Stereocontrolled synthesis of (*E*)- and (*Z*)-poly(*p*-phenylenevinylene)s via ruthenium-catalyzed hydrosilylation of *p*-diethynylbenzene

Hiroyuki Katayama *, Masato Nagao, Rie Moriguchi, Fumiyuki Ozawa *

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

Abstract

Stereocontrolled synthesis of poly(phenylenevinylene)s (PPVs) with (*E*)- and (*Z*)-vinylene units has been examined. Ruthenium complex-catalyzed hydrosilylation of *p*-diethynylbenzene with $HSiMe_2Ar$ (Ar = 2-thienyl (Th), 3,5-$(CF_3)_2C_6H_3$) proceeds readily in CH_2Cl_2 at room temperature to give (*E*,*E*)- or (*Z*,*Z*)-bis(2-silylethenyl)benzenes (**3a**, **3b**) in 89–40% yields. The geometries of **3a** and **3b** are clearly dependent on ruthenium catalysts employed. Thus, $RuHCl(CO)(PPh_3)_3$ forms (*E*,*E*)-isomers in over 99% selectivities, whereas $RuCl_2(CO)(PPr^i_3)_2$ affords (*Z*,*Z*)-**3a** and **3b** with 92 and 91% geometrical purities, respectively. The (*E*,*E*)- and (*Z*,*Z*)-isomers of **3a** and **3b** undergo polycondensation with 2,5-dioctyloxy-1,4-diiodobenzene in THF in the presence of a palladium catalyst ([PdCl(η^3-allyl)]_2, Pd(dba)_2) and tetrabutylammonium fluoride hydrate, giving (*E*)-rich and (*Z*)-rich PPVs in high yields.
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Keywords: Hydrosilylation; Alkyne; Polycondensation; Stereocontrolled synthesis; Poly(phenylenevinylene)

1. Introduction

Alkenylsilanes are versatile starting materials in organic synthesis [1]. We recently demonstrated that (*E*)- and (*Z*)-isomers of alkenylsilanes may be independently synthesized from the same starting materials, simply by the choice of ruthenium catalysts for hydrosilylation of terminal alkynes [2,3]. Thus, the treatment of RC≡CH (R = Ph, *p*-tolyl, Cy, *n*-hexyl) with HSi-Me_2Ar (Ar = Ph, 3,5-$(CF_3)_2C_6H_3$, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$) in CH_2Cl_2 in the presence of $RuHCl(CO)(PPh_3)_3$ catalyst (**1**) forms (*E*)-RCH=CHSi-Me_2Ar in over 99% selectivities. On the other hand, the same starting materials are converted into (*Z*)-RCH= CHSiMe_2Ar in 91–99% selectivities using Ru(Si-Me_2Ph)Cl(CO)(PPr^i_3)_2 (**2**) instead of **1** as the catalyst. Both reactions proceed readily at room temperature in almost quantitative yields. We also reported mechanistic details of the (*E*)- and (*Z*)-selective catalytic processes [2,4].

Having the highly selective catalysts giving (*E*)- and (*Z*)-alkenylsilanes in hand, we examined in this study stereocontrolled synthesis of poly(*p*-phenylenevinylene)s (PPVs, **5**) having (*E*)- and (*Z*)-vinylene units (Scheme 1). While π-conjugated polymers of this type are highly expected electrooptical materials and their optical properties are known to be dependent on stereoregularity of the polymer backbone [5], stereocontrolled synthesis of both geometrical isomers of PPVs has so far been extremely limited [6].

2. Results and discussion

2.1. Hydrosilylation of p-diethynylbenzene

Our synthetic route to PPVs consists of two catalytic reactions. One is ruthenium-catalyzed hydrosilylation of *p*-diethynylbenzene to give bis(2-silylethenyl)benzene (**3**). The other is palladium-catalyzed polycondensation of **3** with 2,5-dioctyloxy-1,4-diiodobenzene (**4**), which is based on the Hiyama cross-coupling reaction [7]. Since polycondensation proceeds via a number of repetitions of a catalytic reaction, the parent catalysis should be as efficient as possible. Although the palladium-catalyzed

