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Thorpe–Ingold Effect on the Helicity of Chiral Alternating Silylene-Divinylarene Copolymers

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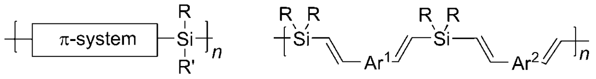
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The concept of the Thorpe–Ingold effect has been used to rationalize the helicity of the silylene-spaced divinylarene copolymers having chiral substituents. Diisopropylsilylene-spaced divinylbenzene copolymers having chiral 2-methylbutoxy substituents have been shown to exhibit a helical conformation. The presence of the bulky isopropyl substituents on silicon would render each of the monomeric units in these copolymers to favor a syn–syn conformation. The copolymer would thus be more folded to form helical morphology as revealed by the notable enhancement of the circular dichroic intensity. The reversible temperature-dependent circular dichroism (CD) profiles further support the stable helical conformation for the copolymers **4b** and **5b**.

Keywords: aggregation · circular dichroism · copolymerization · fluorescence · helical structures

Introduction

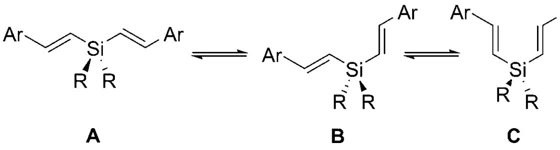
Alternating silylene-conjugated chromophore copolymers **1**[1] (Scheme 1) are known to exhibit a range of fascinating photophysical properties, such as intrachain chromophore-chromophore aggregation,[2] fluorescence resonance energy transfer (FRET)[3] and photoinduced electron transfer[4] between neighboring chromophores, as well as electroluminescent applications.[5] The folding nature of **1** may occasionally play an important role in dictating some of these interesting photophysical properties. We recently found that the size of the substituent on the silylene spacer would furnish the Thorpe–Ingold effect[6,7] on the conformation of the silylene-spaced divinylarene copolymers **2** (Scheme 1).[2c,4b] Thus, intrachain aggregration becomes more prominent when the methyl substituent in **2a** is replaced by the isopropyl group (e.g., **2b**).[2c] Similarly, the rate of the intrachain photoinduced electron transfer is enhanced when R in **2b** is the bulky isopropyl substituent in comparison with **2a** having a methyl group.[4b] The origin of this folding character may arise from the conformational equilibrium of the divinylsilane moiety in **2** [Eq. (1)].[2c,4b]



1

2a R = Me
b R = *i*Pr

Scheme 1. Silylene-conjugated and silylene-spaced divinylarene copolymers.



(1)

When dimethylsilylene-spaced divinylarene copolymers are incorporated with chiral substituents, copolymers **3** (Scheme 2), for example, show characteristic circular dichroitic properties at relatively high concentration. No CD curves are, however, observed at low concentration.[8] Presumably, aggregation of polymer **3** plays a pivotal role to enhance the circular dichroitic properties.[9,10] It is envisaged that, when the methyl substituent on silicon in **3** is changed

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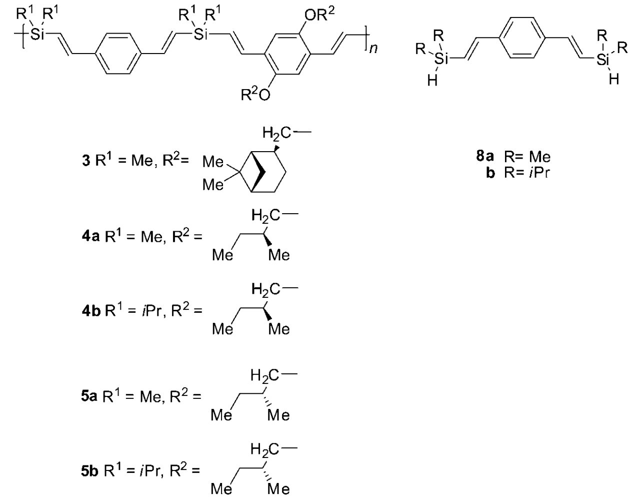
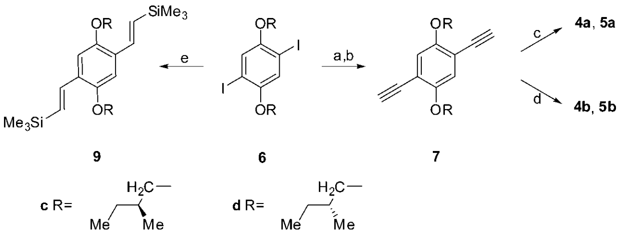


