Al	3910	1.74	8
Cp_2ZrCl_2/2Red-Al[e]	-	-	-
Cp_2ZrCl_2/Red-Al[f]	4870	1.73	11
Cp_2ZrCl_2/Red-Al[g]	2600	1.55	20
Cp_2ZrCl_2/Red-Al[h]	2070	1.48	27
Cp_2ZrCl_2/Red-Al[i]	1890	1.36	30
Cp_2ZrCl_2/Red-Al[j]	4030	1.69	13
Cp_2ZrCl_2/Red-Al[k]	890	1.50	nd[l]
$Cp(C_5Me_5)ZrCl_2$/Red-Al	5140	1.86	5
$(C_5Me_5)_2ZrCl_2$/Red-Al	mixture of dimer, trimer, and tetramer		
Cp_2HfCl_2/Red-Al	7230	1.90	1
Cp_2HfCl_2/Red-Al/MS4A[d]	1930	1.38	30
Cp_2HfCl_2/2Red-Al[e]	-	-	-
$Cp(C_5Me_5)HfCl_2$/Red-Al	7510	1.92	<1

[a] Reactions in neat at 25 ℃ for 1 day, a catalyst concentration of 1 mol%, and conversion of phenylsilane of >99%, except where stated otherwise. [b] The molecular weights (in Dalton, estimated to be reliable to within ±5%) were measured by GPC and calibrated with respect to polystyrene standards. [c] Determined by ^1H NMR and GPC. [d] [MS4A] = 1000wt% of metallocene dichloride. [e] No reaction observed. [f] 5 mol% catalyst used in this reaction. [g] The $PhSiH_3$/toluene ratio is 5/1. [h] The $PhSiH_3$/THF ratio is 5/1. [i] Reaction temperature 80 ℃. [j] Reaction time 5 days. [k] $PhCH_2SiH_3$ used in this reaction. [l] Not determined.

spectrum were visually separated as linear polysilane (4.2 ~ 4.8 ppm) and cyclic oligosilane (4.9 ~ 5.3 ppm). The formation of the cyclic oligosilane was estimated by integration of the GPC peaks and ^{1}H NMR peaks, and was used as cross-checking means of the cyclic/linear ratio. The two methods were roughly correlative. Similarly, the other group 4 metallocene-based combination catalysts were tested for the dehydrocoupling of phenylsilane under various reaction conditions. The dehydropolymerization results are summerized in Table 1.

