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Temperature-dependent helix–helix transition of an optically active poly(diarylsilylene)†

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The poly(diarylsilylene) copolymer mainchain helix in $(Ar^*_2Si)_x(Ar_2Si)_{1-x}$ [Ar* = 3-(S)-2-methylbutylphenyl, Ar = 4-butylphenyl, $x = 0.2$] undergoes a thermally driven inversion of helical screw sense with a transition temperature of -10 °C.

Functional organic and polymeric materials with potential for application in devices in capacities such as switches, data storage, transmission and displays are attracting much attention owing to their relatively low cost, ease of fabrication of large area thin films, processability, and chemical tunability of optoelectronic properties through choice of substituents,[1] and particularly those with physical responses to stimuli, arising from higher order structural regularity.[2] Polymers adopting a preferential screw sense helical backbone conformation offer the possibility of a two state, switchable material if the opposite screw sense is energetically accessible and the helix–helix transition reversible.[3] Such helical inversions are rare and for discrete molecules in dilute solution responding to a change in temperature, have been reported only twice, first for a polypeptide, poly(β-propyl-L-aspartate)[4a] and very recently for a polyisocyanate, poly[3-{(S)-sec-butoxycarbonyl}phenyliso-cyanate].[4b] There is one example of a solid state helix inversion, for a polypeptide,[5] and change of sign of optical activity upon aggregation of other polyisocyanates,[6] polypeptides[7] and poly-thiophenes[3,8] is known.

Recently we showed using circular dichroism (CD) spectroscopy that poly(diarylsilylene)s (of significance owing to their electroluminescence (EL) properties)[9] with enantiopure chiral sidechains adopt preferential helical screw sense backbone conformations in solution.[10] Incorporation of the (S)-2-me-thylbutylphenyl group in polymers of the type [(Ar′)(Ar″)Si]$_n$ (Ar′, Ar″ = 4-butylphenyl, 4-(S)-2-methylbutylphenyl or 3-(S)-2-methylbutylphenyl) afforded optically active materials with positive or negative Cotton effects in the CD spectra (solution state) for polymers with one or two chiral centres per silicon, respectively. We then set out to find poly(diarylsilylene)s which

† Electronic supplementary information (ESI) available: polymer synthe-ses, fluorescence excitation and NMR data for **1**–**3**. See http://www.rsc.org/suppdata/cc/a9/a909368k/

could exhibit either positive or negative Cotton effects, dependent upon the application of an external stimulus. Such materials could potentially find application in a polymer-based chiroptical photonic device (e.g. circularly polarised EL device or semiconducting small molecule chirality sensor). Now we report our preliminary findings that the copolymer, poly[{bis-3-(S)-2-methylbutylphenyl}$_{0.2}$-co-(bis-4-butylphenyl)$_{0.8}$sily-lene] **1** undergoes a reversible, thermally driven helix–helix transition in solution with a transition point at -10 °C.

1: $x = 0.2$
2: $x = 0.5$
3: $x = 0.8$
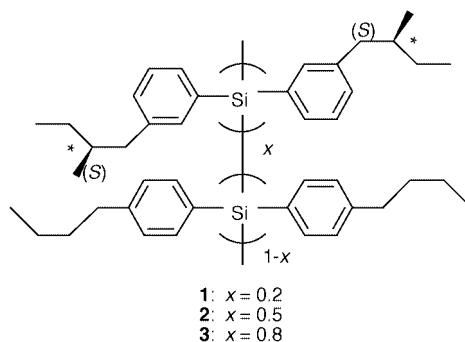
Poly(diarylsilylene) copolymers **1**–**3** were obtained by the Wurtz coupling of the appropriate dichlorosilane monomer mixtures in toluene at 70 °C and the compositions, as verified by ^{13}C NMR spectroscopy, corresponded to the nominal addition ratios (for preparative and NMR details see ESI†). Polymer-isation and spectroscopic data are given in Table 1.

The polymers show relatively narrow ($\Delta\nu_{1/2}$ ca. 16 nm) UV absorptions (peak maximum ca. 396 nm) due to the conjugated Si backbone σ–σ* transition, mirror image fluorescence emission spectra, small Stokes' shifts (ca. 13 nm) and fluorescence anisotropies in the range 0.20–0.38, indicating regular, semi-flexible polymer molecules with long segment lengths.[10] The CD and UV spectra of **1** are shown in Fig. 1. A negatively signed Cotton effect is evident in the CD spectrum at -70 °C, coincident with the absorption due to the Si σ–σ* transition, whereas at 50 °C, the effect is positive and at -10 °C the signal is approximately zero. This indicates a change in the

Table 1 Polymerisation and spectroscopic data for **1**–**3**

| | T^a/°C | UV[b] | CD[b] | | | | | | |
		$\varepsilon/\lambda_{max}$/fwhm	$\Delta\varepsilon/\lambda_{max}$	$10^4\,g_{abs}$	FL λ_{max}	FL-A[c]	$10^{-3}\,M_w$[d]	PDI[e]	Yield[f] (%)
1	20	24 300/397/14.0	0.24/393	0.10	408.5	0.20–0.30	474	2.77	5.9
2	20	25 700/399/14.6	−0.61/400	−0.24	410.5	0.20–0.30	271	2.88	3.9
3	20	10 400/393/19.0	−1.06/392	−1.02	407.5	0.34–0.38	8	1.34	3.3

[a] UV and CD data in isooctane at 20 °C; fluorescence (FL) and fluorescence anisotropy (FL-A) data in toluene at room temperature (21 °C). [b] ε and $\Delta\varepsilon$ units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}; λ_{max} units: nm; fwhm = full width (nm) at half maximum of λ_{max}. [c] Fluorescence anisotropy measured over region of backbone σ–σ* transition. [d] Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards; eluent: THF. [e] PDI = polydispersity index; M_w/M_n; given for isolated high M_w fractions. [f] Isolated yields of high M_w fraction.

