A New Stereoselective Approach to (*E*)-Poly(arylenevinylene)s

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Abstract: A new synthetic protocol for the one-pot, stereoselective synthesis of (*E*)-poly(arylenevinylene)s via palladium-catalyzed Hiyama cross-coupling of dihaloarenes with cyclic *gem*-bis(silyl)ethene or isopropoxydimethylvinylsilane is described.

Key words: poly(arylenevinylene)s, cross-coupling, palladium catalyst, organometallic reagents, silicon derivatives

Poly(arylenevinylene)s (PAV) constitute a group of π-conjugated polymers that have attracted considerable interest because of their potential applications in electronic and optoelectronic devices including light-emitting diodes, solar cells, plastic lasers, fluorescent sensors, rechargeable batteries, field-effect transistors, etc.[1] In the context of their wide applications, synthetic design of PAV has attracted a great deal of recent interest.[2]

Conventional approaches to poly(arylenevinylene)s involve dehydrohalogenative polycondensation of bis(halomethyl)benzenes (Gilch reaction),[3] thermolysis of sulfonium polymer precursors (Wessling route),[4] Wittig–Horner polycondensation of xylylene diphosphonates with phthalaldehydes,[5] palladium-catalyzed Heck reaction of ethylene[6] or divinylarenes[7] with dihaloarenes as well as palladium-catalyzed Suzuki–Miyaura coupling of difunctional arylboronic derivatives with di(haloalkenyl)arenes.[8]

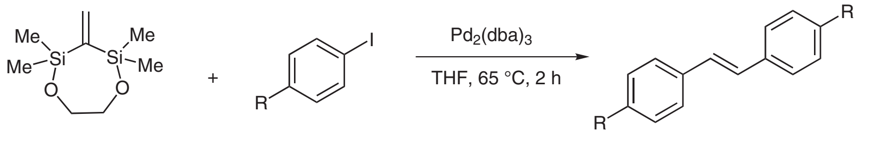
The palladium-catalyzed and fluoride-promoted cross-coupling of unsaturated organosilicon compounds with aryl halides (Hiyama coupling) has been recently employed as a mild and efficient alternative to the well-established Stille and Suzuki reactions due to commercial availability, high stability, and low toxicity of the silicon derivatives.[9] Although there are many reports on the successful applications of the Hiyama coupling in the synthesis of molecular π-conjugated organic frameworks, the potential use of this particular method for the synthesis of arylenevinylene oligomers and polymers has not been so far fully exploited. Recently, Ozawa and co-workers reported a stereocontrolled synthesis of *trans*- and *cis*-oligo(arylenevinylene)s using Hiyama-type polycondensation of substituted 1,4-diiodobenzenes with 1,4-bis(silyl-ethenyl)benzenes.[8c,10] An interesting silicon-assisted alternative for the synthesis of PAV seems to be also palladium-catalyzed poly-Heck reaction of bisarene-diazonium salts with vinyltriethoxysilane.[11] However, application of this particular method has been limited because of commercial unavailability of bisarene-diazonium salts, whose synthesis from very toxic aryl diamines is challenging even for the most common PAV precursors.

Therefore, we wish to report herein the first, unprecedented, one-pot, palladium-catalyzed Hiyama-type strategy for the stereoselective synthesis of (*E*)-poly(arylenevinylene)s using aryl dihalides and isomeric bis(silyl)ethenes as new double-bond equivalents.

During the course of our studies on the reactivity of geminal bis(silyl)alkenes towards carbon electrophiles, we have unexpectedly found that 2,2,4,4-tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane (**1**), in the reaction with 2 equivalents of aryl iodides (iodobenzene and 4-iodoanisole), under standard cross-coupling conditions forms exclusively (instead of the expected 1,1-diarylethenes) *cine*-substitution products – (*E*)-stilbene and (*E*)-4,4′-dimethoxystilbene, respectively, with perfect stereoselectivity and almost quantitative yield (Scheme 1).[12]

Although *cine*-substitution of 1-aryl-1-silylethenes in palladium-catalyzed cross-coupling with aryl iodides or aryldiazonium salts has been previously reported,[13] the simultaneous *ipso*- and *cine*-substitution of geminally silylated ethenes under Hiyama conditions is unprecedented.