As shown in Table 1, the dehydrocoupling of phenylsilane with Cp'_2MCl_2/Red-Al combination catalysts rapidly produces linear polyphenylsilanes. The linear selectivity drastically increases in the order of Cp_2Ti (64%) < Cp_2Zr (92%) < $Cp(C_5Me_5)Zr$ (95%) < Cp_2Hf (99%) < $Cp(C_5Me_5)Hf$ (<99%). The change of linear selectivity is more steep than other catalytic combination systems: Cp_2TiCl_2/2MeLi (55%) < Cp_2ZrCl_2/2MeLi (75%), Cp_2ZrCl_2/2BuLi (75%) < $Cp(C_5Me_5)ZrCl_2$/2BuLi (80%) < Cp_2HfCl_2/2MeLi (85%).[9,10] The coordinating environment around metal center at the Cp_2MCl_2/Red-Al combination catalysts could be different from other catalytic system such as Cp_2MCl_2/2R'Li.[7,8,10,12] Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; $Na[H_2Al(OCH_2CH_2OMe)_2]$) will be quantitatively converted into $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ after reacting with dichlorometallocene. The coordinating structure of the present catalytic system might be similar to or different from the zwitter ionic structure of the $Cp_2ZrCl_2/2BuLi/(C_6F_5)_3B$ catalytic system.[9,11] The $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety may influence by simply coordinating to the metal through H, Cl-bridge or H, OMe-bridge between group 4 metal and Al metal. In any case, the favorable steric demand exerted by the Cp ring and cocatalyst moiety could prevent the formation of inactive dimer of metallocene hydride and suppress the cyclic oligomer formation by chain cleavage reaction, leading to the greater chain elongation.[8,9] However, overriding steric demand should result in low dehydrocoupling activity. The order of dehydrocoupling activity for the various zirconocenes is found to be the same as the sequence of Tilley[5] and Harrod[9]: $(C_5Me_5)_2Zr$ << Cp_2Zr < $Cp(C_5Me_5)Zr$. The $(C_5Me_5)_2ZrCl_2$/Red-Al combination catalyst thus slowly produces a mixture of dimer, trimer, and tetramer. The dehydrocoupling of $PhCH_2SiH_3$ yields only low-molecular weight oligomers because an alkylsilane $PhCH_2SiH_3$ was less reactive than an arylsilane $PhSiH_3$, as seen in other catalyst system[12]. The molecular weight of polymer is influenced by higher catalyst concentration (1 mol% vs 5 mol%), but it is a little affected by longer reaction time (1 day vs 5 days). The linear selectivity and molecular weight decrease with adding solvent and with heating, which was also similarly observed in other catalytic systems.[5,9] This is because the dilution and heating could hamper the tight coordination of $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety to the metal center. Interestingly, the linear selectivity and molecular weight decrease drastically by adding 4 Å molecular sieve (MS4A). We suspect that the interaction of $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety with MS4A might prevent the close coordination of $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety to the metal center. The MS4A is known to significantly increase the optical yield of products in the some metal complex-mediated organic reactions.[13,14] The exact molar ratio of Red-Al to dichlorometallocene is necessary to replace both chlorines to attain high reactivity. This supports the results of previous studies by Harrod and Tilley.[10,15] The inactivity observed for higher molar ratio of Red-Al to dichlorometallocene could be due to over-complexation of Red-Al moieties on the metal, blocking the empty coordination site necessary for the dehydrocoupling of silane. The present experimental results suggest that the better catalyst affording higher linear-selectivity and higher-molecular-weight polymer can be properly designed by tuning the steric and electronic character of the catalyst environment including ligand and cocatalyst moieties. The detailed studies are in progress and will be separately reported as a full article.

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References and Notes

1 R. West, *J. Organomet. Chem.*, **300**, 327 (1986).

2 "Silicon-Based Polymer Science", Advances in Chemistry Series 224 ed by J. M. Ziegler and F. W. G. Fearon, American Chemical Society, Washington, D.C. (1990).

3 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989) and references cited therein.

4 F. Gauvin, J. F. Harrod, and H. G. Woo, *Adv. Organomet. Chem.*, **42**, 363 (1998) and references cited therein.

5 T. D. Tilley, *Acc. Chem. Res.* **26**, 22 (1993) and references cited therein.

6 J. Y. Corey, *Adv. Silicon. Chem.*, **1**, 327 (1991) and references cited therein.

7 J. P. Banovetz, R. M. Stein, and R. M. Waymouth, *Organometallics*, **10**, 3430 (1991).

8 N. Choi, S.-Y. Onozawa, T. Sakakura, and M. Tanaka, *Organometallics*, **16**, 2765 (1997).

9 V. K. Dioumaev and J. F. Harrod, *Organometallics*, **13**, 1548 (1994).

10 H. Li, F. Gauvin, and J. F. Harrod, *Organometallics*, **12**, 575 (1993).

11 V. K. Dioumaev and J. F. Harrod, *Organometallics*, **15**, 3859 (1996).

12 W. H. Campbell, T. K. Hilty, and L. Yurga, *Organometallics*, **8**, 2615 (1989).

13 E. Hagiwara, A. Fujii, and M. Sodeoka, *J. Am. Chem. Soc.*, **120**, 2474 (1998).

14 T. Iida, N. Yamamoto, S. Matsunaga, H.-G. Woo, and M. Shibasaki, *Angew. Chem., Int. Ed. Engl.*, **37**, 2223 (1998).

15 T. D. Tilley, *Comments Inorg. Chem.*, **10**, 37 (1990).