Novel Silicon-Substituted, Soluble Poly(phenylenevinylene)s: Enlargement of the Semiconductor Bandgap

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A poly(phenylenevinylene) with a silicon substituent and an *epi*-cholestanoxy substituent in the aromatic rings was prepared by a nonaqueous polymerization reaction. The polymer is soluble in most polymer solvents and can be processed to produce free-standing films. The silicon substituent has the effect of *enlarging* the semiconductor gap with a concomitant change in the polymer's color from orange [bis(3-*epi*-cholestanoxy)PPV] to yellow. The monomer was prepared by an unusual oxygen-to-carbon rearrangement of the silicon substituent.

In the continued quest for blue-fluorescing conjugated polymers,[1] where the semiconductor bandgap is wider than in currently known processable, dialkoxy PPVs, we designed PPVs with a silicon substituent. Though trimethylsilyl and trihexylsilyl groups were targeted first, they were found to produce an insoluble polymer. The substituent which eventually led to a processable polymer was the dimethylthexylsilyl group. To provide additional solubilizing properties, the other substituent on the new PPV was the *epi*-cholestanoxy group[2,3] (see Scheme 2).

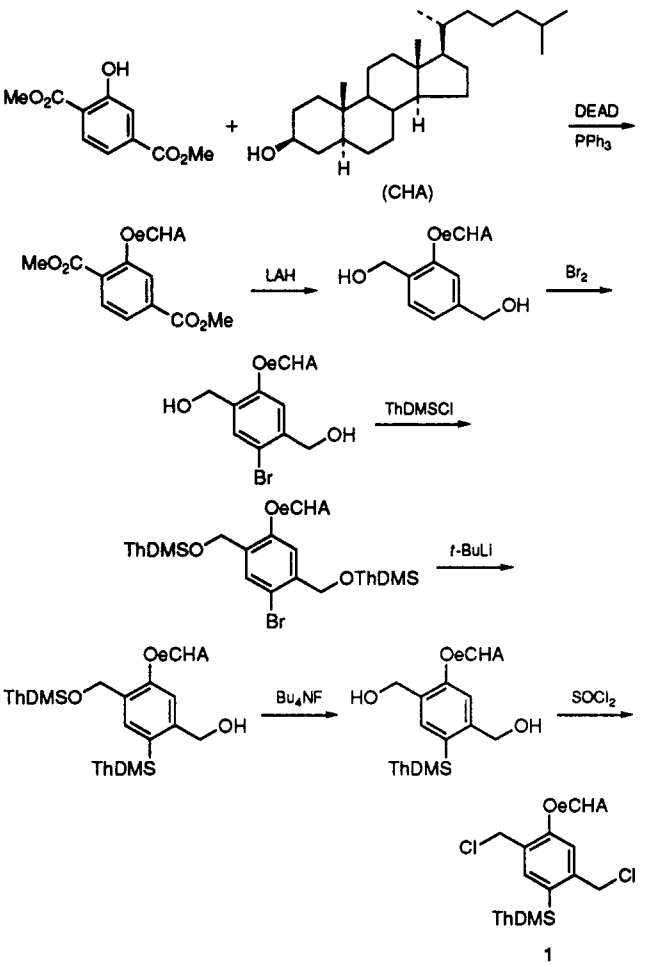
Here we report the preparation of polymer **2** and the synthesis of the monomer **1**. The latter was prepared via a very efficient 1,4-oxygen-to-carbon silicon rearrangement,[4] as detailed in Scheme 1.

The first four synthetic steps afforded products in 82, 83, 87, and 85%, respectively. The rearrangement step proceeded in 71% and the remaining two steps yielded products in 85 and 42%, respectively. Spectroscopic and other characterization data were in good agreement with the structures proposed for all synthetic intermediates and monomer **1**.

The polymerization reaction was carried out in nonaqueous medium with potassium *tert*-butoxide as base (Scheme 2).

Whereas bis(*epi*-cholestanoxy)PPV is light orange (λ_{max} = 510 nm),[5] the silylated polymer **2** is yellow; an observation which is consistent with a shorter absorption wavelength (λ_{max} = 450 nm; Figure 1). The polymer is soluble in chloroform, xylenes, toluene, and THF. It can be purified by reprecipitation from chloroform with methanol.

