Substituent Effects on Catalytic Synthesis and Properties of Poly(phenylsilane)

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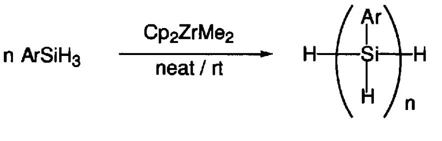
Catalytic dehydrogenative polymerization of phenylsilanes with electron-withdrawing substituents using dimethylzirconocene as a catalyst afforded the corresponding polysilanes with rather high molecular weights. Significant substituent effects were observed on the electronic spectra of the polymers.

Polysilanes have attracted much attention owing to their unique electronic properties based on the delocalized σ-electrons over the silicon backbone and their potential applications for the new materials such as microelectronics and integrated optics.[1] Although polysilanes having functional groups are interesting synthetic targets to explore the novel optoelectronic properties of the polymers, the direct syntheses by the conventional Wurtz-type coupling polymerizations are usually difficult.[2,3] While the dehydrogenative coupling of trihydrosilanes catalyzed by group-4 metallocenes[4] in mild condition provides a possible way to introduce the functionality into the polysilane, the molecular weights of the resulting polymers are usually low. We have investigated polymerization of various phenylsilanes using dimethylzirconocene as a catalyst and found that phenylsilanes with electron-withdrawing substituents produce the corresponding poly(phenylsilane)s with rather high molecular weights. Unique absorption spectra of these polysilanes are also demonstrated.

In a typical polymerization experiment, a mixture of dimethylzirconocene (1 mol%) and a substituted phenylsilane (0.5 ml) in a Schlenk flask was stirred at room temperature in a glovebox (Eq. 1). The reaction started with evolution of hydrogen gas and produced after a few days a viscous oil or solids depending on the substituents. After the catalyst was oxidized by air exposure, the product mixture was diluted with toluene and then filtered through a Florisil column (100 ~ 200 mesh, 10 cm x 2 cm ϕ). Removal of volatiles yielded off-white tacky solids. The resulting polymers were usually soluble in organic solvents, but less soluble if the molecular weights are high. The polymers were analyzed by ^{1}H and ^{29}Si NMR spectroscopies[5] and gel permeation chromatography (GPC; polystyrene standards).



$$n\,ArSiH_3 \xrightarrow[\text{neat / rt}]{Cp_2ZrMe_2} H\!\left(\!\begin{array}{c} Ar \\ | \\ -Si- \\ | \\ H \end{array}\!\right)_{\!n}\!H \qquad (1)$$

Table 1. Various substituted poly(phenylsilane)s [$(ArSiH)_n$] prepared by the dehydrogenative coupling using Cp_2ZrMe_2[a]

Entry	Ar	Time/d	$\overline{M}_w/10^3$ [b]	$\overline{M}_w/\overline{M}_n$	Yield/%[c]
1	Ph	0.5	3.6 (0.6)	1.6	94 (32)
2	p-$CH_3C_6H_4$	1	2.3 (0.3)	1.5	90 (27)
3	m,m'-$(CH_3)_2C_6H_3$	2	2.2 (0.2)	1.5	85 (26)
4	p-$CH_3OC_6H_4$	0.8	3.5 (0.5)	1.7	82 (30)
5	p-$(CH_3)_2CHOC_6H_4$	2	2.8 (0.1)	1.3	98 (12)
6[d]	p-$(CH_3)_2NC_6H_4$	7	0.6	1.5	56 (–)[e]
7[f]	p-FC_6H_4	2	7.0 (0.2)	1.9	81 (21)
8[f]	p-$CF_3C_6H_4$	2	9.9 (1.2)	1.4	64 (9)
9	m-$CF_3C_6H_4$	2	17.2 (2.0)	1.9	95 (16)
10	m,m'-$(CF_3)_2C_6H_3$	2	1.0 (0.3)	1.2	98 (–)[e]
11	C_6F_5	2	1.1 (0.3)	1.5	76 (–)[e]

[a] Neat, unless otherwise noted. [b] The average of 2 - 6 experiments. The standard deviation is shown in parentheses. [c] The population of the cyclic oligomers in the polymer determined by ^{1}H NMR is in parentheses. [d] In toluene. [e] Not determined. [f] The catalyst could not be removed.