Since the starting compound **1** can be easily prepared with high yield in a two-step process from inexpensive chlorodimethylvinylsilane and ethylene glycol using silyla-



Scheme 1

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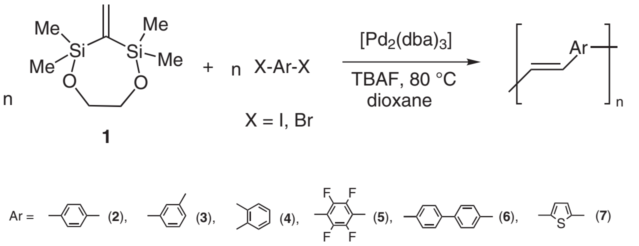
tion–ruthenium-catalyzed silylative coupling–*exo*-cyclization sequence,[14] this novel bis(silyl)ethene transformation is expected to be an attractive alternative for the synthesis of arylenevinylene polymers.

We began our investigations with the cross-coupling between cyclic 1,1-bis(silyl)ethene **1** and 1,4-diiodobenzene using $Pd_2(dba)_3$ as a catalyst and TBAF as an activator. Under standard cross-coupling reaction conditions (30–40 °C), the expected product was not observed, whereas at 55 °C the low conversion of diiodoarene has been detected (ca 40%). Increasing the temperature to 80 °C completed this reaction in 16 hours with only 0.5 mol% loading of $Pd_2(dba)_3$ per silyl group.

These optimal conditions were applied to the other aryl diiodides providing almost quantitative yields (94–98%) of the desired polymeric products (Table 1).[15] Only 1,4-diiodotetrafluorobenzene gave the expected polymer with lower yield (Table 1, entry 5) and an increase of the amount of Pd catalyst (from 0.5 to 2 mol% per silyl group) as well as a longer reaction time did not appreciably affect the rate of this process.

Table 1 Synthesis of (*E*)-Poly(arylenevinylene)s via Palladium-Catalyzed Cross-Coupling of Cyclic 1,1-Bis(silyl)ethene with Aryl Dihalides[a]



Entry	Aryl dihalide	Time (h)	Product[17]	Yield (%)[b]
1	1,4-$I_2C_6H_4$	16	**2**	96
2	1,4-$Br_2C_6H_4$	24	**2**	94
3	1,3-$I_2C_6H_4$	24	**3**	98
4	1,2-$I_2C_6H_4$	24	**4**	97
5	1,4-$I_2C_6F_4$	48	**5**	35
6	4,4′-$I_2C_6H_4$-C_6H_4	24	**6**	98
7	4,4′-$Br_2C_6H_4$-C_6H_4	24	**6**	95
8	2,5-$I_2C_4H_2S$	24	**7**	97

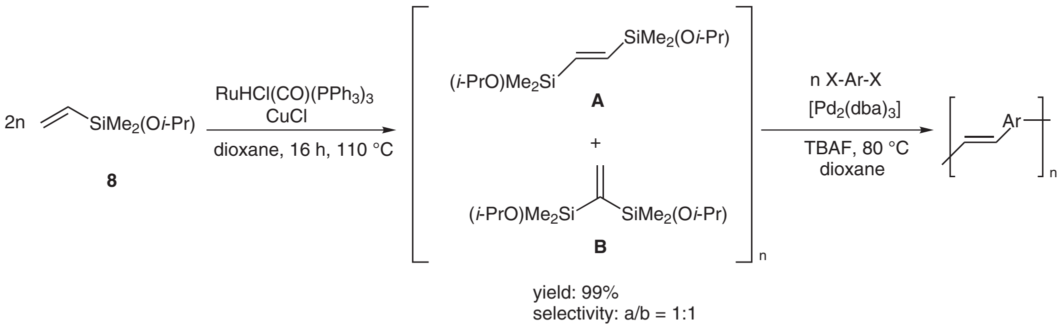
[a] [1]:[XArX]:[TBAF]:[$Pd_2(dba)_3$] = 1:0.9:2.4:0.01, dioxane, 80 °C.
[b] Isolated yields of products.