* Corresponding authors. Tel.: +82-6-6605-2885; fax: +82-6-6605-2978.
E-mail address: katayama@a-chem.eng.osaka-cu.ac.jp (H. Katayama).
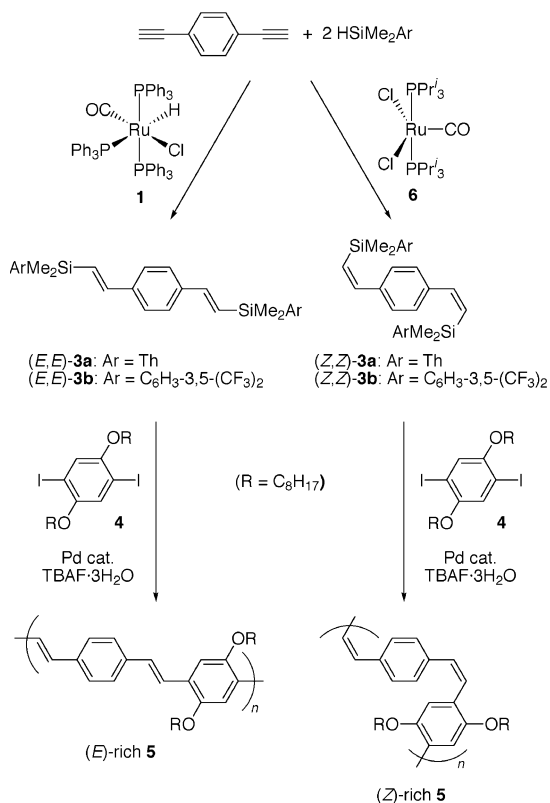
Scheme 1.

cross-coupling using organosilicon reagents often requires a heated condition, alkenylsilanes with a silacyclobutane structure [8] and those with 2-thienyl (Th) [9] and 3,5-$(CF_3)_2C_6H_3$ [2] substituents have recently been shown to be sufficiently reactive at room temperature [7]. Furthermore, since the ruthenium-catalyzed hydrosilylation of terminal alkynes successfully proceeds with the hydrosilanes of the type $HSiMe_2Ar$ [2], we chose $HSiMe_2Th$ and $HSiMe_2[C_6H_3$-3,5-$(CF_3)_2]$ as hydrosilylation reagents.

The reaction of *p*-diethynylbenzene with 5 molar quantity of $HSiMe_2Th$ in CH_2Cl_2 in the presence of 10 mol% of **1** was completed in 1 h at room temperature, giving (*E,E*)-**3a** in almost perfect selectivity as confirmed by ^1H-NMR analysis of the crude product. The analytically pure (*E,E*)-**3a** [(*E,E*)/(*E,Z*) > 99/1] was obtained in 75% yield by silica-gel column chromatography. Similarly, hydrosilylation of *p*-diethynylbenzene with $HSiMe_2[C_6H_3$-3,5-$(CF_3)_2]$ gave (*E,E*)-**3b** in 89% isolated yield [(*E,E*)/(*E,Z*) = 99/1]. The use of hydrosilanes in excess to *p*-diethynylbenzene is of particular importance for obtaining the doubly hydrosilylated products in high yields; otherwise, the reactions were not completed in 24 h at room temperature, and considerable amounts of single hydrosilylation products $HC≡CC_6H_4CH=CHSiMe_2Ar$ and their reduction pro-

ducts $H_2C=CHC_6H_4CH=CHSiMe_2Ar$ were formed in addition to **3**.

We next examined (*Z*)-selective hydrosilylation. As already reported [2], silylruthenium complex **2** exhibits extremely high catalytic activity. However, this complex is rather difficult to prepare. While the ruthenium hydrides $RuHCl(CO)L_2$ (L = PPr_3^i, PCy_3) coordinated with bulky phosphine ligands have been known to serve as precursors of (*Z*)-selective catalysts [2,10], we found $RuCl_2(CO)(PPr_3^i)_2$ (**6**) as a better alternative. Thus, complex **6** is synthesized easily in high yield [11] and exhibits the stereoselectivity, comparable to **2** and slightly higher than $RuHCl(CO)L_2$ [12].