Scheme 1



The effect of silylation on the electronic properties of the monomer or polymer was not easy to predict since the electronic effect of organosilicon substitution on an aromatic ring is "schizophrenic"; i.e., for Me_3Si[6] σ°_p = 0.0,

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(1) Williams, E. W. *Luminescence and the Light Emitting Diode*; Pergamon Press: New York, 1978. Bloor, D. *Nature* **1992**, *356*, 19. A blue LED with an efficiency of 0.01–0.05% has been made from poly(*p*-phenylene): Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36. The efficiency of another blue emitter based on poly(alkylfluorene) was not reported: Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, *11B*, L1941.

(2) Wudl, F.; Höger, S.; Zhang, C.; Pakbaz, K.; Heeger, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 197.

(3) In previous publications we refer to this substituent as a "cholestanoxy" group. The method of synthesis causes an inversion of configuration at the 3-carbon (oxy-substituted site); hence, the correct name should be "*epi*-cholestanoxy".

(4) The synthesis of a number of other silicon-substituted PPV precursors by this rearrangement process will be published elsewhere; Wudl, F.; Höger, S., unpublished.

(5) Wudl, F.; Höger, S.; Zhang, C.; Pakbaz, K.; Heeger, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 197.

(6) Exner, O. As quoted in Isaacs, N. S. *Physical Organic Chemistry*; Wiley: New York, 1987; Chapter 4.

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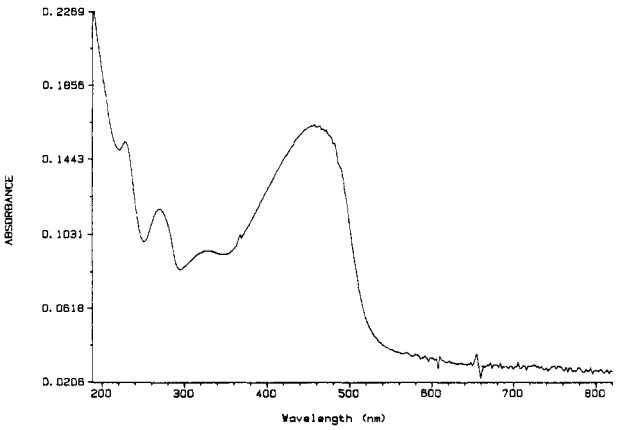
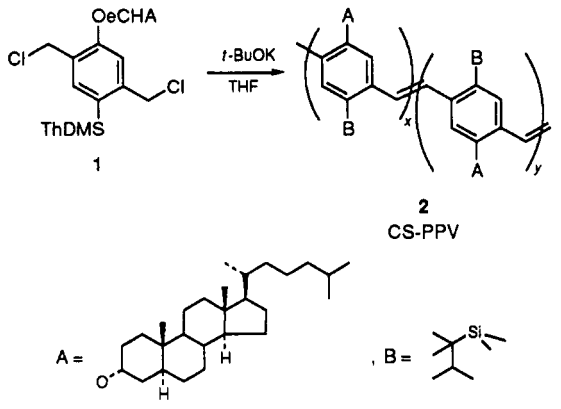


Figure 1. Ultraviolet–visible spectrum of polymer **2** as a neat film.

Scheme 2



yet $\sigma^{\circ}_{m} = 0.11$. This implies that the trimethylsilyl group is *as strong an inductive* electron-withdrawing group (EWG) as methoxy ($\sigma^{\circ}_{m} = 0.10$) yet has the same *resonance* electronic effect as the "reference substituent" H.

It appears, from the electronic spectroscopy of **2**, that the silyl substituent acts as an EWG or that it increases the semiconductor bandgap of the PPV backbone, an effect which is opposite to that of a cholestanoxy group.

A consequence of the above is that the photo- and electroluminescence of thin films of the polymer is a beautiful light-green color.[7]

