

New Entry to the Construction of Si–Si Linkages: Sm/SmI₂-Induced Efficient Reductive Coupling of Organochlorosilanes

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Using the Sm/SmI₂ mixed system, organochlorosilanes (R₃SiCl) undergo reductive dimerization reactions to give the corresponding disilanes in moderate to good yields. The Sm/SmI₂ mixed system also can be applied successfully to the polymerization of 1,4-bis(dimethylchlorosilyl)benzene and dichloromethylphenylsilane, which affords the σ - π conjugate poly(disilanylenephylene) ($M_w/M_n = 1.2$, $M_n = 2480$) and poly(methylphenyl)silane ($M_w/M_n = 1.5$, $M_n = 4650$) with a sharp molecular distribution.

Introduction

Reductive dimerization of organochlorosilanes is a well-known method for the construction of the Si–Si linkage.^{1–3} Although synthetic methods such as the electroreduction of chlorosilanes,⁴ dehydrogenative coupling of primary silanes,⁵

sonochemical coupling of dichlorosilanes,⁶ and anionic polymerization of masked disilenes⁷ have been reported, the Wurtz-type condensation of halosilanes by alkali metals such as metallic sodium still is used most frequently.⁸ However, the Wurtz coupling method often requires drastic reaction conditions and the formation of disiloxanes resulting from an oxide film on the sodium surface is an undesirable side reaction. The higher reducing potential of alkali metals as well as the highly exothermic nature of the alkali-metal-mediated reaction makes this method inapplicable for the synthesis of a variety of functional silicon compounds. Therefore, milder, safer, and more efficient methods are needed.

Samarium diiodide (SmI₂) has been widely employed as a single-electron reducing agent in organic synthesis.⁹ Thus, samarium diiodide in THF was considered as a mild reducing agent for dimerization of chlorosilanes. However, in the reaction of chlorosilanes with SmI₂ in THF, the in situ formed iodosilanes (from chlorosilanes and SmI₂) induce silylative ring opening of the THF solvent, and the desired reductive dimerization of triorganochlorosilanes does not take place.¹⁰ Recently, we have found that the combination of samarium diiodide and samarium metal, i.e., the Sm/SmI₂ system, exhibits a higher reducing ability compared that of with SmI₂ or Sm metal alone.¹¹ Furthermore, Sm/SmI₂ can be prepared in solvents other than THF, e.g., in 1,2-dimethoxyethane (DME), which does not undergo ethereal C–O bond cleavage by iodosilanes under the conditions used for Sm/SmI₂-induced reductions. Herein we report a novel Sm/SmI₂-induced reductive coupling of orga-

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Table 1. Sm/SmI₂-Induced Reductive Dimerization of Dimethylphenylchlorosilane^a

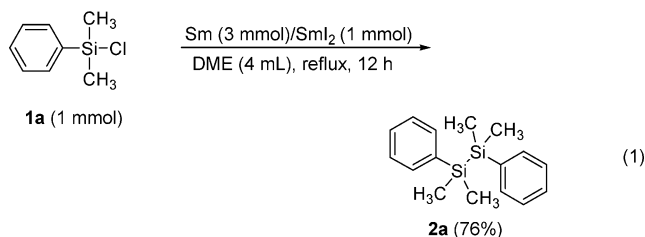
run no.	amt of Sm (mmol)	amt of SmI ₂ (mmol)	solvent	reacn time (h)	yield of 2a ^b (%)
1	3	1	THF	24	0 ^c
2	3	1	CH ₃ CN	24	NR
3		1	DME	12	NR
4		3	DME	12	trace
5	3	1	DME	5	46 ^d
6	3	1	DME	12	76 ^d
7	3	0.5	DME	24	54 ^d
8 ^e	3	1	DME	36	NR
9	3		DME	24	NR

