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# Solution DFWM $\chi^{(3)}$ non-linear optical properties of poly[(arylene)silylene]s and poly[(arylene)(ethynylene)silylene]s containing tetra- or hypercoordinate silicon

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The third-order optical nonlinearities of a series of conjugated poly[(arylene)(ethynylene)silylene]s, and also of a complementary series of poly[(arylene)silylene] statistical copolymers without acetylene groups, have been studied in chloroform solution by using the degenerate four-wave mixing technique with a Q-switched Nd : YAG laser–oscillator at 1064 nm and a pulse duration of *ca*. 6 ns. The polymers contain a variety of arylene groups including carbazole and anthracene. The electronic and nuclear contributions of the  $\chi^{(3)}$ susceptibility and the thermal nonlinearity of the solutions were separated. The  $\chi^{(3)}$  susceptibilities of some poly[(arylene)(ethynylene)silylene]s were found to be as high as  $|\text{Re }\chi^{(3)}| = 0.95 \times 10^{-10}$  esu for solutions of concentration 50 g l<sup>-1</sup>. The results show that the presence of a single 8-(dimethylamino)naphthyl ligand at silicon affording pentacoordination has a beneficial effect on the  $\chi^{(3)}$  properties. Comparison of the results for the poly[(arylene)silylene]s with those for the poly[(arylene)(ethynylene)silylene]s suggests that the absence of acetylene groups in the former case has in general a deleterious effect on the  $\chi^{(3)}$  properties. Confirmation of the order of magnitude of the non-linear response has been confirmed by Z-scan measurements with picosecond laser pulses on hybrid sol–gel silica films of two of the poly[(arylene)(ethynylene)silylene]s containing arylene amide groups.

High and fast optical nonlinearities of organic and organometallic materials are attracting considerable attention because of their potential uses in optical computation, tele-communications, integrated optics, and opto-electronic devices.<sup>1–3</sup> A wide variety of organic polymers with conjugated  $\pi$ -electron systems have been studied for third-order nonlinear optics.<sup>4,5</sup> The magnitude of third-order nonlinear optical susceptibilities ( $\chi^{(3)}$ ) has been found to be affected by factors such as  $\pi$ -delocalization length, donor–acceptor groups, chain orientation and packing density, conformation and dimensionality.<sup>6</sup>

Poly[(arylene)ethynylene]s have interesting photo- and electroluminescent properties and show large third-order nonlinear optical susceptibilities  $(\chi^{(3)})$  similar to those for poly[diacetylene]s,7 giving rise to strong nonlinear optical effects such as two- and four-wave mixings, and self-action. Solution Z-scan  $\chi^{(3)}$  measurements on the corresponding silicon-containing poly[(arylene)(ethynylene)silylene]s of general structure  $-[-C \equiv C - SiR^1R^2 - C \equiv C - Ar - ]_n$  have been determined at 590 nm  $[Re(\chi^{(3)}) = -9.3 \times 10^{-13} \text{ esu})^8$  and at 1064 nm in the near-resonant region  $[\text{Re}(\chi^{(3)}) = 4.0 \times 10^{-13}]$ esu].<sup>9</sup> Here, we report the considerably higher values obtained by the degenerate four wave mixing (DFWM) technique for solutions of a variety of poly[(arylene)(ethynylene)silylene]s, and also the third-order nonlinear optical susceptibilities of a complementary series of poly[(arylene)silylene] statistical copolymers without acetylene groups.<sup>10</sup> We also

describe the preparation and characterization of poly[(arylene)(ethynylene)silylene]s various new and the corresponding starting materials. Some of the poly[(arylene)(ethynylene)silylene]s contain hypercoordinate silicon resulting from the presence of the 8-(dimethylamino) naphthyl ligand.<sup>11</sup> Few such polymers are known although the chemical and electronic behaviour of silicon is highly dependent on the co-ordination number.12

# **Experimental**

Reactions were carried out under dinitrogen using Schlenk tube techniques. Triethylamine was distilled over powdered KOH, and toluene was distilled from CaH<sub>2</sub>. NMR spectra were run on a Bruker AVANCE DPX 200 spectrometer operating at 200 MHz (<sup>1</sup>H), 50.327 MHz (<sup>13</sup>C) or 39.763 MHz (<sup>29</sup>Si). IR spectra were recorded on a Perkin Elmer 1600 FTIR instrument in CCl<sub>4</sub> solution or as Nujol mulls. Mass spectra were obtained by use of a Jeol JMS-DX300 instrument. Elemental analyses were done at the CNRS Service Central d'Analyse. Size exclusion chromatography (SEC) was carried out in THF at a flow rate of 0.9 ml min<sup>-1</sup> by use of a Waters 510 system equipped with 100, 500, 1000 and 10000 Å columns and a UV detector operating at 254 nm. 1-(Bromomethyl)-3,5-dibromobenzene and 2,5-dibromobenzoic acid were commercial samples (Lancaster). The

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poly[(arylene)(ethynylene)silylene]s  $1,^{13,14}$   $2,^{9}$   $3^{9}$  and  $4,^{15}$  as well as the poly[(arylene)silylene] statistical copolymers (**10a–d**, **11**),<sup>10</sup> were prepared as previously described.

