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NOTE

Degenerate four-wave mixing measurements of the $\chi^{(3)}$ non-linear optical properties of poly(arylene-ethynylenesilylene)s†

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The third-order optical non-linearity in solution of a series of poly(arylene-ethynylenesilylene)s containing a variety of backbone arylene groups and substituents at silicon has been studied by using the degenerate four-wave mixing technique at 1064 nm with a 6 ns pulse duration. Thermal grating effects may be neglected under the experimental set-ups employed. The results obtained are greater by more than two orders of magnitude than those previously measured for some of the polymers using the *Z*-scan technique at the same wavelength. The electronic contribution to the fast non-linearity is greater than the nuclear (orientational) contribution by a factor of at least 4. The presence of a single 8-(dimethylamino)naphthyl ligand at silicon affording pentacoordination has a beneficial effect on the $\chi^{(3)}$ properties. The high $\chi^{(3)}$ properties of the polymers (e.g. $|\mathrm{Re}(\chi^{(3)})| = 9.5 \times 10^{-12}$ esu for $[\text{—C}\equiv\text{C—SiPh}_2\text{—C}\equiv\text{C} - (1,4 - \text{C}_6\text{H}_4)\text{—}]_n$ in chloroform [5 g l^{-1}]) confirm the presence of extensive through-Si conjugation along the backbone. **Copyright © 2000 John Wiley & Sons, Ltd.**

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High and fast optical non-linearities of organic and organometallic materials are attracting considerable attention because of their potential uses in optical computing, telecommunications, integrated optics and opto-electronic devices.[1–3] A wide variety of organic polymers with conjugated π-electron systems has been studied for third-order nonlinear optics.[4,5] The magnitude of third-order non-linear optical susceptibilities ($\chi^{(3)}$) has been found to be affected by factors such as π-delocalization length, donor–acceptor functionalities, chain orientation and packing density, conformation and dimensionality.[6] Here we report the results of degenerate four-wave mixing (DFWM) measurements of the $\chi^{(3}$ susceptibility of poly(arylene-ethynylenesilylene)s.

Poly(arylene-ethynylene)s have interesting photo- and electro-luminescent properties and show large $\chi^{(3)}$-susceptibilities similar to those for polydiacetylenes,[7] giving rise to strong non-linear optical effects such as two- and four-wave mixings, and self-action. *Z*-scan $\chi^{(3)}$ measurements on some similar silicon-containing polymers of general

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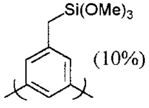
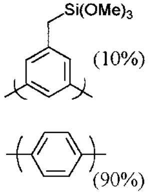
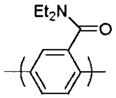
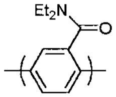
Table 1 Properties of polymers $[—C{\equiv}C—SiR^1R^2—C{\equiv}C—Ar—]_n$ (**1–8**)

Polymer	Polymer substituents		Si coord. no.	Colour	Molecular weight data			Solution DFWM ($\chi^{(3)}$) measurements[e]	
	$(R^1R^2)Si^a$	Ar^b			$M_w{}^c$	$M_w/M_n{}^c$	n^d	$\lvert n_2\rvert(cm^2\,W^{-1})$	$\lvert Re(\chi^{(3)})\rvert$(esu)
1	Ph_2Si	An	4	Red	23 500	3.2	56	19×10^{-14}	9.5×10^{-12}
2	$(l\text{-}Np)_2Si$	An	4	Orange	8 800	2.8	17	0.15×10^{-14f}	0.075×10^{-12f}
3	Me(NpN)Si	An	5	Red	12 400	2.7	28	11×10^{-14}	5.5×10^{-12}
4	$(NpN)_2Si$	An	6	Orange	20 000	3.2	34	6.3×10^{-14}	3.1×10^{-12}
5	Ph_2Si	 An (90%)	4	Red	13 000	2.9	36	1.5×10^{-14}	0.75×10^{-12}
6	Ph_2Si		4	Yellow	25 700	3.5	94	2.0×10^{-14f}	1.0×10^{-12f}
7	Ph_2Si		4	Brown	3 390	1.8	9	0.63×10^{-14}	0.32×10^{-12}
8	Me(NpN)Si		5	Brown	2 310	1.5	6	17×10^{-14}	8.5×10^{-12}

[a] NpN = 1-(8-dimethylamino)naphthyl.
[b] An = 9,10-anthrylene.
[c] Determined by SEC with reference to polystyrene standards.
[d] Number of units calculated from value of M_w.
[e] In $CHCl_3$ solution ($5\,g\,l^{-1}$) at 1064 nm with 6 ns pulse duration.
[f] Measured with 30 ns pulse duration.

