First Optically Active Diarylpolysilanes: Facile Helical Screw Sense Control with Only (*S*)-Enantiopure Side Chains

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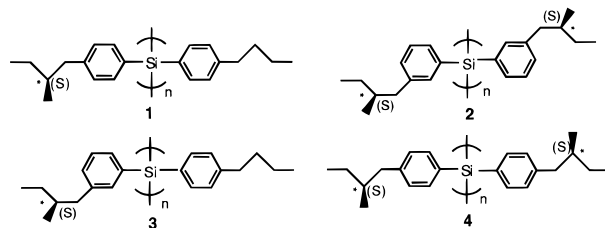
Received May 20, 1999
Revised Manuscript Received August 20, 1999

Organic polymer-based light-emitting diodes (LEDs) are attractive for several reasons, including low cost, ease of fabrication of large area thin films, processability, and chemical tunability of emission wavelength through choice of substituents, compared with inorganic semiconducting LEDs such as III−V and II−VI wide band gap materials.[1] An additional advantage is that circular polarization (CP) of emitted light may be obtained by suitable chemical modification of the polymer higher order structure, rather than by use of circularly polarizing filters, which for the same luminescence output intensity may require the device to be driven harder, increasing power consumption and decreasing the lifetime. The first example of CP electroluminescence was reported for a soluble poly(*p*-phenylenevinylene) copolymer containing enantiopure chiral side chains.[2] Among polysilanes,[3−5] of interest for their unique optical and electronic properties,[6] the greatest reported electroluminescence (EL) efficiency has been that of a diarylpolysilane, bis(*p*-*n*-butylphenyl)polysilane,[7,8] for which emission at 407 nm was observed in these labs. We are now investigating diarylpolysilanes containing enantiopure chiral side chains and report here the first synthesis of optically active helical diarylpolysilane homopolymers bearing (*S*)-2-methylbutyl groups and the effects on, and facile control of, the sign and intensity of the Cotton effect associated with a preferential P (plus) or M (minus) polymer helical screw sense in the circular dichroism (CD) spectra by the number per Si repeat unit and aryl ring substitution position of only (*S*)-enantiomer chiral substituents.

For a helical polymer backbone conformation, the presence of chiral side chains, and their resulting stereorelationship with each other, may induce a preferential screw sense of the polymer main chain. For the polysilanes of interest here, this would result in the appearance of a Cotton effect in the circular dichroism (CD) spectrum, coincident with the UV absorption due to the $\sigma-\sigma^*$ transition of the electronically delocalized silicon main chain. The lowest energy polysilane $\sigma-\sigma^*$ transition is sensitive to both electronic and steric substituent effects:[6,9] the former through silicon−silicon and silicon−side substituent orbital overlaps and the latter through their effects on the main chain global and local conformations. Though still a subject of much debate (especially

in the solid state) polysilane backbone conformations in the solution state have been discussed in terms of microscopic helical or all-trans domains within mesoscopic segments.[10] For bisaryl-substituted polysilanes, while the substituent contribution to the unusually long UV λ_{max} values from aryl ring-backbone orbital mixing is indicated theoretically,[11a] it has also been suggested that they may adopt an all-trans conformation.[11b]

Polysilanes are generally optically inactive, due either to the adoption of an all-trans conformation or, in the case of a helical polysilane, to equivalent amounts of both P (plus) and M (minus) screw sense helices. When the relative energies of P and M screw senses are altered, however, as has been demonstrated in a number of dialkyl-[12] and alkyl-arylpolysilane[13] systems, through the incorporation of enantiopure chiral side chains or end groups,[14] optical activity is exhibited. Force field calculations[15] for the model diarylpolysilane H−(SiPh$_2$)$_{30}$−H produce local minima at torsion angles of 165 and 195°, corresponding to a 15$_7$ helical conformation and suggesting a non-all-trans structure. On the basis of these calculations and to obtain diarylpolysilanes with a prevailing screw sense, we designed four diarylpolysilanes of the type [(Ar′)(Ar″)Si]$_n$ (Ar′, Ar″ = *p*-*n*-butylphenyl, *p*-(*S*)-2-methylbutylphenyl, or *m*-(*S*)-2-methylbutylphenyl) in which the number of chiral alkyl pendants per Si repeat unit is either one or two, as indicated in **1**−**4**.[16]