### Preparation of 1-(trimethoxysilylmethyl)-3,5-dibromobenzene

A mixture of 1-(bromomethyl)-3,5-dibromobenzene (5 g, 15.2 mmol) and trichlorosilane (1.6 ml, 15.9 mmol) in tri-*n*-propylamine (4.5 ml) was kept at 95 °C for 20 h and then evaporated to dryness. The resulting solid [1-(trichlorosilylmethyl)-3,5-dibromobenzene] was heated with methanol (15 ml) and triethylamine (15 ml) for 20 h under reflux. The excess of methanol and triethylamine was removed under vacuum and the resulting mixture was extracted with *n*-pentane. Distillation of the combined extracts gave 1.33 g (23% overall yield) of the desired compound (89–95 °C, 0.05 mbar). IR [CCl<sub>4</sub>,  $\bar{\nu}$ /cm<sup>-1</sup>]: 3109vw, 2944s, 2843s, 1925vw, 1756vw, 1726vw, 1702vw, 1584s, 1552s, 1461m, 1423s, 1402m, 1361w, 1286w, 1192s, 1174s, 1090vs. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.5–7.3 (m, 3 H), 3.57 (s, 9 H), 2.16 (s, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -49.20.

### Preparation of 2,5-dibromobenzoyl chloride<sup>16</sup>

A mixture of 2,5-dibromobenzoic acid (5.0 g, 17.8 mmol) and phosphorus pentachloride (3.7 g, 17.8 mmol) was heated at 65 °C for 30 min with evolution of hydrogen chloride. Phosphorus oxychloride (bp 106 °C) was distilled out of the resulting brown liquid under atmospheric pressure. The distillation was then continued under reduced pressure affording 2,5-dibromobenzoyl chloride (88–95 °C, 1 mbar) which crystallized as a white solid (4.72 g, 89% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.2 (m, 1 H), 7.6 (m, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  165.23, 139.97, 137.62, 136.52, 135.99, 121.69, 120.40.

### Preparation of N,N-diethyl-2,5-dibromobenzamide

A solution of 2,5-dibromobenzoyl chloride (4.72 g, 15.3 mmol) in freshly distilled diethyl ether (50 ml) was added rapidly to diethylamine (3.89 g, 53.2 mmol). An exothermic reaction resulted with formation of a copious white precipitate. Stirring was continued for 1 h and the mixture was filtered. Evaporation of the filtrate under reduced pressure gave the desired product (5.3 g) as a white crystalline solid which was purified by distillation under reduced pressure (4.38 g, 85.4% yield). Mp 52.4–53.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.4 (m, 3 H), 3.8 (m, 1 H), 3.4 (m, 1 H), 3.2 (m, 2 H), 1.27 (t, 3 H), 1.10 (t, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  167.28, 140.88, 134.67, 133.41, 130.75, 121.95, 118.35, 43.18, 39.46, 14.36, 12.91. Calc. for C<sub>11</sub>H<sub>13</sub>Br<sub>2</sub>NO: C, 39.43; H, 3.91; N, 4.18. Found: C, 39.79; H, 3.89; N, 4.26.

### Preparation of N-(2,5-dibromobenzoyl)carbazole

Following the method used to prepare N-benzoylcarbazole,<sup>17</sup> carbazole (2.51 g, 15.0 mmol) and sodium hydride (0.75 g of 60% dispersion in mineral oil, 17.5 mmol) were stirred in a mixture of DMF (60 ml) and toluene (60 ml) at 0 °C for 15 min. A solution of 2,5-dibromobenzoyl chloride in DMF (40 ml) was then added drop by drop. After being stirred for 4 h the reaction mixture was hydrolysed with 7% H<sub>2</sub>SO<sub>4</sub> and was extracted with toluene. The combined extracts were dried over MgSO<sub>4</sub> and the solvents were pumped off to afford the crude product. Recrystallization from absolute ethanol gave beige crystals of the compound (3.40 g, 53.2% yield). Mp 125.2-126.0 °C. IR [CCl<sub>4</sub>,  $\bar{\nu}$ /cm<sup>-1</sup>]: 3065w, 2986w, 1898vw, 1685vs, 1600w, 1490m, 1479m, 1454s, 1445vs, 1418vw, 1388s, 1356m, 1342m, 1330vs, 1303s, 1268vw, 1238w, 1214m, 1156w, 1138vw, 1122w, 1089w, 1034m. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.1–7.3 (m, 11 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  164.48, 138.91, 137.91, 133.94, 133.89,

130.59, 126.40, 125.66, 123.38, 121.05, 118.86, 117.42, 114.72. M<sup>+</sup> 429 (EI). Calc. for  $C_{19}H_{11}Br_2NO$ : C, 53.18; H, 2.58; N, 3.26. Found: C, 52.42; H, 2.62; N, 3.27.

# Preparation of 1-bromo-4-(2-ethyl-1-hexyloxy)benzene

A mixture of 4-bromophenol (30.00 g, 0.173 mol), 1-bromo-2ethylhexane (33.47 g, 0.173 mol) and sodium carbonate (18.38 g, 0.173 mol) was heated under reflux in DMF (80 ml) for 16 h. The resulting yellow suspension was filtered at RT and the solid was washed with diethyl ether. The filtrate and washings were extracted with water followed by NaOH solution (5%) and then water again. The organic layer was dried over  $K_2CO_3$  and evaporated to give a yellow liquid (33.34 g). Distillation (108–115 °C, 0.05 mbar) afforded 1-bromo-4-(2-ethyl-1-hexyloxy)benzene (colourless liquid; 19.55 g, 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.4 (m, 2 H), 6.8 (m, 2 H), 3.86 (d, 2 H), 1.8 (m, 1 H), 1.4 (m, 8 H), 1.0 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 158.94, 132.58, 116.74, 112.90, 71.14, 39.76, 30.93, 29.51, 24.26, 23.50, 14.55, 11.55.