Treatment of *p*-diethynylbenzene with 2 molar quantity of $HSiMe_2Th$ in CH_2Cl_2 in the presence of 10 mol% of **6** at room temperature for 5 h afforded (*Z,Z*)-**3a** in 92% geometrical purity [i.e. (*Z,Z*)/(*E,Z*) = 92/8] and 59% isolated yield. While the single hydrosilylation product (11%) was also formed in the reaction system, this could be removed by column chromatography. Similarly, (*Z,Z*)-**3b** [(*Z,Z*)/(*E,Z*) = 91/9] was prepared in 40% isolated yield.

1,4-bis(2-Silylethenyl)benzenes thus obtained were characterized by elemental analysis and ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy. The ^1H-NMR spectra of (*E,E*)-**3a** and (*E,E*)-**3b** exhibited olefinic proton signals at δ 6.95 and 6.57 ($^3J_{HH}$ = 19.1 Hz) and δ 6.97 and 6.54 ($^3J_{HH}$ = 19.1 Hz), respectively. On the other hand, the corresponding signals of (*Z,Z*)-isomers appeared with a smaller H–H coupling [**3a**: δ 7.43 and 5.99 ($^3J_{HH}$ = 14.8 Hz); **3b**: δ 7.47 and 5.93 ($^3J_{HH}$ = 15.0 Hz)]. The four aromatic protons of the central benzene ring exhibited only one singlet for all compounds, showing the symmetrically substituted structures of **3**.

2.2. Palladium-catalyzed polycondensation

Table 1 lists the results of polycondensation between equimolar amounts of **3** and 2,5-dioctyloxy-1,4-diiodobenzene (**4**). Except for run 9, the reactions were carried out at room temperature in THF in the presence of palladium catalyst and 2 molar quantity of tetrabutylammonium fluoride hydrate (TBAF·3H_2O), which was added as an activator of **3** [7,13]. The (*E,E*)-isomers of **3a** and **3b** were polymerized without notable loss of the geometrical purity of vinylene unit, giving (*E*)-rich poly[(1,4-phenylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] (**5**) in almost quantitative yields (runs 1, 2). The catalyst precursors [PdCl($η^3$-allyl)]$_2$, Pd(dba)$_2$, and Pd(OAc)$_2$ gave comparable results with each other for the reactions of (*E,E*)-**3a** (runs 1,3,4), while for (*E,E*)-**3b** only [PdCl($η^3$-allyl)]$_2$ exhibited the catalytic activity. Phosphine-coordinated complexes such as Pd(PPh$_3$)$_4$ were much less reactive (run 5).

Polycondensation of (*Z,Z*)-isomers was similarly examined (runs 6–9). Using [PdCl($η^3$-allyl)]$_2$ as an

Table 1
Palladium-catalyzed polycondensation between **3** and **4**

Run	**3** [a]	Catalyst	Yield (%) of **5** [b]	M_n (M_w/M_n) [c]	$(E):(Z)$ [d]
1	(E,E)-**3a**	[PdCl(η^3-allyl)]$_2$	> 99	5700 (1.62)	> 99: < 1
2	(E,E)-**3b**	[PdCl(η^3-allyl)]$_2$	> 99	6300 (2.30)	99:1
3	(E,E)-**3a**	Pd(dba)$_2$	95	5000 (1.39)	> 99: < 1
4	(E,E)-**3a**	Pd(OAc)$_2$	> 99	5700 (1.64)	> 99: < 1
5	(E,E)-**3a**	Pd(PPh$_3$)$_4$	0	–	–
6	(Z,Z)-**3a**	[PdCl(η^3-allyl)]$_2$	97	1600 (1.20)	45:55
7	(Z,Z)-**3b**	[PdCl(η^3-allyl)]$_2$	98	3100 (1.27)	46:54
8	(Z,Z)-**3a**	Pd(dba)$_2$	97	3700 (1.37)	34:66
9 [e]	(Z,Z)-**3a**	Pd(dba)$_2$	83	1900 (1.27)	38:62

All reactions were run in THF in the presence of palladium catalyst and TBAF·3H$_2$O at room temperature for 24 h, except for run 9. Initial concentration: [**3**]$_0$ = [**4**]$_0$ = 0.10 M, [catalyst]$_0$ = 5 (for [PdCl(η^3-allyl)]$_2$) or 10 mol% (for other complexes), [TBAF·3H$_2$O]$_0$ = 0.20 M.
[a] Geometrical purity: (E,E)-**3a** (> 99%), (E,E)-**3b** (99%), (Z,Z)-**3a** (92%), (Z,Z)-**3b** (91%). The minor isomer has (E,Z) geometry in all cases.
[b] Isolated yield.
[c] Determined by GPC based on polystyrene standards.
[d] Determined by ^{1}H-NMR spectroscopy.
[e] The reaction was carried out at 0 °C for 4 h.