Scheme 2. Various silylene-spaced divinylarene copolymers.

to the bulky isopropyl group, conformation **C** shown in Equation (1) would be favored for each of the monomeric units in these silicon-containing copolymers. As such, the polymer might favor a helical conformation. We now wish to report the first example of the Thorpe–Ingold effect on the helicity of the silylene-spaced divinylarene copolymers **4** and **5** (Scheme 2).

Results and Discussion

Enantiomerically pure 2-methylbutoxy group has commonly been used as the chiral auxiliary in optically active polymers.[10] We chose to use the same chiral substituent for the syntheses of **4** and **5** which were based on the known hydrosilylation strategy as outlined in Scheme 3. The corresponding monomeric model compounds **9** (Scheme 3) were also prepared for comparison.



Scheme 3. Syntheses of **4** and **5**. a) TMSC≡CH, Pd(PPh_3)$_2$Cl$_2$, CuI, Et_3N, 92–95%: b) KOH, 87–90%; c) **8a**, Rh(PPh_3)$_3$Cl, 82–85% (**4a**: M_n=17400, PDI=2.09 **5a**: M_n=16300, PDI=2.22); d) **8b**, Rh(PPh_3)$_3$Cl, 78–80% (**4b**: M_n=19500, PDI=2.25 **5b**: M_n=21200, PDI=2.19); e) Pd(OAc)$_2$, Bu_4NOAc, 86–91%.

The CD curves and absorption spectra of **4** and **5** in dodecane at ambient temperature are shown in Figure 1. It is noteworthy that CD signals were observed for **4b** and **5b** at a relatively low concentration (10 mg L)$^{-1}$. Since the degree of polymerization of **4b** and **5b** were similar, mirror-image curves for **4b** and **5b** were therefore expected. On the other hand, the circular dichroitic intensities were too weak to be observed for **4a** and **5a** at the same concentration. However, **4a** and **5a** showed CD signals at high concentration (1 g L)$^{-1}$, indicating that aggregation might take place as in the case of **3**.[8] No CD profiles were observed for monomers **9c** or **9d**.

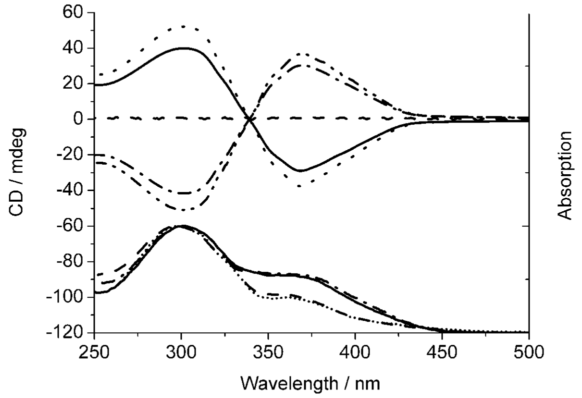


Figure 1. The CD (upper) and absorption (lower) spectra of polymers **4a** ($10\,mg\,L^{-1}$, -----; $1\,g\,L^{-1}$, •••••, **4b** ($10\,mg\,L^{-1}$, ——), **5a** ($10\,mg\,L^{-1}$, short •••••; $1\,g\,L^{-1}$, dash-dot-dot) and **5b** ($10\,mg\,L^{-1}$, –•–•) in dodecane at ambient temperature.