# Preparation of phenyl[4-(2-ethyl-1-hexyloxy)phenyl]dichlorosilane

The Grignard reagent made by heating under reflux for 3 h 1-bromo-4-(2-ethyl-1-hexyloxy)benzene (5.72 g, 20.1 mmol) and magnesium (0.49 g, 20.1 mmol) in THF (50 ml) was added drop by drop to a vigorously stirred solution of trichlorophenylsilane (4.25 g, 20.1 mmol) in THF (50 ml). Stirring was continued overnight and the mixture was then pumped to dryness and the residue extracted with *n*-pentane. Evaporation of the combined extracts afforded 7.51 g of the crude product which was distilled under reduced pressure (145–158 °C, 0.15 mbar) to give phenyl[4-(2-ethyl-1-hexyloxy)phenyl]dichlorosilane (colourless liquid; 5.12 g, 67% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.0–7.0 (m, 9 H), 3.96 (d, 2 H), 1.8 (m, 1 H), 1.4 (m, 8 H), 1.0 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  162.76, 136.36, 134.53, 132.98, 132.06, 128.73, 122.85, 115.05, 70.82, 39.73, 30.94, 29.52, 24.29, 23.50, 14.55, 11.56.

# Preparation of phenyl[4-(2-ethyl-1-hexyloxy)phenyl]diethynylsilane

Monoacetylene Grignard reagent was prepared by bubbling acetylene through a solution of the Grignard reagent prepared from magnesium (0.91 g, 37.4 mmol) and bromoethane (4.09 g, 37.5 mmol) in THF (70 ml). A solution of phenyl[4-(2-ethyl-1hexyloxy)phenyl]dichlorosilane (5.00 g, 13.12 mmol) in THF (50 ml) was added rapidly to the monoacetylene Grignard reagent at -78 °C. The mixture was allowed to warm to room temperature overnight, and stirring was continued for 3 d. The reaction mixture was pumped to dryness and the residue taken up in diethyl ether to give a solution which was washed successively with aqueous acetic acid (10%), aqueous sodium bicarbonate, and water. The organic layer was dried over  $MgSO_4$  and evaporated to give a brown oil (4.28 g). The latter was distilled under reduced pressure (170–185  $^{\circ}\text{C},$  0.1 mbar) to phenyl[4-(2-ethyl-1-hexyloxy)phenyl]diethynylsilane afford (red oil; 2.49 g, 53% yield). IR [neat,  $\bar{v}/cm^{-1}$ ]: 3951vw, 3584vw, 3275s, 3071w, 3052w, 3023w, 3001w, 2959vs, 2928vs, 2872s, 2859s, 2526vw, 2040vs [v(C=C)], 1899w, 1820vw, 1778vw, 1595vs, 1563m, 1503s, 1488w, 1466m, 1430m, 1400w, 1380m, 1311m, 1279vs, 1249vs, 1182s, 1159w, 1119vs, 1090m, 1030m, 998w, 971w, 938vw, 928vw, 896vw, 826s, 814m, 789w, 741m, 697vs, 630m, 601s. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.0-7.0 (m, 9 H), 3.93 (d, 2 H), 2.79 (s, 2 H), 1.8 (m, 1 H), 1.4 (m, 8 H), 1.0 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 162.00, 136.84, 135.18, 132.24, 130.94, 128.61, 121.93, 115.04, 97.54 (SiC=CH), 84.27 (SiC=CH), 70.69, 39.75, 30.96, 29.52, 24.30, 23.50,  $\overline{14.55}$ , 11.56. <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  -48.2. M<sup>+</sup> 360 (FAB<sup>+</sup>, no matrix).



Fig. 1 Experimental optical bench for the DFWM study. M = mirror, BS = beamsplitter, PD = photodiode, P = glass prism,  $PR = 90^{\circ}$  polarization rotator, D = diaphragm.

Calc. for C<sub>24</sub>H<sub>28</sub>OSi: C, 79.95; H, 7.83. Found: C, 79.90; H, 7.73.

# **Preparation of 5**

A mixture of diethynyldiphenylsilane (1.84 g, 7.92 mmol), 9,10dibromoanthracene (2.40 g, 7.14 mmol), 1-(trimethoxysilylmethyl)-3,5-dibromobenzene (0.29 g, 0.78 mmol), bis(triphenylphosphine)palladium(II) dichloride (8.7 mg, 0.0124 mmol), copper(I) iodide (35.7 mg, 0.187 mmol) and tri-



Fig. 2 Wave vectors and polarization diagrams for the two series of DFWM experiments. (a) experimental measurements of  $\chi^{(3)}$  susceptibility of the polymer solutions, (b) experiment for separation of electronic and nuclear contributions. Pumping waves  $= E_1$  and  $E_2$ , probe wave  $= E_3$ , phase conjugated wave  $= E_4$  ( $E_4$  is the result of diffraction of the pumping waves on the reflecting  $(\delta n_1)$  and transmitting  $(\delta n_2)$  refractive index gratings).



Fig. 3 The DFWM reflection coefficient as a function of the pumping wave intensity for the first (a) and second (b) series of experiments for a chloroform solution of polymer 1.

phenylphosphine (81.9 mg, 0.312 mmol) in toluene (60 ml) and triethylamine (60 ml) was stirred at 85 °C for 20 h and then filtered. The residue was washed with THF and the filtrate was evaporated to dryness affording a red solid (1.64 g) which was dissolved in THF and the solution filtered. Addition of *n*-pentane precipitated the polymer (1.04 g, 32% yield). IR [CCl<sub>4</sub>,  $\bar{\nu}$ /cm<sup>-1</sup>]: 2158, 2132 [ $\nu$ (C=C)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.0–7.3 (m, 18.3 H), 3.63 (s, 1 H; OCH<sub>3</sub>), 2.27 (s, 0.22 H; CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  135.65, 135.53, 135.15, 133.24, 131.19, 130.29, 128.97, 128.83, 128.59, 128.03, 127.77, 118.94, 106.21 (C=C), 102.28 (C=C), 51.47. <sup>29</sup>Si NMR (CDCl<sub>3</sub>) [INVGATE; delay time 15 s]:  $\delta$  –47.13 (7.4 Si; SiC=C), -47.33 (1.6 Si; SiC=C), -48.68 (0.5 Si; SiCH<sub>2</sub>), -48.89 (0.5 Si; SiCH<sub>2</sub>).