It is worth noting that all the coupling processes proceeded in stereoselective manner to yield products containing only (*E*)-vinylene units in the polymer chain. Moreover, the application of more available and cheaper aryl dibromides to our new silicon-assisted methodology has significantly broadened its utility. The conversion of 1,4-dibromobenzene and 4,4′-dibromobiphenyl has been only slightly lower than that of 1,4-diiodobenzene under the analogous reaction conditions (Table 1, entry 2, 7).

With the optimized conditions established for cyclic 1,1-bis(silyl)ethene, we turned our attention towards the one-pot synthesis of PAV by successive silylative coupling – Hiyama coupling proceeding via (*E*)-1,2-bis(silyl)ethene intermediate. In the first step, unsaturated organosilicon precursors were synthesized using ruthenium hydride catalyzed silylative coupling of the respective vinylsilane and then the post reaction mixture was treated with an appropriate dihaloarene under the Hiyama cross-coupling conditions (Scheme 2). In this process, isopropoxydimethylvinylsilane (**8**) was used to facilitate the next palladium-catalyzed cross-coupling.

The silylative coupling of **8** successfully proceeded in the presence of [$RuHCl(CO)(PPh_3)_3$] (2 mol%) in dioxane, and the starting vinylsilane was efficiently transformed into an almost equimolar mixture of isomeric (*E*)-1,2-bis(isopropoxydimethylsilyl)ethene **A** and 1,1-bis(isopropoxydimethylsilyl)ethene **B** (Scheme 2) in 16 hours at 110 °C. Moreover, the use of CuCl (2 mol%) as a co-catalyst caused a slight increase in the catalytic activity of the ruthenium–hydride complex. Although toluene or chlorobenzene could also be employed without affecting either the activity of the catalytic system or the selectivity of this process, the use of dioxane seemed to be the most favorable due to its higher effectiveness in the following palladium-catalyzed coupling.

Similarly to the reactions with **1**, palladium-catalyzed coupling of the isomeric bis(silyl)ethenes **A** and **B** with aryl dihalides in the presence of TBAF and $Pd_2(dba)_3$ (1 mol%) catalyst proceeded stereoselectively to give satisfactory yields of the desired poly(arylenevinylene)s



Scheme 2

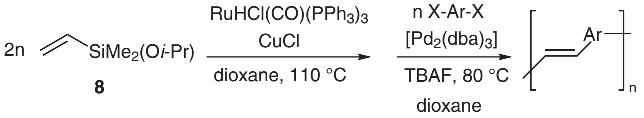
(Table 2).[16] This particular reaction proceeded via competitive stereospecific coupling of (*E*)-bis(silyl)ethene intermediate and afore-mentioned rearrangement of geminal bis(silyl)ethene derivatives. The results of the one-pot silylative coupling–Hiyama coupling are depicted in Table 2.

p-Arylene polymers were isolated by simple filtration from the reaction mixture. The PAV containing *o*-phenylene or thienylene units were isolated by column chromatography. All polymers were washed with acetone in order to remove traces of oligomers and catalyst and dried under vacuum. Due to the lack of polar lateral substituents, these polymers were found to be only poorly soluble in $CHCl_3$ and partly in THF. Molecular weights of THF soluble fractions of polymers obtained were measured by GPC using THF as an eluent and polystyrene standards.

Due to the insolubility of the resulting products, the matrix-assisted laser desorption–ionization mass spectrometry (MALDI-MS) was also applied for estimation of their molecular weights. The MALDI-MS spectra of **2** and **5** in ditranol as a matrix revealed only short chain polymers: 11–18-mer and 6–10-mer, respectively. The LSIMS of these compounds in NBA as matrix revealed chains till 25-mer characterized by very low intensity peaks and high polydispersity. The polymers in solution subjected on UV light (366 nm) emit intensive blue (**2**–**6**) or green (**7**) light. Representative physical properties of the selected products are presented in Table 3.