catalyst precursor, moderately (Z)-rich **5** was obtained in high yields both from (Z,Z)-**3a** and **3b** (runs 6, 7). The (Z) content of vinylene unit was somewhat improved by using Pd(dba)$_2$ in place of [PdCl(η^3-allyl)]$_2$ (run 8), but no further improvement was observed even at lower reaction temperature (run 9). Since the isolated polymer was thermally stable [14], the (Z) to (E) isomerization of vinylene unit is considered to take place during the polymerization.

(E)- and (Z)-rich **5** were isolated as an orange powder or a gummy paste, respectively, which were highly soluble in THF, toluene, and CHCl$_3$, and insoluble in MeOH and hexane. Fig. 1 shows the ^{1}H-NMR spectra. The ratio of (E)- and (Z)-vinylene units was determined by peak integration of the signals at around δ 4.0 and 3.5, which are assignable to OCH$_2$ protons of octyloxy groups, adjacent to (E)- and (Z)-vinylene units, respectively [6a,b].

3. Conclusion

We have described that hydrosilylation of *p*-diethynylbenzene catalyzed by RuHCl(CO)(PPh$_3$)$_3$ (**1**) and RuCl$_2$(CO)(PPr$^i_3$)$_2$ (**6**) leads to almost geometrically pure (E,E)- and (Z,Z)-bis(2-silylethenyl)benzenes (**3**), respectively. The products could be utilized as monomers for palladium-catalyzed polycondensation with 2,5-dioctyloxy-1,4-diiodobenzene (**4**) in the presence of TBAF·3H$_2$O, giving (E)- and (Z)-rich PPVs (**5**). Although the (Z)-regularity still has an ample space to be improved, this study represents a new stereocontrolled way of synthesizing PPVs.

4. Experimental

4.1. General considerations

All manipulations were conducted under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing successively through the columns of an activated copper catalyst (BASF, R3-11) and P$_2$O$_5$ (Merck, SICAPENT). IR spectra were recorded on a JASCO FT/IR-410 instrument. NMR spectra were recorded on a Varian Mercury 300 spectrometer (^{1}H-NMR, 300.11 MHz; ^{13}C-NMR, 75.46 MHz). Chemical shifts are reported in δ (ppm), referred to ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). Flash column chromatography was performed with Merck silica gel 60 (230–400 mesh). Gel permeation chromatography was carried out on a JASCO GPC system equipped with an RI detector and three GPC columns (Shodex KF-801, KF-803L, KF-805L). Melting points were measured on a Yanaco MP-S3 instrument. Elemental analyses were carried out with a Perkin-Elmer 2400II CHN analyzer.