# **Preparation of 6**

A mixture of diethynyldiphenylsilane (0.29 g, 1.25 mmol), *N*,*N*-diethyl-2,5-dibromobenzamide (0.42 g, 1.25 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.8 mg, 0.0026 mmol), copper(I) iodide (5.3 mg, 0.0278 mmol) and triphenylphosphine (13.3 mg, 0.0507 mmol) in toluene (15 ml) and triethylamine (10 ml) was stirred at 80 °C for 20 h and then filtered. The filtrate was evaporated to dryness affording a brown solid which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the resulting solution filtered. Addition of *n*-pentane to the filtrate precipitated the desired product which was isolated by centrifugation (0.46 g, 91% yield). IR [CCl<sub>4</sub>,  $\bar{\nu}$ /cm<sup>-1</sup>]: 2163 [ $\nu$ (C=C)], 1643 [ $\nu$ (C=O)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.1–7.2 (m, 13 H), 4.0–3.0 (m, 4 H), 1.5–0.8 (m, 6 H). <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  –47.6.

### **Preparation of 7**

The polymer (brown solid) was obtained in 93% yield starting from the corresponding pentacoordinate diethynylsilane<sup>9</sup> under the same experimental conditions as those used for **6**. IR [CCl<sub>4</sub>,  $\bar{\nu}$ /cm<sup>-1</sup>]: 2158 [ $\nu$ (C=C)], 1646 [ $\nu$ (C=O)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.5 (s, 1 H), 8.0–7.2 (m, 8 H), 3.9–3.0 (m, 4 H; NCH<sub>2</sub>), 2.7 (s, 3 H; NCH<sub>3</sub>), 2.6 (s, 3 H; NCH<sub>3</sub>), 1.4–0.8 (m, 6 H; NCH<sub>2</sub>C<u>H<sub>3</sub></u>), 0.6 (s, 3 H; SiCH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$ – 56.8– – 57.8 (m).

### **Preparation of 8**

The polymer (light brown solid) was obtained in 68% yield starting from *N*-(2,5-dibromobenzoyl)carbazole under experimental conditions essentially the same as those used for **6**. IR [Nujol,  $\bar{v}/\text{cm}^{-1}$ ]: 2162 [v(C=C)], 1682 [v(C=O)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.1–6.6 (m). <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  –47.5– 48.0 (m).

### **Preparation of 9**

The polymer (red solid) was obtained in 57% yield starting from phenyl[4-(2-ethyl-1-hexyloxy)phenyl]diethynylsilane and 9,10-dibromoanthracene under experimental conditions essentially the same as those used for **6**. IR [Nujol,  $\bar{\nu}$ /cm<sup>-1</sup>]: 2126 [ $\nu$ (C=C)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.9–6.5 (m, 17 H; Ar), 3.79 (d, 2 H; OCH<sub>2</sub>), 1.61 (d, 1 H; CH), 1.5–1.0 (m, 8 H; CH<sub>2</sub>), 0.9–0.6 (m, 6 H; CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  105.92 (C=C), 102.75 (C=C). <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  –47.4.

### DFWM measurements of $\chi^{(3)}$

DFWM experiments were made by using a Q-switched Nd : YAG laser-oscillator at 1064 nm with a pulse duration of ca. 6 ns. The original beam was passed through a Faraday isolator, followed by an Nd : YAG amplifier and was then directed into the DFWM optical bench (Fig. 1). Two beam splitters BS1 and BS2 provided two counter-running pumping beams  $E_1$  and  $E_2$  (with equal energy of ca. 10 mJ) and probe beam  $E_3$  (with energy of ca. 1 mJ). The probe beam entered the polymer cell at an angle of  $5 \times 10^{-3}$  rad with respect to



Scheme 1

the pump-wave directions. Two series of experiments with different mutual polarization orientations of the pumping and probe beams were performed (Fig. 2). The phase conjugated (PC) wave was recorded for both polarization orientations. The reflection coefficient of the PC wave was found to increase quadratically with increasing pump intensity (Fig. 3). To determine the absolute value of the susceptibility of the polymers, the DFWM reflection coefficient was calibrated with respect to that for neat chloroform.

# **Results and discussion**

# Preparation and properties of new monomers and polymers

The new starting monomer phenyl[4-(2-ethyl-1-hexyloxy)phenyl]diethynylsilane was prepared by treatment of the corresponding dichlorosilane with monoacetylene Grignard reagent (Scheme 1). Its spectral properties are very similar to those of diphenyldiethynylsilane<sup>13,14</sup> with the same IR  $\nu$ (C=C) frequency and <sup>29</sup>Si NMR chemical shift, the <sup>13</sup>C NMR acetylene resonances being shifted slightly downfield.

The new dibromoarene monomer 1-(trimethoxysilylmethyl)-3,5-dibromobenzene was prepared from 1-(bromomethyl)-3,5dibromobenzene (Scheme 2). N,N-Diethyl-2,5-dibromobenzamide and N-(2,5-dibromobenzoyl)carbazole were prepared from 2,5-dibromobenzoic acid (Scheme 3).

Following the route previously described,<sup>13</sup> the new polymers **5–9** (Table 1) were prepared by palladium-catalysed cross-coupling polymerization between the appropriate diethynylsilane and dibromoarene (Scheme 4).

The red polymer 5 was synthesized from a mixture of 10% 1-(trimethoxysilylmethyl)-3,5-dibromobenzene (Scheme 3) and 90% 9,10-dibromoanthracene, the molecular weight being half that of the corresponding polymer 1 with anthryl groups.<sup>13,14</sup> Two v(C=C) IR absorbances are observed both at higher frequency than that of the single absorption observed for 1, the <sup>29</sup>Si and acetylene <sup>13</sup>C NMR chemical shifts being the same as in 1. Several <sup>29</sup>Si NMR resonances are observed, the number and relative intensities suggesting that the trimethoxysilyl-containing monomer is distributed non-randomly within the polymer chains.