^a Reaction conditions: PhMe₂SiCl (1 mmol), solvent (4 mL), reflux (DME, 84 °C; THF, 65 °C; CH₃CN, 82 °C). ^b NMR yield. ^c Silylative ring opening of THF with silyl iodide (formed in situ from the substrates chlorosilanes and SmI₂) took place exclusively. ^d Isolated yields based on **1a**. ^e At room temperature.

nochlorosilanes in DME, an efficient Si–Si bond formation under mild conditions.¹²

Results and Discussion

As a starting point for the synthesis of disilanes, initially, we chose to study the conversion of dimethylphenylchlorosilane to the disilane mediated by the Sm/SmI₂ reagent (eq 1). After



extensive studies concerning different solvents, ratios of Sm/SmI₂, and reaction temperatures (Table 1), we observed that the best result was obtained when the reaction was conducted

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Table 2. Sm/SmI₂-Induced Reductive Dimerization of Organochlorosilanes^a

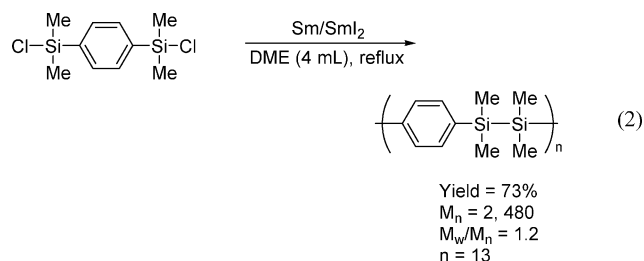
run no.	chlorosilane 1	disilane	2	yield ^b
1	Me ₂ PhSiCl	Me ₂ PhSiSiPhMe ₂	a	76
2	MePh ₂ SiCl	MePh ₂ SiSiPh ₂ Me	b	90
3	Ph ₃ SiCl	Ph ₃ SiSiPh ₃	c	80
4	MePhHSiCl	MePhHSiSiHPhMe	d	64 ^c
5	Ph ₂ HSiCl	Ph ₂ HSiSiHPh ₂	e	70
6	(vinyl)Ph ₂ SiCl	(vinyl)Ph ₂ SiSiPh ₂ (vinyl)	f	85
7 ^d	^t BuMe ₂ SiCl	^t BuMe ₂ SiSiMe ₂ ^t Bu	g	81

^a Unless otherwise noted, organochlorosilanes (1 mmol) were allowed to react with Sm (3 mmol) and SmI₂ (1 mmol) in DME at 84 °C for 12–14 h. ^b Isolated yields based on chlorosilane (**1**) used. ^c Ratio of diastereomers is about 50/50. ^d 20 h.

using a 3:1 molar ratio of Sm to SmI₂ in refluxing 1,2-dimethoxyethane (84 °C) for 12 h (run 6). Control experiments clearly indicated that both samarium powder and samarium diiodide are essential for the formation of Me₂PhSiSiPhMe₂ from dimethylphenylchlorosilane. When samarium powder or samarium diiodide was used alone, no reaction occurred (runs 3, 4, and 9).

In order to investigate the scope and the limitations of this reaction, a number of different organochlorosilanes were reacted with the Sm/SmI₂ system under the optimized reaction conditions (run 6 in Table 1). As Table 2 shows, substituted aromatic chlorosilanes could undergo reductive dimerization to give the corresponding disilanes in good to excellent yield. In the case of diphenylvinylchlorosilane (run 6), the vinyl group is unaffected under these reaction conditions. It is remarkable that an aliphatic organochlorosilane, *tert*-butyldimethylchlorosilane, also reacted to form disilane using the Sm/SmI₂ system, although longer reaction times (20 h) were required (run 7).

Interestingly, when 1,4-bis(dimethylchlorosilyl)benzene (1 mmol) was treated with Sm (3 mmol)/SmI₂ (1 mmol) in refluxing DME for 24 h, the corresponding poly(disilanyl-phenylene) was formed in good yield (73%) (eq 2). The polymer



was purified by precipitation from its THF solution by addition of EtOH, followed by freeze-drying. The molecular weight distribution of this polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent (M_n = 2480, M_w/M_n = 1.2). This result suggests that the Sm/SmI₂ system is a promising reagent for the construction of a σ–π conjugate system of poly(disilanyl-phenylene).