Experimental Section

Preparation of Dimethyl-2-(3-*epi*-cholestanoloxy)terephthalate. To a stirring solution of 25.0 g (64.3 mmol) of cholestanol, 10.15 g (33.0 mmol) of dimethyl-2-hydroxyterephthalate and 17.8 g (74.0 mmol) of triphenylphosphine in 400 mL of ether was added dropwise 11.8 g (68.0 mmol) of diethyl azodicarboxylate in 80 mL of ether. After this was stirred for 3 days at room temperature, 600 mL of water and 300 mL of ether were added and the aqueous phase was extracted with ether (two times, each 200 mL). The combined organic phase was washed once with 200 mL of water, three times with 100 mL of 7% aqueous NaOH, and once with 200 mL of water and with 200 mL of brine, followed by drying over $MgSO_4$ and evaporation of the solvent. The product was then separated from the triphenylphosphine oxide by passing over a short column of silica gel (hexanes/ether 3:1). The product was dissolved in hot acetone, cooled to room temperature, and precipitated by the addition of methanol. Filtration and washing with methanol yielded after drying in vacuum 30.7 g (82%) of white product. ^{1}H NMR ($CDCl_3$) δ = 0.62–2.03 (m, 46 H), 3.93 (s, 3H), 3.94 (s, 3 H), 4.74 (s, 1 H), 7.55–7.81 (m, 3 H). IR (KBr) 2934, 2867, 1730, 1603, 1572, 1493, 1434, 1415, 1382, 1365, 1291, 1228, 1106, 1076, 1003, 759 cm^{-1}; mp 104–106 °C. MS (FAB) 581.41 (M^+ – cluster).

Preparation of 1,4-Bis(hydroxymethyl)-2-(3-*epi*-cholestanoxy)benzene. While stirring a suspension of 4.6 g (120.0 mmol) of LAH in 100 mL of THF, a solution of 29.9 g (50.2 mmol) of dimethyl-2-(3-*epi*-cholestanoloxy)terephthalate was added at 0 °C dropwise. After 2 h at 0 °C the suspension was allowed to reach room temperature and stirred overnight at room temperature. The reaction was quenched with 10 mL of water, and after 3 h 10 mL of 15% aqueous NaOH was added. The reaction mixture was allowed to stir for 3 h before it was filtered. The residue was washed four times with ether (each 150 mL). The combined organic phase was then washed six times with water (each 200 mL) and once with brine (200 mL) and then dried over $MgSO_4$. Evaporation of the solvent yielded 21.7 g (83.0%) of colorless product. ^{1}H NMR ($CDCl_3$) δ = 0.62–2.02 (m, 46 H), 4.62–4.74 (m, 5 H), 6.82–7.28 (m, 3 H). IR (KBr) 3441, 2928, 2866, 1620, 1498, 1466, 1454, 1444, 1421, 1382, 1365, 1341, 1203, 1160, 1032, 997, 977, 911 cm^{-1}; mp >210 °C. MS (FAB) 524.4.

Preparation of 1-Bromo-4-(3-*epi*-cholestanoxy)-2,5-bis(hydroxymethyl)benzene. To a vigorously stirred two-phase system containing 21.0 g (40.0 mmol) of 1,4-bis(hydroxymethyl)-2-(3-epi-cholestanoxy)benzene in 300 mL of CCl_4 and K_2CO_3 (7.0 g)/$KHCO_3$ (3.5 g) in 100 mL of water was added 9.0 g (56.3 mmol) bromine in 35 mL of CCl_4 dropwise at 0 °C. After 2 h the cooling bath was removed, and the solution stirred for 4 days at room temperature. The mixture was poured into 950 mL of ether and 600 mL of water. The organic phase was extracted with water (300 mL), 5% aqueous $NaHCO_3$ solution three times (each 150 mL), water (300 mL), and brine (300 mL). After drying over $MgSO_4$, the solvent was removed to yield 26.5 g of crude 1-bromo-4-(3-*epi*-cholestanoxy)-2,5-bis(hydroxymethyl)benzene. This was dissolved in 50 mL of THF and added dropwise at 0 °C to a suspension of 4.0 g of LAH in 150 mL of THF added. After 2 h the cooling bath was removed, and the solution stirred overnight at room temperature. The reaction was quenched with 10 mL of water, and after 3 hours 10 mL of 15% aqueous NaOH was added. The reaction mixture was allowed to stir for 3 h before it was filtered. The residue was washed four times with ether (each 150 mL). The combined organic phase was then washed six times with water (each 200 mL) and once with brine (200 mL) and then dried over $MgSO_4$. Evaporation of the solvent yielded 21.1 g (87.0%) of colorless product. ^{1}H NMR ($CDCl_3$) δ = 0.6–2.0 (m, 46 H), 4.65–4.72 (m, 5 H), 7.02 (s, 1 H), 7.46 (s, 1 H). IR (KBr) 3421, 2932, 2865, 1487, 1466, 1455, 1444, 1393, 1382, 1364, 1341, 1301, 1281, 1251, 1150, 1033, 1001, 976, 908 cm^{-1}; mp 120–122 °C.