The fluorescence spectra of **4a** and **4b** (λ_{ex}=300 nm) in dodecane at ambient temperature are shown in Figure 2. At low concentration, the emission profile of **4a** was similar to that of **9c**. At high concentration, λ_{em} of **4a** shifted to longer wavelength, presumably as a result of interchain aggregation. Interestingly, emission maxima of **4b** appeared at 436 and 460 nm even at low concentration and the profile remained unchanged within the concentration range of $10\,mg\,L^{-1}$ to $200\,mg\,L^{-1}$. As a result of the bulky isopropyl substituents, each of the monomeric unit in **4b** would adopt conformation **C** [Eq. (1)] arising from the Thorpe–Ingold effect. Accordingly, **4b** would be more folded. It seems

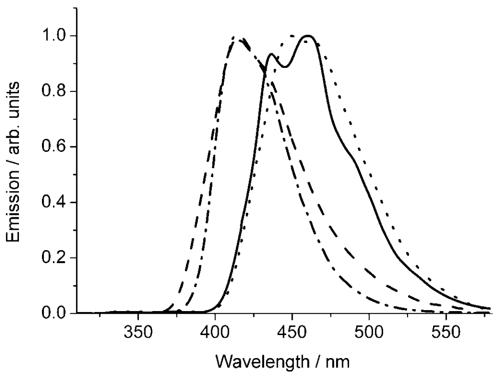


Figure 2. The emission spectra of polymers **4a** ($10\,mg\,L^{-1}$, -----; $1\,g\,L^{-1}$, •••••), **4b** ($10\,mg\,L^{-1}$, ——) and model compound **9c** (–•–•) in dodecane at ambient temperature.

likely that the divinylarene chromophores in **4b** might be in close proximity so that intrachain interaction between these chromophores might take place, resulting in a red shift in the emission profile. In addition, intrachain chromophore–chromphore interactions in **4b** may lead to a more rigid conformation so that structured emission could be observed.

Temperature-dependent CD profiles have been extensively used to elucidate helix–random coil interconversion.[11] We have carried out a similar examination on copolymer **4b**. As shown in Figure 3a, the CD intensities of **4b** decreased as the temperature increased and the circular dichroitic properties were completely lost at 100 °C. The overall process was reversible and the original CD curve was regenerated upon cooling. Relatively speaking, the circular dichroitic properties of **4a** (at 1 gL^{-1}) in dodecane were less sensitive to temperature changes and were only slightly perturbed as with a temperature increase from −10 to 110 °C (Figure 3b).

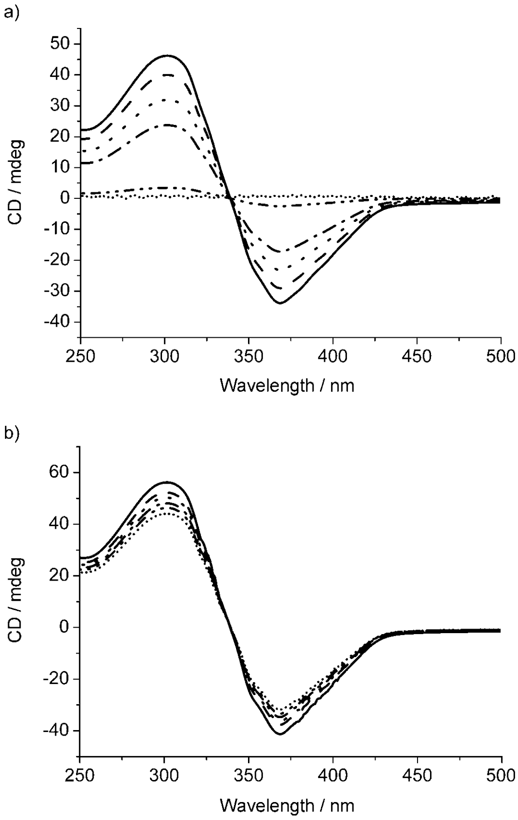


Figure 3. Temperature-dependent CD spectra of a) **4b** in dodecane at 10 mgL^{-1}. b) **4a** in dodecane at 1 gL^{-1}. (0 °C: ——; 20 °C: -----; 40 °C: •••••; 60 °C: –•–•; 80 °C: dash-dot-dot; 100 °C: short •••••).