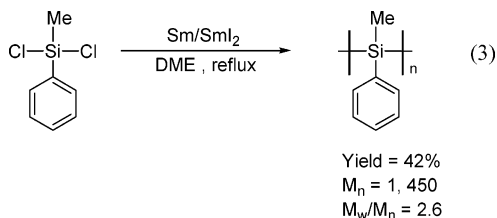
Since the synthesis of disilanes was successful, the reductive polymerization of dichloromethylphenylsilane was also carried out under the aforementioned reaction conditions. When dichloromethylphenylsilane (2 mmol) was treated with Sm (3 mmol)/SmI₂ (1 mmol) in refluxing DME for given times (Table 3), the poly(methylphenyl)silane was obtained in moder-

Table 3. Reductive Polymerization of Dichloromethylphenylsilane Mediated by the Sm/SmI₂-DME System

run no.	amt of MePhSiCl ₂ (mmol)	amt of Sm (mmol)	amt of SmI ₂ (mmol)	amt of Mg (mmol)	time (h)	yield ^a (%)	M _w	M _n	M _w /M _n
1	2	3	1		12	33	3744	1560	2.4
2	2	3	1		24	42	3770	1450	2.6
3	4	3.9	0.1	10	36	38	7040	4400	1.6
4	2	1.5	1	10	24	43	6975	4650	1.5
5 ^b	0.5	2		10	24	0			
6 ^b	0.5		0.5	10	24	0			

^a Isolated yield based on PhMeSiCl₂ used. ^b In the absence of SmI₂ or samarium powder, no reaction occurred.

ate yield (eq 3). When magnesium¹⁴ was used as the core-



ductant, the molecular weight distribution of the poly(methylphenyl)silane ($M_w/M_n = 1.5$, $M_n = 4650$) was much narrower than that of the product prepared by using a Sm/SmI₂ mixed system in the absence of Mg ($M_w/M_n = 2.6$, $M_n = 1450$) (Table 3). However, when samarium powder or samarium diiodide was absent in the reduction system, the reaction failed (runs 5 and 6). The product was identified based on the analysis of ¹H NMR, IR, and UV spectra ($\lambda_{\text{max}} = 334$ nm, which shows the high purity of the polysilane).

Conclusion

In summary, an efficient reductive dimerization of chlorosilanes has been achieved by the Sm/SmI₂ mixed system in DME. A variety of chlorosilanes bearing hydrogen, vinyl, and *tert*-butyl groups can be converted conveniently into the corresponding disilanes. The procedure is applicable for the synthesis of poly(disilanylphenylene) and poly(methylphenyl)silane. Further studies on the application of this method to the synthesis of polysilanes are now underway.

Experimental Section

General Comments. ¹H NMR spectra were recorded on a JEOL JNM-AL (300 Hz) spectrometer using CDCl₃ as the solvent with tetramethylsilane (TMS) as the internal standard. ¹³C NMR spectra were obtained on a JEOL JNM-AL (75 Hz) spectrometer using CDCl₃ as the solvent. Chemical shifts in ¹³C NMR were measured relative to CDCl₃ and converted to δ_{TMS} values by using $\delta 77.0$ ppm. IR spectra were determined on a Perkin-Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 instrument in the analytical section of Osaka University. Elemental analyses were also performed there.

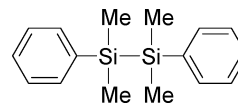
DME was freshly distilled from sodium-benzophenone ketyl prior to use. Unless otherwise noted, chemical reagents were obtained from commercial suppliers and used directly. Samarium powder in oil (99.9%) was purchased from High Purity Chemicals and was used after washing with dry pentane, followed by drying for 4 h under reduced pressure. 1,2-Diiodoethane was purified by washing of its ether solution with saturated sodium thiosulfate, followed by removal of ether under reduced pressure.