Preparation of 1-Bromo-4-(3-*epi*-cholestanoxy)-2,5-bis((dimethylthexylsiloxy)methyl)benzene. 1-Bromo-4-(3-*epi*-cholestanoxy)-2,5-bis(hydroxymethyl)benzene (20.8 g 34.4 mmol), 12.0 g (176.2 mmol) of imidazole, and 16.0 g (89.5 mmol) of dimethylthexylsilyl chloride were stirred in 50 mL DMF at 4 °C for 16 h. The mixture was poured into 300 mL of ether and 200 mL of water. The organic phase was extracted with 200 mL of water, 7% aqueous acetic acid (three times, each 150 mL), 200 mL of water, and 200 mL of brine. After drying over $MgSO_4$ and evaporation of the solvent the oily crude product was heated under vacuum to remove the silanol, followed by treatment with methanol (three times, each 200 mL) while it solidified. Filtration and washing with methanol yielded 26.0 g (85%) white product. ^{1}H NMR ($CDCl_3$) δ = 0.158 (s, 6 H), 0.162 (s, 6 H), 0.58–2.00 (m, 72 H), 4.57 (s, 1 H), 4.66 (s, 2 H), 4.77 (s, 2 H), 7.07 (s, 1 H), 7.53 (s, 1 H). IR (KBr) 2948, 2931, 2866, 1604, 1486, 1465, 1451, 1390, 1378, 1365, 1340, 1252, 1172, 1156, 1131, 1088, 1033, 1009, 987, 887, 874, 831, 777 cm^{-1}; mp 86–88 °C. MS (FAB) 885.3.

Preparation of 1-(3-*epi*-Cholestanol)-2-(dimethylthexylsiloxy)methyl)-4-(dimethylthexylsilyl)-5-(hydroxymethyl)benzene. 1-Bromo-4-(3-*epi*-cholestanoxy)-2,5-bis((dimethylthexylsiloxy)methyl)benzene (24 g, 27.0 mmol) was dissolved in 300 mL of THF and cooled to –78 °C, and 35 mL of a 1.7 M solution of *t*-BuLi in pentane was added dropwise. After 1 h at –78 °C the solution was allowed to warm slowly to –30 °C and kept at this temperature for an additional 3 h. The reaction mixture was poured into 800 mL of ether and 800 mL of water,

(7) Zhang, C.; Höger, S.; Pakbaz, K.; Wudl, F.; Heeger, A. J. *J. Electronic Mater.*, submitted.

and the aqueous phase was extracted twice with 300 mL of ether. The combined organic phase was extracted with water (three times, each 300 mL) and brine (300 mL). After drying over $MgSO_4$ and evaporation of the solvent, the crude product was chromatographed with hexanes/ether (2:1) to yield 15.5 g (71%) white product. ^1H NMR ($CDCl_3$) δ = 0.16 (s, 6 H), 0.38 (s, 6 H), 0.60–2.02 (m, 72 H), 4.66 (s, 1 H), 4.72 (d, 2 H), 4.78 (s, 2 H), 7.00 (s, 1 H), 7.64 (s, 1 H). IR (KBr) 3384, 2945, 2933, 2866, 1596, 1559, 1465, 1445, 1377, 1377, 1363, 1363, 1299, 1281, 1250, 1250, 1230, 1230, 1162, 1086, 1045, 997, 933, 908, 872, 830, 810, 771, 697, 669 cm^{-1}; mp 84–86 °C. MS (FAB) 807.1.

Preparation of 1-(3-*epi*-Cholestanol)-4-(dimethylthexylsilyl)2,5-bis(hydroxymethyl)benzene. 1-(3-*epi*-Cholestanol)-2-((dimethylthexylsiloxy)methyl)-4-(dimethylthexylsilyl)-5-hydroxymethylbenzene (14.8 g, 18.3 mmol) was dissolved in 75 mL of THF, and 42 mL of a 1 M solution of Bu_4NF in THF was added. The mixture was stirred overnight at room temperature and then poured into 400 mL of ether and 400 mL of water. The organic phase was extracted with water (five times, each 200 mL) and 200 mL of brine and dried over $MgSO_4$. After evaporation of the solvent the silanol was removed from the crude product by heating under vacuum to yield 10.34 g (85%) of product. ^1H NMR ($CDCl_3$) δ = 0.37 ppm (s, 6 H), 0.60–2.02 ppm (m, 59 H), 4.64–4.80 (m, 5 H), 7.10 (s, 1 H), 7.36 (s, 1 H). IR (KBr) 3426, 2944, 2932, 2866, 2596, 2558, 1487, 1466, 1444, 1429, 1377, 1364, 1291, 1283, 1250, 1231, 1162, 1162, 1129, 1118, 1046, 1035, 998, 978, 961, 933, 908, 871, 829, 809, 770, 671 cm^{-1}; mp 97–99 °C. MS (FAB) 581.4 [$M^+ - C_6H_{13}$ (thexyl)].