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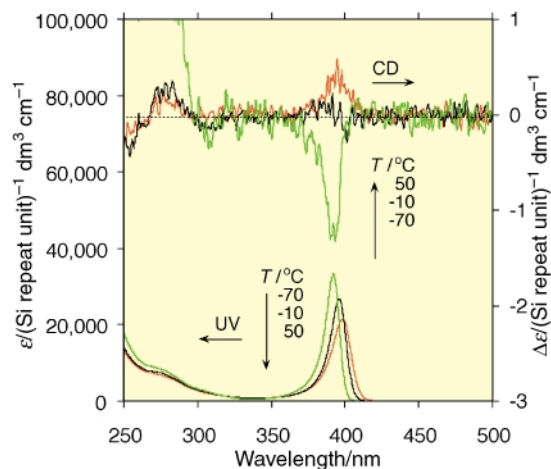
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Fig. 1 CD and UV spectra of **1** at −70, −10 and 50 °C.

backbone from one prevailing helical screw sense to the other. The disymmetric ratio,[11] g_{abs}, defined as the ratio of CD and UV molar absorptivities, $\Delta\varepsilon/\varepsilon$ (and thus more appropriate as a gauge of helicity than simply $\Delta\varepsilon$), is small for **1** at the temperature listed in Table 1 (20 °C), since this is close to the transition temperature. However, at −70 °C, g_{abs} is −0.38, greater than that for **2** (−0.27), but less than that for **3** (−1.57). By comparison, g_{abs} for the related homopolymer, poly[bis{3-(S)-2-methylbutylphenyl}silylene],[10] at 20 °C is −2.00. The lower disymmetric ratios for **1–3**, therefore, are most probably the consequence of the coexistence of both helical screw senses in **1–3**, at all temperatures.

Consistent with the above suggestion, at −10 °C, the CD spectrum of **1** actually has a small negative component at *ca.* 401 nm in addition to the small positive peak at 390 nm. We ascribe these two bands to the two different screw senses, which should be characterised by different screw pitches.[12] It is not possible, however, in the present case to associate a particular screw sense with the sign of the Cotton effect.

The maximum magnitude of the positive Cotton effect for **1** occurs around 50 °C, but it is less than the maximum negative magnitude, as may be seen from the plot of CD intensity $\Delta\varepsilon$ *vs.* *T* in Fig. 2. Above 50 °C, the CD signal intensity decreases again, a feature in common with the poly(diarylpolysilylene) homopolymers in our earlier study,[10] which we attribute to thermal population of the higher energy screw sense state, but additionally, though to a much lesser degree, to thermal broadening of the bands as a result of slight bond length increase (the molar absorptivities for UV and CD spectra decrease with increasing temperature).
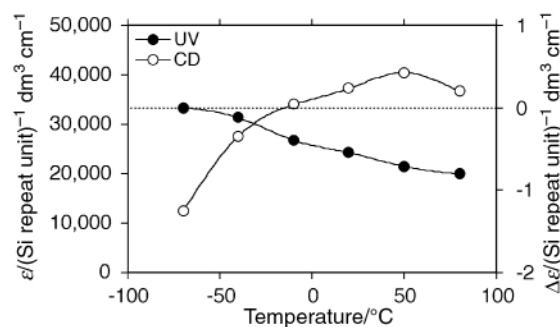

Fig. 2 Plots of CD ($\Delta\varepsilon$) and UV (ε) molar absorptivities per Si repeat unit *vs.* temperature for **1** (cubic spline fitting).

The corollary of this is an increase in $\Delta\varepsilon$ with decrease in temperature (in the absence of helical inversion), which has also been observed by other workers.[4b,13,14] Green *et al.* proposed that the optical activity of poly(alkyl isocyanate)s increases with decreasing temperature due to a diminishing number of helix reversals, allowing greater cooperation of backbone units.[14b]

A temperature cycling experiment comprising three cycles of −70/50 °C with CD and UV spectra recorded at each temperature for **1** indicated that the transition is reversible, negative and positive Cotton effects being observed, respectively. Excluding CD results, the data for polymer **2**, with a ratio of enantiopure chiral monomer to achiral monomer of 0.5:0.5, are similar to those of **1**. Polymer **3** (chiral:achiral = 0.8:0.2) with lower M_w (owing to lower solubility during synthesis) has slightly lower UV molar absorptivity but is otherwise also comparable to **1**, indicating similar polymer structures for **1–3**. The CD data, however, are markedly different: whereas **1** shows negative Cotton effects at low temperature and positive at high temperature indicating a transition from one helical screw sense to the other, **2**, **3** and the above mentioned related homopolymer, poly[bis{3-(S)-2-methylbutylphenyl}silylene],[10] show only negative Cotton effects at all temperatures and thus do not exhibit this phenomenon; *i.e.* this function is specific to **1**. It is apparent, therefore, that a subtle interplay of factors permits such a helix–helix transition, presumably as a result of the enthalpy and entropy terms in the Gibbs free energy equation being of the same sign, such that the free energy difference changes sign as a function of temperature, as was proposed in discussions of helix–helix transitions for certain polyisocyanates.[4b,15]

In conclusion, we have demonstrated a structure-specific, reversible, temperature-dependent helical screw sense inversion for a hybrid organic–inorganic chromophoric and fluorophoric polymer. Further investigation of poly(diarylsilylene) systems is in progress.

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