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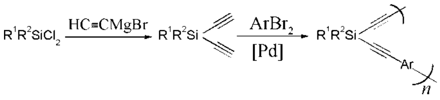
structure [—C≡C—SiR^{1}R^2—C≡C—Ar—]$_n$ [poly(arylene-ethynylenesilylene)s] have been determined at 590 nm [Re($\chi^{(3)}$) = -9.3×10^{-13} esu][8] and 1064 nm in the near-resonant region [Re($\chi^{(3)}$) = 4.0×10^{-13} esu].[9] Here, we report the considerably higher values obtained by using the DFWM technique for solutions of a variety of poly(arylene-ethynylenesilylene)s.

Following the route previously described,[9–11] polymers **1**–**8** (Table 1) were prepared by palladium-catalysed cross-coupling polymerization between the appropriate diethynylsilane (obtained from the corresponding dichlorosilane) and dibromoarene (Eqn [1]).



[1]

Polymers **3, 4** and **8** contain the 8-(dimethylamino)naphthyl ligand, which gives stable hypercoordinate species.[12] Indeed, few polymers containing hypercoordinate silicon are known, although it exhibits very different chemical and electronic behaviour from tetracoordinate silicon.[13] For polymers **1, 3** and **4**, the Im($\chi^{(3)}$) and Re($\chi^{(3)}$) values determined by the *Z*-scan method at 1064 nm (pulse duration 140 ps, intensity 20 GW cm^{-2}) in $CHCl_3$ solution (50 g l^{-1}) have been previously reported.[9]

DFWM experiments were made with a Q-swiched Nd:YAG laser-oscillator at 1064 nm and both co- and cross-polarized pumps, the pulse duration being 6 ns unless otherwise stated (Table 1). The pulse energy of each pumping wave was up to 10 mJ. For both experimental arrangements thermal grating effects may be neglected. In the first case orthogonally polarized probe wave and pumps wrote the grating, which therefore could not be thermal. In the second case the co-polarized probe wave and co-running pump wrote the grating with period $\Lambda \approx 200\,\mu$m with delay time τ_s for the isobar formation given by Eqn [2] (the speed of sound in chloroform is *ca.* $c_s = 10^5$ cm s^{-1}). Thus, in the case of co-polarized probe wave and co-running pump, the fast grating (due to Kerr-like non-linearities) is estimated to predominate over the thermally induced grating if the non-linear susceptibility $\chi^{(3)}$ is greater than 2.4×10^{-13} esu (as is so for all the present polymers). By comparison of the DFWM reflectivity results for the two series of experiments the electronic contribution to the fast non-linearity can be estimated to be greater than the nuclear (orientational) contribution by a factor of at least 4.[14]

$$\tau_s = 2\pi\Lambda . c_s = 34\,\text{ns} \gg 6\,\text{ns} \qquad [2]$$

The values of $|n_2|$ measured for chloroform solutions (using pure chloroform measurements as reference) of (a) starting monomer $Ph_2Si(C{\equiv}CH)_2$, and (b) the previously reported[9] model monomer $Ph_2Si(C{\equiv}C\{9\text{-anthryl}\})_2$ were essentially identical to that observed for the neat solvent $CHCl_3$ ($|n_2| = 3 \times 10^{-15}$ cm^2 W^{-1}),[6] being about one order of magnitude less than that observed for the polymer solutions (Table 1). Hence, it may be concluded that the n_2 values for these two monomers are very much lower than those for the polymers.