The brown polymer **6** was synthesized from N,N-diethyl-2,5-dibromobenzamide, the latter being prepared from 2,5-dibromobenzoyl chloride (Scheme 4). The low molecular weight corresponds to a chain length of about 9 units. The brown polymer 7 containing pentacoordinate silicon was prepared in an analogous way, the molecular weight in this case corresponding to only 6 units. Several <sup>29</sup>Si NMR resonances, in the same region as for polymer **3** also containing pentacoordinate silicon,<sup>9</sup> are observed with the multiplicity reflecting the short chains as well as the unsymmetrical nature of the benzamide moieties.

The light brown polymer 8 was synthesized from N-(2,5-dibromobenzoyl)carbazole, the latter being prepared from carbazole and 2,5-dibromobenzoyl chloride (Scheme 4). The v(C=C) IR absorbance and <sup>29</sup>Si NMR chemical shifts are in the same range as for 6. The molecular weight corresponds to a weight-average chain length of 90 units (Table 1). However, the true molecular weight may in fact be lower since although 8 is much bulkier than 6 the calculations are made with reference to polystyrene standards.

The red polymer 9 has a molecular weight slightly lower than that of the analogous polymer 1 without the side-chain. The spectral characteristics of both polymers are similar suggesting that the 2-ethyl-1-hexyloxyphenyl side-chain at Si has little effect on the electron distribution within the polymer backbone.

# **DFWM** measurements

The laser pulse duration was much longer than the time of termalization of polymer molecular excitation (of the order of



Table 1Properties of polymers -[-C=C-SiR<sup>1</sup>R<sup>2</sup>-C=C-Ar-]<sub>n</sub> (1-9)

	Polymer substituents		Si	Molecular weight data			Solution DFWM ( $\chi^{(3)}$ ) measurements <sup>e</sup>		
Polymer	$(R^1R^2)Si^a$	$\mathrm{Ar}^{b}$	coord. no.	$M_{\mathbf{w}}^{c}$	$M_{ m w}/M_{ m n}{}^c$	n <sup>d</sup>	Colour	$ n_2 /cm^2 W^{-1}$	$ \operatorname{Re}\chi^{(3)} /esu$
1	Ph <sub>2</sub> Si	An	4	23500	3.2	56	red	$190 \times 10^{-14 f}$	$95 \times 10^{-12f}$
2	(1-Ňp),Si	An	4	8800	2.8	17	orange	$1.5 \times 10^{-14}$	$0.75 \times 10^{-12}$
3	Me(NpN)Si	An	5	12400	2.7	28	red	$110 \times 10^{-14g}$	$55 \times 10^{-12g}$
4	$(NpN)_2Si$	An Si(OMe) <sub>3</sub>	6	20000	3.2	34	orange	$63 \times 10^{-14g}$	$31 \times 10^{-12g}$
5	Ph <sub>2</sub> Si	(10%)	4	13000	2.9	36	red	$15 \times 10^{-14h}$	$7.5 \times 10^{-12h}$
6	Ph <sub>2</sub> Si	An (90%) $Et_2N \rightarrow O$	4	3390	1.8	9	brown	$6.3\times10^{-14h}$	$3.1 \times 10^{-12h}$
7	Me(NpN)Si		5	2310	1.5	6	brown	$170 \times 10^{-14g}$	$85 \times 10^{-12g}$
8	Ph <sub>2</sub> Si		4	40500	3.4	90	cream	$5.7 \times 10^{-14}$	$2.8 \times 10^{-12}$
9		An	4	19300	2.3	40	red	$10 \times 10^{-14}$	$10 \times 10^{-12}$

<sup>*a*</sup> NpN = 1-(8-dimethylamino)naphthyl. <sup>*b*</sup> An = 9,10-anthrylene. <sup>*c*</sup> Determined by SEC with reference to polystyrene standards. <sup>*d*</sup> Number of units calculated from value of  $M_w$ . <sup>*e*</sup> At 1064 nm with 6 ns pulse duration in CHCl<sub>3</sub> solution (measured at, or linearly extrapolated to, 50 g l<sup>-1</sup>). <sup>*f*</sup> Concentration, 2.5 g l<sup>-1</sup>. <sup>*g*</sup> Concentration, 5 g l<sup>-1</sup>. <sup>*h*</sup> Concentration, 12.5 g l<sup>-1</sup>.

tens of picoseconds<sup>5</sup>). Therefore, the thermally-induced grating of the solvent refractive index must be taken into consideration for the theoretical description of the DFWM process. To interpret the experimental results we used the plane wave approximation for the interacting beams  $E_m = E_m \exp(i[\omega_m t - k_m r])$  (m = 1, 2, 3, 4), and the approximation of constant intensities for the probe and pumping beams. The latter approximation is correct because the PC-wave intensity in the nonlinear cell was much less than the probe and pumping wave intensities,  $|E_4|^2 \ll |E_3|^2 \ll |E_1|^2 = |E_2|^2$ . For these reasons the equation for the PC wave amplitude can be written in the following form

$$\frac{\partial E_{4i}}{\partial z} = -ik_0 \left[ \left( \frac{\partial n}{\partial \rho} \right) \Delta \rho (E_1 E_3^*) E_{2i} + \frac{1}{2n_0} \left( \chi_{ijkl}^{(3)} E_{1j} E_{2k} E_{3l}^* + \chi_{ikjl}^{(3)} E_{2k} E_{1j} E_{3l}^* \right) \right]$$
(1)

where  $k_0$  is the undisturbed wave number of the optical beams,  $n_0$  is the refractive index of the medium,  $\chi_{ijkl}^{(3)}$  is the fast optical non-linear susceptibility of the polymer, (i,j,k,l) are the Cartesian coordinates x,y,z indicating the directions of the wave polarizations),  $(\partial n/\partial \rho)$  is the gradient of the refractive index changes due to thermal variation of the chloroform density, and  $\Delta \rho (E_1 \ E_3^*)$  is the amplitude of the chloroform density grating thermally-induced by the interference field of the optical waves.