The structure of the resulting polymers was proved by FT-IR and ^{1}H NMR spectroscopy. The presence of (*E*)-vinylene functionality was unambiguously confirmed by the appearance of FT-IR bands attributable to CH bending of *trans*-vinylene at 936–971 cm^{-1}. Unfortunately, the corresponding ^{1}H NMR signals fall in the region of aromatic protons and could be assigned only for (*E*)-poly(1,4-phenylenevinylene) oligomers **2** ($J = 19$ Hz) and (*E*)-poly(tetrafluorophenylenevinylene)s **5** ($J = 16$ Hz). It may be noted that the presence of 1,1-diarylenevinylene defects in the polymers, which are usually formed during other palladium-catalyzed processes was not detected.

Table 2 One-Pot Synthesis of (*E*)-Poly(arylenevinylene)s via Sequential Ruthenium-Catalyzed Silylative Coupling–Palladium-Catalyzed Cross-Coupling of Isopropoxydimethylvinylsilane[a]



Entry	Aryl dihalide	Time (h)	Product	Yield (%)[b]
1	1,4-$I_2C_6H_4$	16	**2**	98
2	1,4-$Br_2C_6H_4$	24	**2**	92
3	1,3-$I_2C_6H_4$	24	**3**	90
4	1,2-$I_2C_6H_4$	24	**4**	90
5	1,4-$I_2C_6F_4$	48	**5**	43
6	4,4′-$I_2C_6H_4$-C_6H_4	24	**6**	98
8	2,5-$I_2C_4H_2S$	24	**7**	90

[a] Silylative coupling conditions: [8]:[$RuHCl(CO)(PPh_3)_3$]:[CuCl] = 1:0.02:0.02; dioxane (1 M), 110 °C, 16 h. Hiyama coupling conditions: [$ViSiMe_2$(O*i*-Pr)]:[XArX]:[TBAF]:[$Pd_2(dba)_3$] = 2:0.9:2.4:0.01, dioxane, 80 °C.

[b] Isolated yields of products

Table 3 Physical Properties of the Polymers **2**–**7**

Compound	UV λ_{max} ([nm)	M_n	M_w/M_n
2	369.8	1530[a]	–
3	307.2	840[a]	–
4	299.4	2670[b]	1.27
5	305.8	2200[a]	–
6	338.2	11700[b]	1.19
7	384.0	3220[b]	1.18

[a] Calculated by MALDI-MS.

[b] Calculated by GPC.

In conclusion, we have developed a new, efficient, highly stereoselective, one-pot synthetic methodology for the construction of (*E*)-poly(arylenevinylene)s based on palladium-catalyzed Hiyama cross-coupling of cyclic bis(silyl)ethene or sequential silylative coupling–Hiyama cross-coupling of isopropoxydimethylvinylsilane with aryl dihalides. The availability of starting materials, the simplicity of the experimental technique, and the use of aryl dibromides instead of aryl diiodides are favorable features of this new catalytic approach to stereodefined PAV polymers.

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References and Notes

(1) For reviews, see: (a) *Functional Organic and Polymeric Materials*; Richardson, T. H., Ed.; John Wiley and Sons: Chichester England, **2000**. (b) Samuel, I. P. W.; Turnbull, G. A. *Chem. Rev.* **2007**, *107*, 1272. (c) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. *Chem. Rev.* **2007**, *107*, 926. (d) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339. (e) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (f) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. *Chem. Rev.* **2005**, *105*, 1491. (g) Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402. (b) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163. (c) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875.

(3) (a) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 1337. (b) Hsieh, B. R.; Yu, Y.; Van Laeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094.

(4) (a) Wessling, R. A.; Zimmerman, R. G. US 3 401 152, **1968**. (b) Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3241. (c) Batten, J. H.; Duran, R. S. *Macromolecules* **1998**, *31*, 3148.