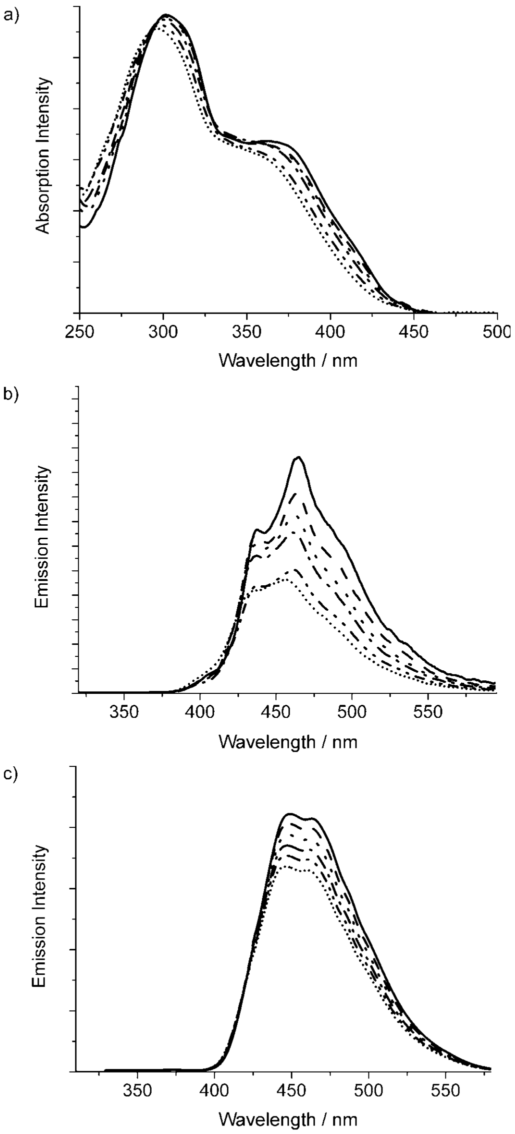


Figure 4. Temperature-dependent a) absorption spectra of **4b** in dodecane at 10 mgL^{-1}; b) fluorescence spectra of **4b** in dodecane at 10 mgL^{-1}; c) fluorescence spectra of **4a** in dodecane at 1 gL^{-1}. (0 °C: ——; 20 °C: -----; 40 °C: •••••; 60 °C: –•–•; 80 °C: dash-dot-dot; 100 °C: short •••••).

Temperature-dependent absorption and emission spectra of **4b** in dodecane are shown in Figure 4. It is interesting to note that the emission profiles appear to be significantly changed as the temperature increased. The conformational change may provoke variations in the chromophore–chromophore interactions in **4b**. These results appear to be consistent with the temperature-dependent CD profiles of **4b** (Figure 3a). Relatively speaking, the emission properties of **4a** at high concentration were only slightly perturbed with temperature (Figure 4). Again, these results were in agreement with the variable temperature CD experiments on **4a** (Figure 3b).

Figure 5 shows the change of the circular dichroitic intensities of **4b** in dodecane in multiple thermal stages. The CD signals were monitored at 300 nm and 368 nm at 0 °C, 30 °C, 60 °C, and 100 °C. The signals disappeared at 100 °C as a result of conformational changes and gradually appeared again at 60 °C and 30 °C, and completely recovered at 0 °C. These CD profiles were reproducible after several thermal cycles.

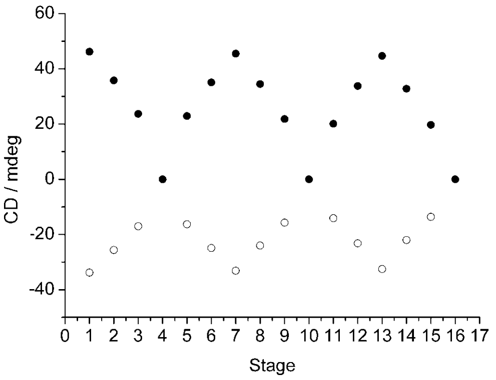


Figure 5. Change of CD intensities of **4b** in dodecane in multiple thermal stages and monitored at 300 nm (●) and 368 nm (○). (stages 1, 7, and 13: 0 °C, stages 2, 6, 8, 12, and 14: 30 °C, stages 3, 5, 9, 11, and 15: 60 °C, stages 4, 10, and 16: 100 °C).