To decrease the contribution of the thermally-induced gratings to the total DFWM reflectivity, in the first series of experiments the polarization of the probe beam  $E_3$  was the same as that for the co-running pump  $E_1$  being crosspolarized with respect to the polarization of the other pump  $E_2$  (Fig. 2a). In this case only a large-scale grating was induced by the interference field of the pumping wave  $E_1$  and the corunning probe  $E_3$ . The spatial period of the large-scale interference grating ( $\Lambda$ ) was about 200 µm. The delay time ( $\tau_s$ ) for the isobar formation of this thermal grating is estimated to be  $\tau_s = 2\pi/\Lambda c_s = 34$  ns (the speed of sound in chloroform is *ca*.  $c_s = 10^5$  cm s<sup>-1</sup>). Under the present experimental conditions the laser pulse duration was much less than this delay time. Therefore, the large-scale thermally-induced grating of the solution density variation ( $\delta\rho$ ) was determined by the full thermodynamic equation system which can be written in the following form<sup>18,19</sup>

$$\left(\frac{\partial^2}{\partial t^2} - c_s^2 \nabla^2\right) \frac{\partial(\partial \rho)}{\partial t} = -\alpha \frac{F c_s^2}{\rho_0 C_p} \frac{4\pi^2}{\Lambda^2} \\ \times \frac{n_0 c}{4\pi} E_1 E_3^* \exp\left(\frac{i2\pi x}{\Lambda}\right),$$
(2)

where  $\alpha$  is the absorption coefficient of the polymer,  $F = (\partial \rho / \partial T)$  is the volume coefficient of thermal expansion of chloroform,  $C_p$  is the specific heat at the constant pressure,  $\rho_0$  is the undisturbed chloroform density, and  $c_s$  and c are the velocities of sound and light, respectively.

The solution of eqn. (2) for optical pulses with the temporal form  $(1 - \exp(-t/\tau_{on})) \exp(-t/\tau_{off})$  gives the following expression for the maximum of the thermally-induced grating amplitude ( $\Delta \rho = \delta \rho \exp(-ix2\pi/\Lambda)$ )

$$\Delta \rho_{\max} \approx \alpha \tau_{\rm S} \frac{F}{\rho_0 C_{\rm p}} \frac{4\pi^2}{\Lambda^2} \frac{n_0 c}{4\pi} E_1 E_3^* \\ \times \left[ \frac{\tau_{\rm off}^3 / \tau_{\rm S}^3}{1 + (\tau_{\rm off}^2 / \tau_{\rm S}^2)} - \frac{\tau_1^3 / \tau_{\rm S}^3}{1 + (\tau_1^2 / \tau_{\rm S}^2)} \right],$$
(3)

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where  $\tau_1 = \tau_{off} \tau_{on}/(\tau_{on} + \tau_{off})$ ,  $\tau_{off}$  and  $\tau_{on}$  being the switch-off and switch-on times of the optical pulse.

The expression (3) indicates that the amplitude of the thermally-induced grating strongly decreases as the ratio  $\tau_{off}/\tau_s$  decreases. To make the contribution of the thermal grating negligible it is necessary to operate with pulses of duration much less than  $\tau_s = 34$  ns. Under our experimental conditions the ratio was of the order of  $\tau_{off}/\tau_s \approx 0.17$ . By using eqns. (1), (2) and (3) and taking into account the values of the chloroform parameters  $(\partial n/\partial T) = (\partial n/\partial \rho) (\partial \rho/\partial T) = 6 \times 10^{-4}$  K<sup>-1</sup>,  $\alpha \leq 0.05$  cm<sup>-1</sup>,  $\rho C_p = 1$  J cm<sup>-3</sup> K<sup>-1</sup>, it is possible to estimate that the fast grating (due to the Kerr-like nonlinearities) predominates over the thermally-induced grating if the nonlinear susceptibility  $\chi^{(3)}$  is greater than 2.4 × 10<sup>-13</sup> esu. This condition is achieved even in the case of the polymer solutions of relatively low nonlinear susceptibility (Tables 1 and 2).

In the second series of experiments (with the probe wave cross-polarized to the pumps [Fig. 2(b)] a scalar density grating was not induced. Therefore, the thermal grating under both our experimental conditions is estimated to be negligibly small in comparison with the grating induced due to the fast Kerr-like non-linearity, the DFWM reflection coefficient being determined by the formula

$$R_{il} = \left| \frac{E_{4i}}{E_{3i}} \right|^2 = \left( \frac{kl}{2n_0} \right)^2 |\chi_{ijkl}^{(3)} E_{1j} E_{2k} + \chi_{ikjl}^{(3)} E_{2k} E_{1j}|^2, \quad (4)$$

(l is the length of the nonlinear medium).

Two terms in the expression are indicative of two possible refractive index gratings: the large-scale reflection grating, and the small-scale transmission grating. For both series of experiments the  $\chi^{(3)}_{ijkl}$ -susceptibility components were the same:  $\chi^{(3)}_{xyxy}$ , for the first series;  $\chi^{(3)}_{xyyx}$ , for the second.