The results of the catalytic polymerization are summarized in Table 1. The weight-average molecular weight (M_w) of the unsubstituted poly(phenylsilane) obtained in our experiment was 3500 (entry 1), being comparable to those reported.[4] Polymerization of phenylsilanes substituted by electron-donating groups afforded the corresponding poly(phenylsilane)s with Mw of 2100 ~ 4200 (entries 2 ~ 6), which were a little lower or comparable with that of poly(phenylsilane); phenylsilanes with electron-donating substituents have been reported[6] not to polymerize with a conventional zirconocene catalyst system. p-(Dimethylamino)phenylsilane gave only a low-molecular-weight oligomer (entry 6), probably because of the strong coordination ability of an amino group to the metal center.[7] In contrast, phenylsilanes with electron-withdrawing groups afforded polymers with high molecular weights, except for entries 10 and 11. m-(Trifluoromethyl)phenylsilane produced the polymer with M_w of 17.2 x 10^3 (entry 9). The molecular weights are the highest among those for poly(phenylsilane)s obtained by dehydrogenative coupling; recent records were polysilanes with M_w of 13.8 x 10^3 and M_w of 11.9 x 10^3 reported by Harrod[8] and Tanaka,[6] respectively. On the other hand, the polymerization of m,m'-bis(trifluoromethyl)phenylsilane and (pentafluoro)phenylsilane gave only low-molecular-weight oligomers.[5] The results indicate that the degree of polymerization is strongly affected by both electronic and steric effects of the substituents. Electron-withdrawing and less bulky substituents are favorable for the catalytic polymerization.

Whereas the σ-bond metathesis is the most accepted mechanism for the polymerization,[4] the electronic nature of the transition state still remains open. The mechanism for dehydrogenative coupling of phenylsilanes should be consistent with the present substituent effects. It is noteworthy that Waymouth et al. have reported that the polymerization of m- and p-(trifluoromethyl)phenylsilanes catalyzed by $Cp_2Zr[Si(SiMe_3)_3]Me$ is faster than that of phenylsilane, while the molecular weights of their polymers are very low (M_w = 1540 ~ 2870);[9] it is suggested that the molecular weight is related to the polymerization rate but also sensitive to the reaction conditions.

The ^{1}H NMR spectra of these substituted poly(phenylsilane)s in benzene-d_6 exhibited a major broad signal at

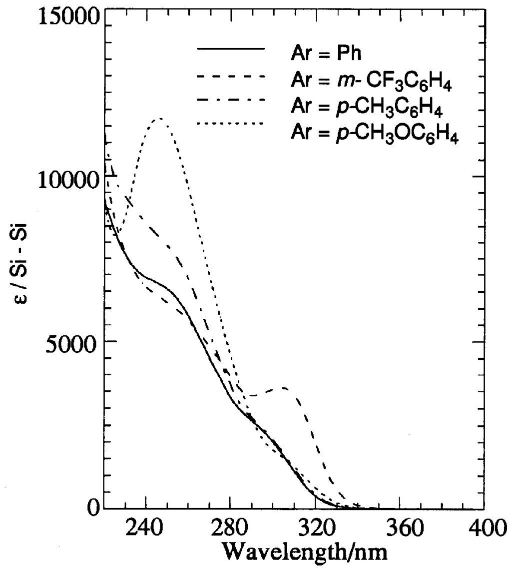


Figure 1. UV spectra of various substituted poly(phenylsilane)s [(ArSiH)$_n$] (THF, 25 °C).

3.6 ~ 4.8 ppm due to SiH for linear polysilane together with a minor broad signal at 4.8 ~ 5.6 ppm assignable to SiH in cyclic oligomers.[4] In the ^{29}Si NMR spectra of the polymers, a broad resonance with three peaks was observed in the range of –53 ~ –66 ppm, in substantially consistent with the reported feature for poly(phenylsilane).[10]

Figure 1 shows UV absorption spectra of a series of substituted poly(phenylsilane)s in THF. These polysilanes showed two absorption maxima (λ_{max}) at ca. 250 nm and ca. 300 nm; the absorption coefficient per Si-Si bond of the former band (ε_1) is much larger than that of the latter (ε_2). The absorption maxima of these polysilanes are remarkably blue-shifted in comparison with those of poly(diarylsilane)s; the λ_{max} for the σ-σ* transition of poly(di-*p*-ethylphenylsilane) is reported to be 389 nm (ε/Si-Si = 10.2 x 10^3).[11] The large blue-shift in poly(phenylsilane)s is indicative of the folded conformation of the main chain, as suggested by Waymouth et al.[3d] Interestingly, $\varepsilon_1/\varepsilon_2$ ratios in the poly(phenysilane)s are strongly dependent on the electronic effects of the substituents; the $\varepsilon_1/\varepsilon_2$ value is increased by an electron-donating substituent but decreased by an electron-withdrawing substituent.[12] The σ→σ* and σ→π* transitions are candidates of the electronic transitions responsible for these two bands. On the basis of the intense absorption of the longer-wavelengh band observed in the polymer derived from *m*-(trifluoromethyl)phenylsilane and the expected low intensity of the σ→σ* band for the polysilanes with the folded silicon chain, the 300 nm band is tentatively assigned to be the σ→σ* transition coupled significantly with the σ→π* transition. Further works on the absorption and emission properties of these poly(phenylsilane)s are in progress.