(5) (a) Hörhold, H. H.; Helbig, M. *Macromol. Chem. Macromol. Symp.* **1987**, *12*, 229. (b) Saito, H.; Ukai, S.; Iwatsuki, S.; Itoh, T.; Kubo, M. *Macromolecules* **1995**, *28*, 8363. (c) Peng, Z.; Zhang, J.; Xu, B. *Macromolecules* **1999**, *32*, 5162.

(6) (a) Greiner, A.; Heitz, W. *Macromol. Chem. Rapid Commun.* **1988**, *9*, 5281. (b) Kiji, J.; Okano, T.; Ooue, A. *J. Mol. Catal. A: Chem.* **1999**, *3*, 147.

(7) (a) Weitzel, H. P.; Müllen, K. *Macromol. Chem.* **1990**, *13*, 563. (b) Suzuki, M.; Lim, J. C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574. (c) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.

(8) (a) Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060. (b) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350. (c) Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, *71*, 2699. (d) Grisorio, R.; Mastrorilli, P.; Nobile, F.; Romanazzi, G.; Suranna, G. P. *Tetrahedron Lett.* **2005**, *46*, 2555.

(9) (a) Hiyama, T. In *Handbook of Organopalladium Chemistry for Organic Synthesis*, Vol. 1; Negishi, E., Ed.; Wiley-Interscience: New York, **2002**, 285. (b) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, J. P., Eds.; Wiley-VCH: Weinheim, **1998**.

(10) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet.Chem.* **2003**, *49*, 676.

(11) Sengupta, S.; Sadhukhan, S. K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2235.

(12) **Reaction of Cyclic 1,1-Bis(silyl)ethene (1) with Aryl Iodides**

The glass reactor (100 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated heating oil bath) was evacuated and flushed with argon. Compound **1** (1 g, 4.95 mmol) and anhyd THF (20 mL) were added to the reactor. At r.t. 14.8 mmol of TBAF (1 M soln in THF) was added and the mixture was stirred for 10 min. After this time, 9.9 mmol of the respective aryl iodide and 56.8 mg (9 μmol) of $Pd_2(dba)_3$ were added and the reaction mixture was stirred under argon for 2 h at 65 °C. After the reaction was completed (GC-MS analysis) the volatiles were evaporated under vacuum and the crude product was chromatographed on silica gel (eluent: hexane–EtOAc, 10:1) to afford the analytically pure products. Isolated yields: (*E*)-stilbene, 96%; (*E*)-4,4′-dimethoxystilbene, 92%.

(13) (a) Hatanaka, Y.; Hiyama, T. *J. Organomet.Chem.* **1994**, *97*, 465. (b) Ikenaga, K.; Matsumoto, S.; Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1988**, 873. (c) Babudri, F.; Farinola, G. M.; Lopez, L. C.; Mattinelli, M. G.; Naso, F. *J. Org. Chem.* **2001**, *66*, 3878.

(14) Pawluc, P.; Marciniec, B.; Hreczycho, G.; Gaczewska, B.; Itami, Y. *J. Org. Chem.* **2005**, *70*, 370.

(15) **Synthesis of PAV from Cyclic 1,1-Bis(silyl)ethene (1)**

$[Pd_2(dba)_3]$ (9.16 mg, 0.01 mmol), dioxane (4 mL), 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane (**1**, 202 mg, 1 mmol), TBAF (640 mg, 2.4 mmol), and respective dihaloarene (0.9 mmol) were placed in an evacuated and flushed with argon 25 mL flask. The mixture was heated at 80 °C for 16–48 h under an argon atmosphere. The degree of conversion of the substrates was estimated by GC and TLC analyses. Then, the reaction mixture was cooled and the precipitated solid was filtered and washed extensively with acetone. The final product was separated using filtration (**2**, **6**) or chromatography column (**3**–**5**, **7**) with silica (THF–EtOAc). The desired products were obtained by combining both fractions of solids to afford the desired polymeric products.