Experiments the  $\chi_{ijkl}$ -susception y components were the same.  $\chi_{xyxy}^{(3)}$ , for the first series;  $\chi_{xyyx}^{(3)}$ , for the second. Eqn. (4) allows the  $\chi_{xyxy}^{(3)}$  or  $\chi_{xyyx}^{(3)}$  (and  $n_2$ ) values for the polymer to be determined by using the results of the measurements of the DFWM reflection coefficient in the solution. The value of the DFWM efficiency in neat chloroform was used as a calibration value for the  $n_2$  determinations. The  $|\chi_{xyxy}^{(3)}|$  value was calculated from the  $n_2$  value by using the relationship  $n_2$ (cm<sup>2</sup> W<sup>-1</sup>) =  $5.2 \times 10^{-2} \chi^{(3)} [\text{esu}]/n_0^{2.20}$  Measurements on chloroform solutions of the various polymers were made (Tables 1 and 2). For all the polymers the values measured are much higher than that found for neat chloroform, *ca.*   $n_2 = 3 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1}$ .<sup>6</sup> The determined  $|\chi_{xyxy}^{(3)}|$  value is much greater than the literature  $\chi^{(3)}$  value for CS<sub>2</sub>,  $\chi^{(3)} = 6.8 \times 10^{-13} [\text{esu}]$ .<sup>21</sup>

In order to study the influence of the solvent on the nonlinear susceptibility of the polymers, the DFWM experiment was also performed for solutions of polymer **3** in THF and toluene, the results of the  $\chi^{(3)}$  (and  $n_2$ ) measurements being essentially the same as in CHCl<sub>3</sub>. It should be noted that the molecular interactions of the various solvents with the polymer are different: the THF molecules with a large dipole moment might be expected to interact with the polymer molecules more strongly than do chloroform molecules. However, the experimental results indicate only a weak effect of the solution molecular interaction on the  $\chi^{(3)}$  susceptibility. This is consistent with the predominance of the electronic contribution of the nonlinear susceptibility over the orientational (nuclear) component, the latter effect being more sensitive to intermolecular interactions.<sup>21</sup>

In order to separate the electronic and nuclear contributions in the fast Kerr-like nonlinear  $\gamma^{(3)}$  susceptibility we have compared the results for two experimental series [Fig. 2(a) and 2(b)]. The second series of experiments was performed for the chloroform solution of polymer 1 containing tetracoordinate Ph<sub>2</sub>Si groups, which had shown the highest susceptibility in the previous series. The separation of electronic and nuclear (orientational) contributions is based on different spatial symmetries of the  $\chi^{(3)}$  tensor.<sup>22,23</sup> In isotropic media the four independent  $\chi^{(3)}$  tensor elements reduce to three according to the relation  $\chi^{(3)}_{xxxx} = \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyyx} + \chi^{(3)}_{xyyx}$ , where by convention the order of the indices corresponds to the diffracted field  $(E_4)$ , the pump  $(E_1)$ , the other pump  $(E_2)$  and the probe field  $(E_3)^{22}$ . If the response is purely nuclear (orientational) the relative magnitude of the elements becomes  $\chi_{xyyx}^{(3)} = -0.5\chi_{xxxx}^{(3)}, \chi_{xxyy}^{(3)} = \chi_{xyxy}^{(3)} = 0.75\chi_{xxxx}^{(3)}, {}^{22,24}$  For a purely electronic response in an isotropic medium the tensor elements have the next relative values:  $\chi^{(3)}_{xyyx} = \chi^{(3)}_{xxyy} = \chi^{(3)}_{xyyx} =$  $\chi_{xxxx}^{(3)}/3.^{22,23}$  The  $\chi_{xyyx}^{(3)}$  susceptibility was determined in the experiment with the probe wave cross-polarized to both pumps. By comparing the result of the last experiment with the results of the previous experiments (in which the probe wave was co-polarized to one of the pumps giving rise to the  $\chi^{(3)}_{xyxy}$  susceptibility) it is possible to determine the ratio of the electronic and nuclear (orientational) contributions to the fast nonlinearity:  $|\chi_{xxxx}^{(3)}(\text{electronic})| / |\chi_{xxxx}^{(3)}(\text{nuclear})| = 3-6$ . It can hence be concluded that the electronic contribution is much larger than the nuclear (orientational) contribution for the  $\chi^{(3)}$ susceptibilities of the present series of poly[(arylene)(ethynylene)silylene]s and poly[(arylene)silylene]s.

### $\chi^{(3)}$ properties of the polymers

For the poly[(arylene)(ethynylene)silylene]s the DFWM measurements were made on chloroform solutions at concentrations ranging from 50 to 2.5 g  $l^{-1}$  (Table 1). The value of  $n_2$ measured for the monomer  $Ph_2Si(C=CH)_2$  as well as for the previously reported<sup>9</sup> model monomer  $Ph_2Si(C=C{9-anthryl})_2$ were similar to that observed for the solvent CHCl<sub>2</sub>  $(3 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1})$ , being about one order of magnitude less than that observed for the polymers. Except for 6 and 7, the polymers were of sufficient chain length for the  $\chi^{(3)}$  effects to be at a maximum<sup>25</sup> the highest value being observed for 1 containing tetracoordinate  $Ph_2Si$  groups ( $\chi^{(3)} = 3.1 \times 10^{-12}$ esu at a concentration of 2.5 g  $1^{-1}$ ). Based on number density considerations ( $\approx 0.25$  wt.% polymer in the solution), this value might be expected to be greater by a factor of 400 for the neat polymer suggesting  $\chi^{(3)}$  activity as high as that for derivatives of poly[(1,4-vinylene)phenylene].<sup>26</sup>

For purposes of comparison, where necessary the values of  $n_2$  and  $\chi^{(3)}$  have been linearly extrapolated to the reference concentration (50 g l<sup>-1</sup>), the absorbances for all the solutions being negligible (<0.05 cm<sup>-1</sup>). The results obtained are greater by an order of magnitude than those previously