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References and Notes

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5 Poly(*m,m'*-dimethylphenylsilane): ^{1}H NMR (300 MHz, C_6D_6, *δ*) 1.99 (m, Me), 4.1 ~ 5.6 (m, SiH), 6.5 ~ 7.8 (m, Ar*H*); ^{29}Si NMR (59.6 MHz, C_6D_6, *δ*) –62 ~ –53. Poly[(*p*-methoxy)phenylsilane]: ^{1}H NMR (300 MHz, C_6D_6, *δ*) 3.21 (m, OMe), 4.3 ~ 5.6 (m, SiH), 6.6 ~ 8.0 (m, Ar*H*); ^{29}Si NMR (59.6 MHz, C_6D_6, *δ*) –63 ~ –54. Poly[(*p*-isopropoxy)phenylsilane]: ^{1}H NMR (300 MHz, C_6D_6, *δ*) 1.05 (m, OPr-*i*), 4.1 ~ 4.2 (m, SiH), 6.6 ~ 6.8 (m, Ar*H*), 7.3 ~ 8.1 (m, Ar*H*); ^{29}Si NMR (59.6 MHz, C_6D_6, *δ*) –66 ~ –53. Poly[(*p*-fluoro)phenylsilane]: ^{1}H NMR (300 MHz, C_6D_6, *δ*) 3.9 ~ 4.6 (m, SiH), 6.4 ~ 7.7 (Ar*H*); ^{29}Si NMR (59.6 MHz, C_6D_6, *δ*) –65 ~ –54. Poly[(*m*-trifluoromethyl)phenylsilane]: ^{1}H NMR (300 MHz, C_6D_6, *δ*) 3.6 ~ 5.2 (m, SiH), 6.2 ~ 8.1 (Ar*H*); ^{29}Si NMR (59.6 MHz, C_6D_6, *d*) –68 ~ –52. Poly[(*p*-trifluoromethyl)phenylsilane]: ^{1}H NMR (300 MHz, THF-d_8, *δ*) 3.6 ~ 5.1 (m, SiH), 6.6 ~ 7.9 (Ar*H*); ^{29}Si NMR (59.6 MHz, THF-d_8, *δ*) –64 ~ –60.

The structure of the polymers obtained from (pentafluoro)-phenylsilane and *m,m'*-bis(trifluoromethyl)phenylsilane was not determined because of their low solubility in the solvents. These two polymers may not be the linear polysilanes.

6 Y. Obora and M. Tanaka, 45th Symposium on Organometallic Chemistry, Japan, Tokyo, September, 1998, Abstr., No. PA116.

7 Since (dimethylamino)phenylsilane is solid, the experiment of entry 6 was performed in a toluene solution. This diluted condition will be another reason for the production of the low-molecular-weight polysilane; high concentration or neat condition is known to be necessary for good results in the dehydrogenative polymerization with metallocene catalysts.[4]

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10 Since the NMR signals of our polysilanes are rather broad, we assigned them as atactic structures, although there is a controversy on stereochemistry of poly(phenylsilane) obtained by dehydrogenative coupling. J. P. Banovetz, K. M. Stain, and R. M. Waymouth, *Organometallics*, **10**, 3430 (1991); N. Choi, S.-Y. Onozawa, T. Sakakura, and M. Tanaka, *Organometallics*, **16**, 2765 (1997); B. J. Grimmond and J. Y. Corey, *Organometallics*, **18**, 2223 (1999); V. K. Dioumaev, K. Rahimian, F. Gauvin, and J. F. Harrod, *Organometallics*, **18**, 2249 (1999).

11 R. D. Miller and R. Sooriyakumaran, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 823 (1983).

12 UV spectra of *p*-FC_6H_4- and *p*-$CF_3C_6H_4$-substituted polysilanes are not given in Figure 1, because the catalyst used could not be removed from these polysilanes. The $\varepsilon_1/\varepsilon_2$ ratios for these polysilanes are however similar to that for *m*-$CF_3C_6H_4$-substituted polysilanes.