(14) We presented the preliminary results for the polysilane synthesis using the SmI₂/Sm/Mg-mixed system at the International Symposium for "Rare Earth '04 in Nara, Japan" Nov 9, 2004 (DP-15, DI-08). For the combination of SmI₂ and Mg metal, see ref 11a.

Representative Procedure for the Reductive Dimerization of Organochlorosilanes Mediated by the Sm/SmI₂-DME Mixed System.

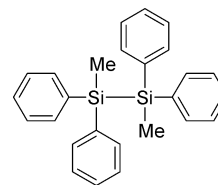
In a 20 mL two-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (4 mmol), 1,2-diiodoethane (1 mmol), and freshly distilled (sodium-benzophenone ketyl) DME (4 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h, resulting in the formation of a dark blue solution of SmI₂. After the addition of the substrates (1 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C and the reaction mixture was treated at reflux for about 12 h. After it was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 mol/L, 20 mL) and extracted with methyl *tert*-butyl ether (3 × 10 mL). The combined organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed under reduced pressure. Products were isolated by HPLC (silica gel 40–63 μm), with hexane or a mixture of hexane and dichloromethane (9:1) as eluent.

Spectral and Analytical Data. (a) **1,1,2,2-Tetramethyl-1,2-diphenyldisilane (2a)** [1145-98-8].



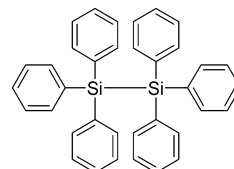
Yield: 103 mg (76%). Mp: 33–35 °C (lit.^{15a} mp 34–35 °C). ¹H NMR (300 MHz, CDCl₃): δ 0.32 (s, 12 H), 7.25–7.55 (m, 10 H). ¹³C NMR (75 MHz, CDCl₃): δ -3.93, 127.78, 128.49, 133.98, 139.10. IR (neat): 3049, 2956, 1427, 1259, 1105, 792, 698 cm⁻¹. MS: m/z (relative intensity) 270 (10, M⁺), 255 (5), 135 (100).

(b) **1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (2b)** [1172-76-5].



Yield; 177 mg (90%). Mp: 143–145 °C (a white solid from ethanol) (lit.^{15b} mp 142–146 °C). ¹H NMR (300 MHz, CDCl₃): δ 0.65 (s, 6 H), 7.24–7.38 (m, 20 H). ¹³C NMR (75 MHz, CDCl₃): δ -5.14, 127.03, 128.14, 134.44, 135.80. IR (KBr): 3021, 1420, 1255, 1100 cm⁻¹. MS: m/z (relative intensity) 394 (10, M⁺), 379 (15), 197 (100).

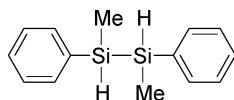
(c) **1,1,1,2,2,2-Hexaphenyldisilane (2c)** [1450-23-3].



Yield: 207 mg (80%). Mp: 371 °C (a white solid from ethanol) (lit.^{15b} mp 365–367 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.25–

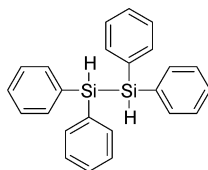
7.70 (m, 30 H). ^{13}C NMR (75 MHz, CDCl_3): δ 128.16, 130.40, 135.29, 136.79. IR (KBr): 3040, 1423, 1105, 792, 698 cm^{-1} . MS: m/z (relative intensity) 518 (5, M^+), 259 (100).

(d) **1,2-Dimethyl-1,2-diphenyldisilane (2d)**.