In summary, we have demonstrated the first example using the concept of the Thorpe–Ingold effect to describe the helicity of the silylene-spaced divinylarene copolymers having chiral substituents. The presence of the bulky isopropyl substituents on silicon would render each of the monomeric units in these copolymers to favor conformation **C**, shown in Equation (1). The copolymer would thus be more folded to form a helical morphology as revealed by the notable enhancement of the circular dichroitic intensity. The reversible temperature-dependent CD profiles further supported the stable helical conformation for the copolymers **4b** and **5b**.

Experimental Section

General.

Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1.0 mL min^{-1}). Waters styragel HR2, HR3, HR4 (7.8 × 300 mm) were employed using polystyrene as standard (M_n values range from 375 to 3.5 × 10^6). Absorption spectra and emission spectra were measured with a Hitachi U-3310 and a Hitachi F-4500 fluorescence spectrophotometers, respectively. CD spectra were recorded on a JASCO J-815 spectropolarimeter. Mass spectra (HRMS) were recorded on a JEOL SX-102 mass spectrometer.

Synthesis

6c[12] **and 6d**: 1,4-Diiodo-2,5-bis(*S*-2-methylbutoxy)benzene and 1,4-diiodo-2,5-bis(*R*-2- methylbutoxy)benzene. To a solution of 2,5-diiodobenzene-1,4-diol[13] (9.20 g, 25.4 mmol) and *R*-2-methyl-butyl tosylate[14] (12.1 g, 53.5 mmol) in DMSO (175 mL) KOH was added (4.5 g, 80.2 mmol). The mixture was stirred at room temperature for 36 h, poured into water, and extracted twice with ether. The combined organic extracts were washed with 10 % NaOH, water, and brine successively, dried with ($MgSO_4$), and then filtered. The solvent was removed in vacuo and the residue was recrystallized from $CHCl_3$/MeOH to afford **6d** as a white solid (6.76 g, 53 %): m.p. 75–76 °C $[\alpha]_D^{22} = -7.0$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz): $\delta = 0.97$ (t, $J = 7.4$ Hz, 6H), 1.08 (d, $J = 6.8$ Hz, 6H), 1.28–1.37 (m, 2H), 1.56–1.65 (m, 2H), 1.86–1.93 (m, 2H), 3.72 (dd, $J = 8.7$, 6.2 Hz, 2H), 3.80 (dd, $J = 8.7$, 5.6 Hz, 2H), 7.16 ppm (s, 2H); ^{13}C NMR (100 MHz): $\delta = 11.5$, 16.8, 26.2, 34.9, 74.8, 86.0, 122.3, 152.6 ppm; IR (KBr): $\tilde{\nu} = 2960$, 2920, 2874, 1485, 1460, 1389, 1349, 1263, 1211, 1055, 1007, 991, 850, 792 cm^{-1}; HRMS (EI) ($C_{16}H_{24}I_2O_2$): calcd: 501.9866 found: 501.9856.

6c: m.p. 75–76 °C (lit.[12] m.p. 74–76.5 °C) $[\alpha]_D^{22} = +7.2$ ($c = 0.1$ in $CHCl_3$).