Dichloromethane and THF were dried over CaH$_2$ and sodium benzophenone ketyl, respectively. These solvents were distilled and stored over activated molecular sieves (MS4A) under a nitrogen atmosphere. The following compounds were synthesized according to literatures: RuHCl(CO)(PPh$_3$)$_3$ (**1**) [15], RuCl$_2$(CO)(PPr$^i_3$)$_2$ (**6**) [11], *p*-diethynylbenzene [16], dimethyl(2-thienyl)silane [9], dimethyl[3,5-bis(trifluoromethyl)phenyl]silane [17], 2,5-dioctyloxy-1,4-diiodobenzene (**4**) [18], Pd(dba)$_2$ [19], [PdCl(η^3-allyl)]$_2$ [19]. All other chemicals were obtained
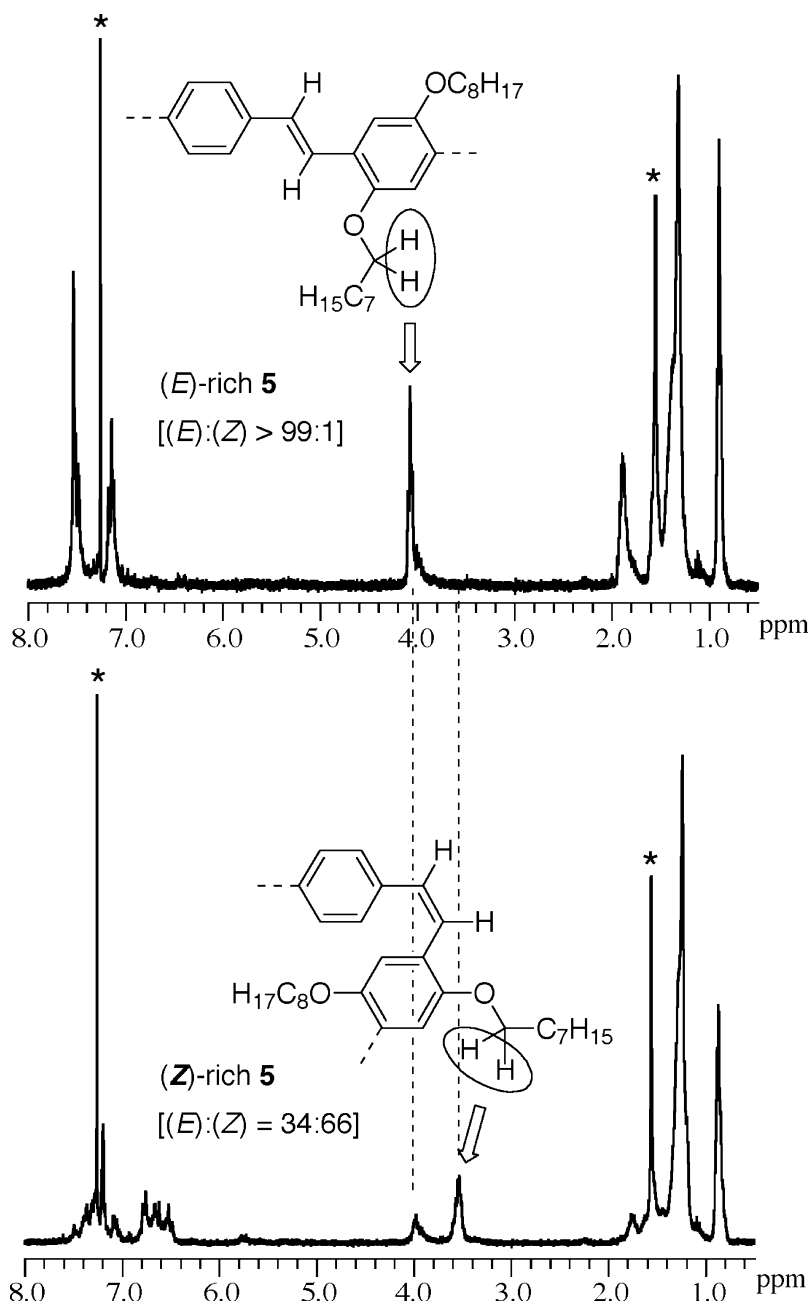
Fig. 1. ^{1}H-NMR spectra of (CDCl$_3$, 300.11 MHz) of (*E*)-rich (top) and (*Z*)-rich **5** (bottom), isolated from the reaction systems of runs 3 and 8 in Table 1, respectively. The starred signals at δ 7.26 and 1.60 are due to residual CHCl$_3$ and water, respectively.

from commercial suppliers and used without further purification.

4.2. Catalytic hydrosilylation of p-diethynylbenzene

A typical procedure for (*E,E*)-selective reaction is as follows. Solid RuHCl(CO)(PPh$_3$)$_3$ (**1**) (144 mg, 151 μmol) was added to a solution of *p*-diethynylbenzene (186 mg, 1.47 mmol) and HSiMe$_2$Th (1.15 g, 8.08 mmol) in CH$_2$Cl$_2$ (5.4 ml) at room temperature (r.t.). The mixture instantly changed into a red solution. After stirring the solution for 1 h, volatile materials were

removed by pumping. The resulting orange solid was purified by flash column chromatography (SiO$_2$, hexane–CH$_2$Cl$_2$ = 9/1) to give analytically pure (*E,E*)-**3a** [(*E,E*)/(*E,Z*) > 99/1] as a white solid (455 mg, 75% yield). Similarly, (*E,E*)-**3b** containing 1% of (*E,Z*)-isomer was obtained in 89% yield, using HSiMe$_2$[C$_6$H$_3$-3,5-(CF$_3$)$_2$] in place of HSiMe$_2$Th.