(16) **One-Pot Synthesis of PAV from Isopropoxydimethylvinylsilane**

The glass minireactor (10 mL, equipped with a magnetic stirring bar, argon bubbling tube and thermostated heating oil bath) was evacuated and flushed with argon. Then, $[RuH(Cl)(CO)(PPh_3)_3]$ (19.05 mg, 0.02 mmol), CuCl (1.98 mg, 0.02 mmol), isopropoxydimethylvinylsilane (0.144 g, 1.0 mmol), and anhyd dioxane (1.0 mL) were added to the reactor (in the case of reaction with 4,4′diiodobiphenyl and 2,5-diiodothiophene 2 mL of dioxane). The reaction mixture was heated at 110 °C for 16 h under an argon flow. After the reaction was completed [GC-MS and ^1H NMR analyses confirmed the formation of the mixture of (*E*)-1,2-bis(isopropoxydimethylsilyl)ethene **A** and 1,1-bis(isopropoxydimethylsilyl)ethene **B**], palladium catalyst $[Pd_2(dba)_3]$ (0.005 mmol), TBAF (1 M solution in THF, 320 mg, 1.2 mmol), and respective dihaloarene (0.45 mmol) were added and the mixture was heated at 80 °C for 16–48 h under an argon atmosphere. The degree of conversion of the substrates was estimated by GC and TLC analyses. Then, the reaction mixture was cooled and the precipitated solid was filtered and washed extensively with acetone. The final product was separated using filtration (**2**, **6**) or chromatography column (**3**–**5**, **7**) with silica (THF–EtOAc). The desired products were obtained by combining both fractions of solids to afford the desired polymeric product.

(17) **Spectroscopic Data of the Selected Products**

(*E*)-Poly(1,4-phenylenevinylene)s (2)

IR (KBr): 740.5 (s), 834.8 (s), 964.7 (s), 1015.2 (s), 1256.0, 1488.6, 1512.8, 1596.6, 1695.9 (s, br), 2922.6, 2953.9, 3021.6 (s) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.15 (s, $SiCH_3$), 0.21 (s, $SiCH_3$), 6.50 (d, *J* = 19.2 Hz, PhCH=), 6.94 (d, *J* = 19.2 Hz, PhCH=), 7.41 (d, *J* = 8.5 Hz, H in phenyl ring), 7.54 (d, *J* = 8.5 Hz, H in phenyl ring) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 0.1, 0.5, 0.8, 29.0, 31.3, 128.2, 128.7, 129.2, 132.4 ppm. Anal. Calcd for $(C_8H_6)_n$: C, 94.07; H, 5.92. Found: C, 91.58; H, 5.43.

(*E*)-Poly(2,3,5,6-tetrafluorophenylenevinylene)s (5)

IR (KBr): 758.7 (s), 938.6, 979.5, 1091.1 (s, br), 1215.7, 1486.4, 1527.7, 1617.3, 1652.9, 2928.8, 2961.1, 3019.3 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, $SiCH_3$), 0.20 (s, $SiCH_3$), 7.09 (d, *J* = 16 Hz, PhCH=), 7.75 (d, *J* = 16 Hz, PhCH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2, 0.6, 29.4, 29.7, 30.3, 125.4, 128.4, 128.9, 130.5, 143.4 ppm. Anal. Calcd for $(C_8F_4H_2)_n$: C, 55.19; H, 1.19. Found: C, 55.37; H, 1.43.

(*E*)-Poly(2,5-thiophenylenevinylene)s (7)

IR (KBr): 790.6 (s, br), 935.8, 1039.4 (s, br), 1070.1, 1258.5, 1444.5, 1618.6, 1655.2, 1722.2, 2924.3, 2957.4, 3065.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, $SiCH_3$), 0.20 (s, $SiCH_3$), 6.40–7.80 (m, H in thiophenyl ring and ArCH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1, 0.9, 14.2, 19.6, 23.1, 29.8, 30.4, 124.2, 125.4, 128.3, 128.7, 128.8, 130.4, 130.8, 143.2 ppm. Anal. Calcd for $(C_6H_4S)_n$: C, 66.62; H, 3.72; S, 29.64. Found: C, 62.58; H, 3.03; S, 28.33.