10c[15] and 10d: 2,5-Bis(*S*-2-methylbutoxy)-1,4-bis(trimethylsilylethynyl)-benzene and 2,5- bis(*R*-2-methylbutoxy)-1,4-bis(trimethylsilylethynyl)-benzene. To a stirred mixture of **6d** (3.97 g, 7.9 mmol), CuI (0.12 g, 0.64 mmol) and $Pd(PPh_3)_2Cl_2$ (0.28 g, 0.40 mmol) in THF (15 mL), Et_3N (3.5 mL, 24.4 mmol) and trimethylsilylacetylene (2.61 mL, 17.4 mmol) in THF (5 mL) were sequentially added. The mixture was stirred at room temperature for 4 h. The solid was filtered through silica gel and the filtrate was evaporated in vacuo to give **10d** (3.22 g, 92 %): m.p. 106–107 °C ($CHCl_3$/MeOH) $[\alpha]_D^{22} = -12.4$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz): $\delta = 0.24$ (s, 18H), 0.96 (t, $J = 7.4$ Hz, 6H), 1.05 (d, $J = 6.8$ Hz, 6H), 1.27–1.34 (m, 2H), 1.58–1.65 (m, 2H), 1.86–1.91 (m, 2H), 3.75 (dd, $J = 8.7$, 6.4 Hz, 2H), 3.80 (dd, $J = 8.7$, 6.2 Hz, 2H), 6.88 ppm (s, 2H); ^{13}C NMR (100 MHz): $\delta = 0.1$, 11.6, 16.6, 26.2, 35.0, 74.1, 99.9, 101.0, 113.8, 116.7, 153.9 ppm; IR (KBr): $\tilde{\nu} = 2960$, 2920, 2876, 2152, 1499, 1463, 1406, 1390, 1274, 1249, 1226, 1208, 1039, 894, 843, 759 cm^{-1}; HRMS (EI) ($C_{26}H_{42}O_2Si_2$): calcd: 442.2723 found: 442.2717.

10c: m.p. 106–107 °C (lit.[15] 109 °C) $[\alpha]_D^{22} = +12.3$ ($c = 0.1$ in $CHCl_3$).

7c and 7d: 2,5-Bis(*S*-2-methylbutoxy)-1,4-diethynylbenzene (7c)[15] and 2,5-bis(*R*-2-methyl- butoxy)-1,4-diethynylbenzene. To a stirred solution of **10d** (2.61 g, 5.9 mmol) in THF (100 mL), MeOH (50 mL) and 20 % aqueous KOH solution (3.5 mL) were added. The mixture was stirred at room temperature for 2 h, poured into water, then extracted twice with CH_2Cl_2. The combined organic extracts were washed with water, and brine, dried with ($MgSO_4$), and then filtered. The solvent was removed in vacuo to give the residue which was chromatographed on silica gel (0.5 % ethyl acetate/hexane) to afford **7d** (1.58 g, 87 %): m.p. 62–63 °C $[\alpha]_D^{22} = -15.2$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz): $\delta = 0.96$ (t, $J = 7.4$ Hz, 6H), 1.04 (d, $J = 6.4$ Hz, 6H), 1.24–1.33 (m, 2H), 1.56–1.61 (m, 2H), 1.88–1.93 (m, 2H), 3.33 (s, 2H), 3.74 (dd, $J = 8.6$, 6.6 Hz, 2H), 3.84 (dd, $J = 8.6$, 6.2 Hz, 2H), 6.94 ppm (s, 2H); ^{13}C NMR (100 MHz): $\delta = 11.5$, 16.6, 26.2, 34.8, 74.4, 79.7, 82.3, 113.1, 117.4, 153.9 ppm; IR (KBr): $\tilde{\nu} = 3269$, 3253, 2957, 2930, 2874, 1494, 1464, 1407, 1382, 1271, 1219, 1199, 1035, 865, 837 cm^{-1}; HRMS (EI) ($C_{20}H_{26}O_2$): calcd: 298.1933 found: 298.1930.

7c: m.p. 62–63 °C $[\alpha]_D^{22} = +15.0$ ($c = 0.1$ in $CHCl_3$).