(*Z,Z*)-Selective reactions were carried out in CH$_2$Cl$_2$ at r.t. for 5 h using *p*-diethynylbenzene, hydrosilanes (2 molar quantity), and RuCl$_2$(CO)(PPr$^i_3$)$_2$ (**6**, 10 mol%). (*Z,Z*)-**3a** [(*Z,Z*)/(*E,Z*) = 92/8] and **3b** [(*Z,Z*)/(*E,Z*) = 91/9] were obtained in 59 and 40% yields, respectively.

No trace of (E,E)-isomer was detected by ^{1}H-NMR spectroscopy.

4.2.1. (E,E)-3a

M.p.: 86 °C. ^{1}H-NMR (CDCl$_3$): δ 7.64 (dd, $J = 4.6$, 0.9 Hz, 2H, Th), 7.41 (s, 4H, C$_6$H$_4$), 7.32 (dd, $J = 3.6$, 0.9 Hz, 2H, Th), 7.22 (dd, $J = 4.6$, 3.6 Hz, 2H, Th), 6.95 (d, $J = 19.1$ Hz, 2H, C$_6$H$_4$C$H=$), 6.57 (d, $J = 19.1$ Hz, 2H, $=$CHSi), 0.48 (s, 12H, SiMe$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 144.9 (s, C$_6$H$_4$CH$=$), 137.9, 134.8, 131.0, 128.2, 126.9, (each s, C$_6$H$_4$ and Th), 126.8 (s, $=$CHSi), −1.3 (s, SiMe$_2$). MS, m/z (rel. intensity, %): 410 [M$^+$, 26], 395 (2), 326 (9), 311 (11), 227 (16), 190 (15), 169 (15), 141 (100), 127 (28), 115 (9), 101 (14), 75 (12). Anal. Calc. for C$_{22}$H$_{26}$S$_2$Si$_2$: C, 64.33; H, 6.38. Found: C, 63.92; H, 6.35%.

4.2.2. (Z,Z)-3a

M.p.: 49 °C. ^{1}H-NMR (CDCl$_3$): δ 7.61 (dd, $J = 4.8$, 0.8 Hz, 2H, Th), 7.43 (d, $J = 14.8$ Hz, 2H, C$_6$H$_4$C$H=$), 7.28 (dd, $J = 3.3$, 0.8 Hz, 2H, Th), 7.18 (dd, $J = 4.8$, 3.3 Hz, 2H, Th), 7.16 (s, 4H, C$_6$H$_4$), 5.99 (d, $J = 14.8$ Hz, 2H, $=$CHSi), 0.32 (s, 12H, SiMe$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 147.8 (s, C$_6$H$_4$CH$=$), 139.1, 138.9, 134.6, 130.8, 130.0, 128.2 (each s, C$_6$H$_4$ and Th), 127.9 (s, $=$CHSi), 0.1 (s, SiMe$_2$). MS, m/z (rel. intensity, %): 410 [M$^+$, 25], 326 (10), 311 (12), 270 (9), 227 (21), 190 (12), 171 (23), 141 (100), 127 (30), 115 (12), 101 (15), 84 (15), 75 (17). Anal. Calc. for C$_{22}$H$_{26}$S$_2$Si$_2$: C, 64.33; H, 6.38. Found: C, 64.08; H, 6.39%.

4.2.3. (E,E)-3b

M.p.: 109 °C. ^{1}H-NMR (CDCl$_3$): δ 7.95 (br s, 4H, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 7.87 (br s, 2H, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 7.45 (s, 4H, C$_6$H$_4$), 6.97 (d, $J = 19.1$ Hz, 2H, C$_6$H$_4$C$H=$), 6.54 (d, $J = 19.1$ Hz, 2H, $=$CHSi), 0.51 (s, 12H, SiMe$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 146.2 (s, C$_6$H$_4$CH$=$), 142.2 (s, C$_6$H$_4$), 137.8, 133.5 (each s, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 130.8 (q, $^2J_{FC} = 33$ Hz, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 127.0 (s, C$_6$H$_4$), 125.1 (s, $=$CHSi), 123.6 (q, $^1J_{FC} = 273$ Hz, CF$_3$), 122.9 (septet, $^3J_{FC} = 4$ Hz, C$_6$H$_3$-3,5-(CF$_3$)$_2$), −2.8 (s, SiMe$_2$). Anal. Calc. for C$_{30}$H$_{26}$F$_{12}$Si$_2$: C, 53.72; H, 3.91. Found: C, 53.56; H, 3.83%.