**Table 2**  $\chi^{(3)}$  Solution properties of  $-[-(SiMePh)_{1.0}(Ar)_{1.3}-]_n$  (10 Ar = 1,4-C<sub>6</sub>H<sub>4</sub>, 11 Ar = 9,10-anthrylene)<sup>a</sup>

Polymer	$M_{\mathbf{w}}$	$M_{ m n}$	$M_{ m w}/M_{ m n}$	$ n_2 /cm^2 W^{-1}$	$ \operatorname{Re} \chi^{(3)} /\mathrm{esu}$
10a 10b 10c	6783 9946 13515	2663 3135 4125	2.5 3.2 3.3	$\begin{array}{c} 1.2 \times 10^{-14} \\ 4.7 \times 10^{-14} \\ 23 \times 10^{-14} \end{array}$	$\begin{array}{c} 0.6 \times 10^{-12} \\ 2.4 \times 10^{-12} \\ 11.5 \times 10^{-12} \end{array}$
10d 11	22774 21700	4019 1350	5.7 16.1	$9.8 \times 10^{-14} \\ 5.6 \times 10^{-14}$	$\begin{array}{c} 4.9 \times 10^{-12} \\ 2.9 \times 10^{-12} \end{array}$

<sup>a</sup> Measured by DFWM technique at 1064 nm with 6 ns pulse duration in CHCl<sub>3</sub> solution (concentration 50 g  $l^{-1}$ ).

reported for 1, 3 and 4 in CHCl<sub>3</sub> solution (50 g l<sup>-1</sup>), as determined by the Z-scan technique at 1064 nm (pulse duration 140 ps, intensity 20 GW cm<sup>-2</sup>).<sup>9</sup> Comparison of results obtained using the two techniques is known to be difficult<sup>5</sup> but may in this case be partly explained by the much lower light beam intensity ( $\approx 1$  MW cm<sup>-2</sup>) used here than that used for the Z-scan study<sup>9</sup> (20 GW cm<sup>-2</sup>). At the greater intensities used in the Z-scan experiment higher order nonlinear susceptibilities ( $\chi^{(5)}$  and  $\chi^{(7)}$ ) giving negative contributions could decrease the overall nonlinear effect of phase modulation.<sup>8</sup> Another reason for the small values of  $n_2$  obtained by Z-scan measurement is possible competing effects such as two photon absorption and stimulated scattering appearing at high beam intensity.

As previously reported,<sup>9</sup> for the series of polymers 2-4 containing naphthyl or naphthylamine groups at silicon smooth trends in the <sup>29</sup>Si and SiC=C <sup>13</sup>C NMR chemical shifts as well as the energy of the v(C=C) IR absorbance are observed with increasing co-ordination number at silicon (reflecting the change in the electronic environment), unlike 1 with phenyl groups at silicon. However, in the case of the  $\chi^{(3)}$  results no such trend is observed, the effect increasing from 2 to 3 and then decreasing on going from 3 to 4, whereas the value for 1 is extremely high. This is consistent with there being a steric effect on the  $\chi^{(3)}$  results perhaps resulting from unfavourable conformations forced on the polymers containing naphthyl or naphthylamine groups. This effect may be offset to some extent by the favourable electronic effect of the naphthylamine group. Indeed, on comparing 6 and 7, the presence of the naphthylamine group can be seen to have a most positive effect in the case of pentacoordinated 7.

Comparison of the results for 1 and 9 shows that the presence of a long chain ether group in the *para* position on one of the silicon phenyl substituents is deleterious to the  $\chi^{(3)}$  properties.

The DFWM measurements for the complementary series of poly[(arylene)silylene] statistical copolymers<sup>10</sup> without acetylene groups were made on chloroform solutions at a concentration of 50 g  $1^{-1}$ . The polymers contain silvlene and arylene units in random sequences of single units and short blocks, electron delocalization along the backbone thus involving both  $\sigma$ -conjugated polysilylene groups and  $\pi$ -conjugated polyarylene blocks. Comparison of the results (Table 2) with those for the poly[(arylene)(ethynylene)silylene]s (Table 1) suggests that the absence of acetylene groups in the former case has in general a deleterious effect on the  $\chi^{(3)}$  properties. An increase in molecular weight on going from 10a to 10d gives rise to an increase in  $\chi^{(3)}$  properties, whereas replacement of a phenylene group (10a-d) by an anthrylene group (11) has little effect. The result for 10c shows that low polydispersity is particularly favourable to high  $\chi^{(3)}$  values.

In conclusion, the very high  $\chi^{(3)}$  properties of some of the poly[(arylene)(ethynylene)silylene]s confirm the presence of extensive through-Si conjugation along the backbone.<sup>9</sup> In particular, the high  $\chi^{(3)}$  values observed for 1 should be noted. The results of this study suggest that the presence of a single 8-(dimethylamino)naphthyl ligand at silicon affording pentacoordination has a beneficial effect on the  $\chi^{(3)}$  properties. Further incorporation of such ligands to give hexacoordinate species is deleterious. In particular, the high  $\chi^{(3)}$  values observed for 1 should be noted.

The nonlinear optical and photorefractive properties of organic–inorganic hybrids made from the polymers by the sol–gel technique are at present being studied and are expected to be of interest in view of the very high solution  $\chi^{(3)}$  values reported here. Polymer 5 contains trimethoxysilyl

groups designed to facilitate incorporation of the materials into gels by formation of covalent bonds. Polymers 6–8 contain amide groups which are known to give rise to homogeneous organic–inorganic polymer hybrids,<sup>27</sup> and 8 also contains a carbazole group of potential use for its photorefractive properties. Initial results<sup>28</sup> obtained by the Z-scan technique with picosecond laser pulses on films of 7 and 8 (5% in a silica matrix) are of the same order of magnitude as those reported here for the solutions.

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