Preparation of 1,4-Bis(chloromethyl)-2-(3-*epi*-cholestanol)-5-(dimethylthexylsilyl)benzene. 1-(3-*epi*-Cholestanol)-4-(dimethylthexylsilyl)-2,5-bis(hydroxymethyl)benzene (7.0 g, 10.5 mmol) was dissolved in 150 mL of THF and cooled to −78 °C, and 8.5 mL of a 2.5 M solution of *n*-BuLi in pentane was added dropwise. To the resulting suspension, after 1 min, was added 2.2 mL $SOCl_2$. The clear solution was stirred for 2 h at −78 °C and then at room temperature overnight. The mixture was poured into 300 mL of ether and 300 mL of water. The organic phase was extracted with water (two times, each 200 mL), 7% aqueous $NaHCO_3$ solution (three times, each 150 mL), water (two times, each 200 mL), and 200 mL of brine and dried over $MgSO_4$. Evaporation of the solvent and chromatography of the crude product (silica gel, hexanes/ether 100:1) yielded 3.0 g (42%) product. ^1H NMR ($CDCl_3$) δ = 0.42 (s, 6 H), 0.62–2.02 (m, 59 H), 4.64 (s, 2 H), 4.66 (br s, 3 H), 6.96 (s, 1 H), 7.43 (s, 1 H). IR (KBr) 2931, 2865, 1596, 1556, 1492, 1466, 1444, 1382, 1365, 1307, 1283, 1252, 1239, 1187, 1162, 1131, 990, 977, 959, 933, 909, 871, 826, 809, 770, 731, 697, 671, 627 cm^{-1}; mp 66–68 °C. MS (FAB) 617.4 [$M^+ - C_6H_{13}$ (thexyl)].

Preparation of Poly[2-(3-*epi*-cholestanol)-5-(dimethylthexylsilyl)-1,4-phenylenevinylene]. Potassium *tert*-butoxide (2.5 g, 22 mmol) in 50 mL of THF was added to a solution of 32.8 g (4.0 mmol) of 1,4-bis(chloromethyl)-2-(3-*epi*-cholestanol)-5-(dimethylthexylsilyl)benzene in 300 mL of THF at 0 °C over 2 min. After stirring for 18 h at 0 °C the resulting yellow solution (which contains small amounts of a yellow gel) was poured into 400 mL of chloroform and 300 mL of water. The chloroform phase was extracted 10 times with water (each 300 mL) and dried over $MgOS_4$, and the polymer precipitated by the slow addition of methanol. Subsequent 3-fold dissolution and precipitation with methanol yielded 450 mg of yellow polymer which was extracted for 3 days with methylene chloride. The NMR spectrum shows a small signal at δ = 1.23 ppm, which indicates the presence of a small amount of *tert*-butyl alcohol in the polymer even after the reprecipitation and extraction. ^1H NMR ($CDCl_3$) δ = 0.4–2.1 (m, 65 H), 4.65 (m, 1 H), 6.8–8.1 (m, 4 H). IR (KBr) 2928, 2865, 1571, 1466, 1455, 1444, 1407, 1377, 1364, 1335, 1313, 1280, 1248, 1232, 1187, 1161, 1129, 1044, 992, 966, 871, 871, 832, 832, 814, 767 cm^{-1}. Elemental Anal. Calcd for $C_{43}H_{70}OSi$: C, 81.82; H, 11.20. Found: C, 81.58; H, 11.10. GPC (PL Gel 10-μm column, $CHCl_3$, 30 °C): $M_w = 2.59 \times 10^6$, $M_n = 3.86 \times 10^5$, M_w/M_n = 6.7; all vs polystyrene. Intrinsic viscosity 2.98 dL/g.

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