9c and 9d: 2,5-Bis-(*S*-2-methylbutoxy)-1,4-bis-(2-trimethylsilanylvinyl)-benzene and 2,5-bis-(*R*-2-methylbutoxy)-1,4-bis-(2-trimethylsilanylvinyl)-benzene. Under N_2, a mixture of **6c**[12] (2.51 g, 5 mmol), trimethylvinylsilane (1.20 g, 12 mmol), $Pd(OAc)_2$ (0.11 g, 0.5 mmol), Bu_4NOAc (6.03 g, 20 mmol) and molecular sieves (4 Å) in dry DMF (150 mL) was stirred at 80 °C for 24 h. After filtration over celite, the solvent was evaporated in vacuo to give the residue which was chromatographed on Et_3N-treated silica gel (CH_2Cl_2/hexane = 1:4) to afford **9c** as a white solid (2.03 g, 91 %): m.p. 102–103 °C $[\alpha]_D^{22} = +15.6$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.18$ (s, 18H), 0.99 (t, $J = 7.4$ Hz, 6H), 1.07 (d, $J = 6.8$ Hz, 6H), 1.25–1.34 (m, 2H), 1.60–1.65 (m, 2H), 1.85–1.92 (m, 2H), 3.79 (dd, $J = 8.8$, 6.0 Hz, 2H), 3.85 (dd, $J = 8.8$, 6.0 Hz, 2H), 6.42 (d, $J = 19.4$ Hz, 2H), 7.04 (s, 2H), 7.32 ppm (d, $J = 19.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -1.0$, 11.6, 16.9, 26.4, 35.2, 74.1, 110.0, 128.0, 129.2, 137.6, 150.6 ppm; IR (KBr): $\tilde{\nu} = 2957$, 2916, 2876, 1591, 1483, 1463, 1420, 1331, 1277, 1248, 1223, 1197, 1044, 994, 865, 837, 736 cm^{-1}; HRMS (EI) ($C_{26}H_{46}O_2Si_2$): calcd: 446.3036 found: 446.3046. **9d** (1.92 g, 86 %) was obtained in a manner similar to that described above, from **6d** as starting material $[\alpha]_D^{22} = -15.2$ ($c = 0.1$ in $CHCl_3$) HRMS (EI) ($C_{26}H_{46}O_2Si_2$): calcd: 446.3036 found: 446.3042.

Polymers 4a and 5a. To a solution of **7c**[15] (298 mg, 1 mmol) and **8a**[2a] (246 mg, 1 mmol) in THF (5 mL) $Rh(PPh_3)_3Cl$ (4.6 mg, 0.1 M) was added under N_2. The mixture was refluxed for 10 h, cooled to room temperature and then poured into MeOH to precipitate. The precipitate was collected and re-dissolved in THF, then precipitated again with MeOH. The product **4a** was collected by filtration and washed with MeOH (0.46 g, 85 %): $M_n = 17400$, PDI = 2.09; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.27$ (s, 12H), 0.94–0.96 (t, 6H), 1.02–1.04 (d, 6H), 1.27–1.35 (m, 2H), 1.55–1.65 (m, 2H), 1.85–1.90 (m, 2H), 3.75–3.80 (m, 2H), 3.80–3.85 (m, 2H), 6.43–6.56

(m, 4H), 6.92–6.96 (d, 4H), 7.05 (s, 2H), 7.42–7.52 ppm (m, 4H); IR (KBr): $\tilde{\nu}=2959$, 2930, 2875, 1597, 1507, 1490, 1459, 1419, 1386, 1318, 1247, 1217, 1196, 1041, 987, 840 cm^{-1}. Polymer **5a** (0.44 g, 82 %) was obtained in a manner similar to that described above, from **7d** and **8a**: $M_n=16300$, PDI = 2.22.

Polymers 4b and 5b. In a manner similar to that described above, a mixture of **7c**[15] (298 mg, 1 mmol), **8b**[2c] (359 mg, 1 mmol) and $Rh(PPh_3)_3Cl$ (4.6 mg, 0.1 M) was converted to **4b** (0.51 g, 78 %): $M_n=19500$, PDI = 2.25; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=0.91$–0.94 (t, 6H), 1.00–1.04 (d, 6H), 1.12–1.20 (d, 24H), 1.22–1.25 (m, 4H), 1.55–1.65 (m, 2H), 1.85–1.90 (m, 2H), 3.80–3.85 (m, 2H), 3.85–3.90 (m, 2H), 6.39–6.53 (m, 4H), 7.01–7.10 (d, 4H), 7.07 (s, 2H), 7.45–7.50 ppm (m, 4H); IR (KBr): $\tilde{\nu}=2956$, 2930, 2862, 1597, 1489, 1462, 1419, 1384, 1321, 1219, 1188, 1049, 991, 881 cm^{-1}. Polymer **5b** (0.52 g, 80 %) was obtained in a manner similar to that described above, from **7d** and **8b**: $M_n=21200$, PDI = 2.19.

Acknowledgements

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