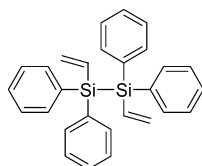
Yield: 78 mg (64%). Colorless oil (lit. 15c mp 105 °C (0.6 mmHg)). ^1H NMR (300 MHz, CDCl_3): δ 0.43 (d, $J = 2.7$ Hz, 6 H), 4.40 (q, $J = 3.3$ Hz, 2 H), 7.25–7.57 (m, 10 H). ^{13}C NMR (75 MHz, CDCl_3): δ -7.52, -7.73, 128.12, 129.17, 135.05, 137.45. IR (neat): 3051, 2954, 2360, 2120, 1427, 1261, 1105, 792, 698 cm^{-1} . MS: m/z (relative intensity) 242 (5, M^+), 227 (5), 121 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{Si}_2$: C, 69.35; H, 7.48. Found: C, 69.38; H, 7.52.

(e) **1,1,2,2-Tetraphenyldisilane (2e)** [16343-18-3].



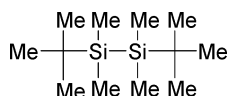
Yield: 128 mg (70%). Mp: 77–78 °C (a white solid from ethanol) (lit. 15d mp 76.5–80.5 °C). ^1H NMR (300 MHz, CDCl_3): δ 5.18 (s, 2 H), 7.45–7.48 (m, 8 H), 7.25–7.38 (m, 12 H). ^{13}C NMR (75 MHz, CDCl_3): δ 128.15, 129.51, 132.51, 136.12. IR (KBr): 3064, 3043, 2360, 2119, 1483, 1425, 1261, 1101, 1066, 1024, 790, 738, 694, 657 cm^{-1} . MS: m/z (relative intensity) 366 (10, M^+), 183 (100). HRMS: m/z calcd, 366.613 08; m/z found, 366.613 15. Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{Si}_2$: C, 78.63; H, 6.05. Found: C, 78.35; H, 6.06.

(f) **1,1,2,2-Tetraphenyl-1,2-divinyldisilane (2f)**.



Yield: 178 mg (85%). Mp: 125–127 °C (a white solid from methanol). ^1H NMR (300 MHz, CDCl_3): δ 5.68 (dd, $J = 3.6$, 20.1 Hz, 2 H), 6.19 (dd, $J = 3.6$, 14.4 Hz, 2 H), 6.52 (dd, $J = 14.4$, 20.1 Hz, 2 H), 7.23–7.62 (m, 20 H). ^{13}C NMR (75 MHz, CDCl_3): δ 128.01, 129.35, 134.42, 134.56, 136.29, 136.45. IR (KBr): 3068, 3049, 2960, 2360, 1593, 1427, 1255, 1116, 794, 732, 698 cm^{-1} . MS: m/z (relative intensity) 418 (5, M^+), 390 (10), 263 (7), 259 (65), 209 (50), 183 (100). Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{Si}_2$: C, 80.32; H, 6.26. Found: C, 80.69; H, 6.29.

(g) **1,2-Di-tert-butyl-1,1,2,2-tetramethyldisilane (2g)**.



Yield: 93 mg (81%) (lit. 15a mp 60 °C (70 mmHg)). ^1H NMR (300 MHz, CDCl_3): δ 0.06 (s, 12 H), 0.88 (s, 18 H). ^{13}C NMR (75 MHz, CDCl_3): δ -3.73, 18.22, 25.59. IR (neat): 2954, 2892, 1251 cm^{-1} . MS: m/z (relative intensity) 230 (4, M^+), 173 (5), 158 (7),

143 (6), 115 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Si}_2$: C, 62.52; H, 13.12. Found: C, 62.48; H, 13.09.

Reductive Dimerization of Chlorodiphenylmethylsilane Mediated by the Sm/SmI₂–DME Mixed System. In a 100 mL two-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (15 mmol), 1,2-diiodoethane (5 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (40 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in the formation of a dark blue solution of SmI₂. After the addition of chlorodiphenylmethylsilane (10 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C and the reaction mixture was refluxed for about 12 h. After it was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 mol/L, 20 mL) and extracted with methyl *tert*-butyl ether (3 × 40 mL). The combined organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol.