4.2.4. (Z,Z)-3b

M.p.: 47 °C. ^{1}H-NMR (CDCl$_3$): δ 7.82 (br s, 4H, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 7.77 (br s, 2H, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 7.47 (d, $J = 15.0$ Hz, 2H, C$_6$H$_4$C$H=$), 6.93 (s, 4H, C$_6$H$_4$), 5.93 (d, $J = 15.0$ Hz, 2H, $=$CHSi), 0.32 (s, 12H, SiMe$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 149.2 (s, C$_6$H$_4$CH$=$), 142.9 (s, C$_6$H$_4$), 138.7, 133.4 (each s, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 130.6 (q, $^2J_{FC} = 33$ Hz, C$_6$H$_3$-3,5-(CF$_3$)$_2$), 128.4 (s, C$_6$H$_4$), 127.6 (s, $=$CHSi), 123.5 (q, $^1J_{FC} = 273$ Hz, CF$_3$), 122.6 (septet, $^3J_{FC} = 4$ Hz, C$_6$H$_3$-3,5-(CF$_3$)$_2$), −1.2 (s, SiMe$_2$). Anal. Calc. for C$_{30}$H$_{26}$F$_{12}$Si$_2$: C, 53.72; H, 3.91. Found: C, 54.16; H, 3.77%.

4.3. Palladium-catalyzed polycondensation

A typical procedure (run 3 in Table 1) is as follows. Solid Pd(dba)$_2$ (10.3 mg, 0.0199 mmol) and a solution of TBAF in THF (1.0 M containing 5 wt% water, Aldrich) were added successively to a solution of (E,E)-3a (82.2 mg, 0.200 mmol) and 2,5-dioctyloxy-1,4-diiodobenzene (4) (117 mg, 0.200 mmol) in THF (1.6 ml). The mixture was stirred at r.t. for 24 h. The resulting deep red sticky suspension was poured into vigorously stirred MeOH (50 ml). The orange–brown solid of polymer (5) thus precipitated was collected by filtration and washed with MeOH (88 mg, 95% yield). (E)-Content of vinylene unit ($> 99\%$) was determined by ^{1}H-NMR analysis. The molecular weight data ($M_n = 5000$, $M_n/M_w = 1.39$) were collected by GPC analysis using polystyrene standards (THF, flow rate 1.0 ml min^{-1}).

4.3.1. (E)-rich 5 [(E)/(Z) = > 99/1]

M.p.: > 380 °C (dec). IR (KBr): 3048, 2926, 2855, 1597, 1510, 1495, 1468, 1421, 1379, 1279, 1260, 1205, 1136, 1043, 964, 849, 805 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.56–7.42 (m, 6H, Ar and CH$=$CH), 7.18–7.05 (m, 4H, Ar and CH$=$CH), 4.08–3.92 (br, 4H, OCH$_2$), 1.94–1.72 (br, 4H, CH$_2$), 1.48–1.20 (br, 20H, CH$_2$), 0.94–0.82 (br, 6H, CH$_3$).

4.3.2. (Z)-rich 5 [(E)/(Z) = 34/66]

IR (KBr): 3046, 2925, 2855, 1603, 1495, 1469, 1422, 1379, 1278, 1205, 1137, 1045, 964, 850 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.54–7.03 (m, 6H, Ar and CH$=$CH), 6.78–6.48 (m, 4H, Ar and CH$=$CH), 4.02–3.86 (br, 1.36H, OCH$_2$ in (E)-olefin fragment), 3.62–3.48 (br, 2.64H, OCH$_2$ in (Z)-olefin fragment), 1.80–1.16 (br, 24H, CH$_2$), 0.91–0.79 (br, 6H, CH$_3$).

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