The real part of $\chi^{(3)}$ for each polymer (Table 1) was evaluated by using the value of Im($\chi^{(3)}$) derived from transmittance measurements together with the relationships $R \sim (|\chi^{(3)}|)^2$ (where R is the DFWM reflectivity) and $(|\chi^{(3)}|)^2 = (|\text{Im}\chi^{(3)}|)^2 + (|\text{Re}\chi^{(3)}|)^2$. Except for **7** and **8**, the polymers were of sufficient chain length for the $\chi^{(3)}$ effects to be at a maximum,[15,16] the highest value being observed for **1** containing tetracoordinate Ph_2Si groups ($|\text{Re}(\chi^{(3)})| = 9.5 \times 10^{-12}$ esu in $CHCl_3$ [5 g l^{-1}]). Based on number density considerations (≈0.5 wt% polymer in the solution), this value might be expected to be greater by a factor of 200 for the neat polymer, suggesting $\chi^{(3)}$ activity at least as high as that for derivatives of poly(1,4-vinylenephenylene).[16,17]

The measurements were made at concentrations lying in the range 2.5–12.5 g l^{-1}. For purposes of comparison, where necessary the values of n_2 and $\chi^{(3)}$ have been linearly extrapolated to the reference concentration (5 g l^{-1}). In each case the absorbance of the solution was found to be negligible (<0.05 cm^{-1}). The results obtained are greater by more than two orders of magnitude than those previously reported for **1** and **4** in concentrated solutions as determined by the *Z*-scan technique at 1064 nm.[9] However, in this previous study the values of n_2 were extracted from the *Z*-scan results with large uncertainties since the data could not be fitted well; indeed, for **3** no satisfactory result could be obtained and apparently identical results were obtained for **1** and **4**. Not only is comparison of results obtained using the two techniques difficult[5,16] but also it should be noted that a much lower light beam intensity (≈1 MW cm^{-2}) was used in the present study than for the *Z*-scan determination (20 GW cm^{-2}).[9] At the greater intensities used in the *Z*-scan experiment, higher-

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order non-linear susceptibilities ($\chi^{(5)}$ and $\chi^{(7)}$) giving negative contributions could decrease the overall non-linear effect of phase modulation.[8] Other reasons for the small values of n_2 obtained by *Z*-scan measurement include possible competing effects such as two-photon absorption and stimulated scattering appearing at high beam intensity. Indeed, the red anthracene-containing polymers (but not the others) show a strong two-photon absorption; transmittance measurements for polymers **1**, **3** and **4** gave $\beta = 5 \times 10^{-9}$ cm W^{-1}, corresponding to Im($\chi^{(3)}$) = 2×10^{-12} esu.

As previously reported,[9] for the series of polymers **2–4** containing naphthyl (Np) or naphthylamine (NpN) groups at silicon, smooth trends in the ^{29}Si and Si*C*≡C ^{13}C NMR chemical shifts as well as the energy of the ν(C≡C) IR absorbance are observed with increasing coordination number at silicon, reflecting the change in the electronic environment. 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** (with phenyl groups at silicon) is very large. These observations are consistent with there being a steric effect on the $\chi^{(3)}$ results perhaps resulting from unfavourable conformations forced on the polymers containing Np or NpN groups. This effect may be offset to some extent by the favourable electronic effect of the NpN group. Indeed, on comparing **7** and **8**, the presence of the naphthylamine group can be seen to have a most positive effect in the case of pentacoordinated **8**. Finally, comparison of the results for **5** and **6** suggests that phenylene groups in the polymer backbone may be preferable to anthrylene groups, although it should be noted that the relative error in the measured values of $|n_2|$ is *ca* 20%.

In conclusion, the very high $\chi^{(3)}$ properties of the polymers compared with those of model monomers confirm the presence of extensive through-Si conjugation along the backbone.[9] 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. The high $\chi^{(3)}$ values observed for **1** are particularly remarkable, although the origin of this effect is not clear.

The non-linear optical and photorefractive properties of organic–inorganic hybrids made from the polymers by the sol–gel technique are at present under investigation and are expected to be of interest in view of the high solution $\chi^{(3)}$ values reported here. Polymers **5** and **6** contain trimethoxysilyl groups designed to facilitate incorporation of the materials into gels by formation of covalent bonds. Polymers **7** and **8** contain amide groups which are known to give rise to homogeneous organic–inorganic polymer hybrids.[18]

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