1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (2b). 15b Yield: 1.812 g (92%). Mp: 144–146 °C. ^1H NMR (300 MHz, CDCl_3): δ 0.66 (s, 6 H), 7.30–7.41 (m, 20 H). ^{13}C NMR (75 MHz, CDCl_3): δ -5.14, 127.03, 128.14, 134.44, 135.80. IR (KBr): 3021, 1420, 1255, 1100 cm^{-1} .

General Procedure for the Reductive Polymerization of 1,4-Bis(dimethylchlorosilyl)benzene Mediated by the Sm/SmI₂–DME System. In a 50 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (8 mmol), 1,2-diiodoethane (2 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (20 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h, resulting in the formation of a dark blue solution of SmI₂. After the addition of 1,4-bis(dimethylchlorosilyl)benzene (2 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for another 24 h. After it was cooled to room temperature, the reaction mixture was treated with EtOH (5 mL), poured into hydrochloric acid (1.5 mol/L, 30 mL), and extracted with methyl *tert*-butyl ether (3 × 40 mL). The combined organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (2 mL) and precipitated by the addition of ethanol (100 mL) to the solution.

Poly(disilanylenephenylene). Yield: 282 mg (73%). ^1H NMR (300 MHz, CDCl_3) δ 0.25–0.46 (m, 12 H), 7.24–7.46 (m, 4 H). IR (KBr): 3066, 3049, 2956, 1427, 1259, 1105, 1066, 1026, 792, 696 cm^{-1} . $M_n = 2480$, $M_w = 2976$, $M_w/M_n = 1.2$.

Polymerization of Dichloromethylphenylsilane with the Sm/SmI₂–DME System. In a 250 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (40 mmol), 1,2-diiodoethane (10 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (100 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in the formation of a dark blue solution of SmI₂. After the addition of dichloromethylphenylsilane (10 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for another 24 h. After it was cooled to room temperature, the reaction mixture was treated with EtOH (20 mL), poured into hydrochloric acid (1.5 mol/L, 40 mL), and extracted with methyl *tert*-butyl ether (3 × 50 mL). The combined organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (50 mL) and precipitated by the addition of ethanol (300 mL) to the solution. The molecular weight of the polymer was determined

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by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent.

Poly(methylphenyl)silane.^{6a} Yield: 0.492 g (41%). ¹H NMR (300 MHz, CDCl₃): δ -0.85–0.86 (m, 3 H), 6.40–7.46 (m, 5 H). IR (KBr), 3056, 2956, 1427, 1250, 1105 cm⁻¹. UV (THF): λ_{max} (log ϵ) 338 nm. $M_n = 1550$, $M_w = 3906$, $M_w/M_n = 2.52$.

Polymerization of Dichloromethylphenylsilane with the Sm/SmI₂/Mg–DME System. In a 50 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (2.5 mmol), 1,2-diiodoethane (1 mmol), magnesium (10 mmol), and freshly distilled (sodium–benzophenone ketyl) DME (20 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h. After the addition of dichloromethylphenylsilane (2 mmol) to the solution, the flask was set in an oil bath maintained at 90 °C. The reaction mixture was refluxed for another 24 h. After it was cooled to room temperature, the reaction mixture was treated with EtOH (5 mL), poured into hydrochloric acid (1.5 mol/L, 30 mL), and extracted with methyl *tert*-butyl ether (3 \times 40 mL). The combined organic layer was washed with

saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (2 mL) and precipitated by the addition of ethanol (100 mL) to the solution. Yield: 0.103 g (43%). ¹H NMR (300 MHz, CDCl₃): δ -0.84 to -0.88 (m, 3 H), 6.41–7.47 (m, 5 H). IR (KBr): 3056, 2956, 1427, 1250, 1105 cm⁻¹. UV (THF): λ_{max} (log ϵ): 338 nm. $M_n = 4650$, $M_w = 6975$, $M_w/M_n = 1.5$.

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