The CD spectrum of **1** (Figure 1a), containing one *p*-(*S*)-2-methylbutylphenyl group per Si repeat unit, exhibits a single positively signed Cotton effect, almost coincident with the UV spectrum, thus indicating that **1** adopts a preferential screw sense helical backbone conformation. In contrast, the CD spectrum of **2** (Figure 1b), containing two *m*-(*S*)-2-methylbutylphenyl groups per Si repeat unit, exhibits only a negatively signed Cotton effect, indicating that the backbone of **2** adopts the opposite (presumably more sterically favored for two bulky chiral substituents) screw sense to **1**. This feature thus permits either helical form to be obtained while employing only the cheaper and more readily available (from natural products) (*S*)-enantiomer substituent. The dissymmetry ratio, g_{abs} (defined[17] as $\Delta\epsilon/\epsilon$), is 4.8×10^{-5} for **1** (25 °C) and -2.0×10^{-4} for **2** (20 °C). The latter value is comparable to those for other enantiopure chiral-containing dialkylpolysilanes (e.g., for [(*S*)-2-methylbutyl](hexyl)polysilane,[18] $g_{abs} = 2.0 \times 10^{-4}$), while the former is about 1/4 that of **2**. The

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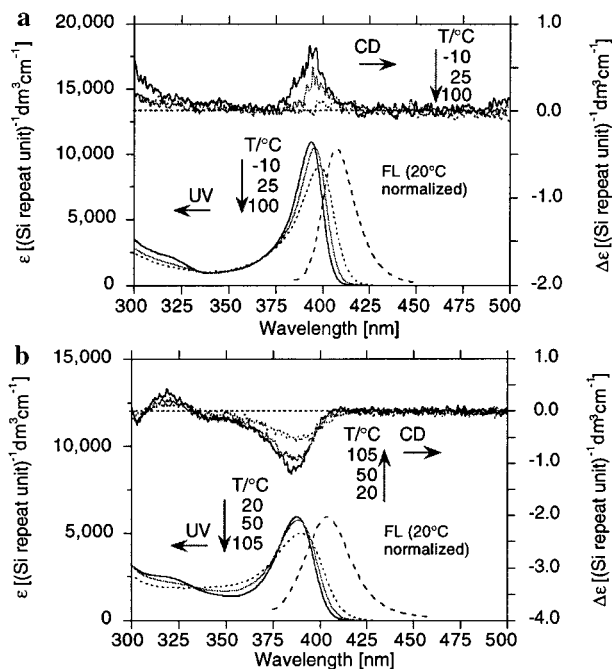(18) Fujiki, M. *Appl. Phys. Lett.* **1994,** *65,* 3251.

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Table 1. Data[a] for Polymers **1**−**4**

compd	UV[b] ϵ/λ_{max}/fwhm	CD[b] $\Delta\epsilon/\lambda_{max}$	$10^{-4}g_{abs}$	FL λ_{max}/nm	FL-A	MW[c]	PDI[d]	phase[e] trans/°C	yield,[f] %
1	10500/396/19.3	0.50/395	0.48	407.5	0.2−0.3	333000	2.8	50	3.3
2	5900/388/24.7	−1.18/385	−2.00	404.0	0.3−0.4	5000	1.1	57, 90	3.3
3	7900/397/21.7	0.27/396	0.34	411.0	0.2−0.3	254000	2.6	55	7.4
4	8400/395/20.5	−1.47/384	−1.75	406.0	0.2−0.3	240000	2.8	93	3.2

[a] Spectra recorded in toluene at 20 °C except for UV and CD of **1** at 25 °C. [b] ϵ units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}. λ_{max} units: nm. fwhm = full width (nm) at half-maximum of λ_{max}. [c] Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards. [d] Polydispersity indices given for isolated high MW fractions. [e] Differential scanning calorimetry (DSC; heating run, 10 K/min) indicates one or two weak endothermic phase transitions (which appear to be first order and thus might derive from a meso−meso phase transition). [f] Isolated yields of high Mw fraction.

Figure 1. Temperature dependence of UV and CD spectra of **1** (a) and **2** (b) in toluene.

CD and UV spectra of **1** and **2** exhibit significant temperature dependence, as may be seen in Figure 1, with the λ_{max} of both shifting to slightly longer values at higher temperatures and the CD signal losing intensity also at the higher temperatures. This is consistent with the loss of helical screw sense preference in some segments (possibly end chain segments, which are less constrained, and segments next to them) and consequent partial cancellation of oppositely signed CD bands.

Similarly for **3** and **4**, the observation of Cotton effects, positive (for one meta chiral substituents per Si repeat unit) and negative (for two para chiral substituents per Si repeat unit), respectively, in the CD spectra indicate optical activity for these polymers, too, and as in the cases of **1** and **2**, the electronic spectra are temperature dependent. However, the dissymmetry ratio for **3** is 3.4×10^{-5} (lower by a factor of 1.5 than that of **1**), indicating less dominant screw sense selectivity, arising from the partial cancellation of oppositely signed CD bands of major and opposite minor screw sense segments. This may be a result of the greater ability of **3** to mitigate steric congestion by phenyl ring rotation to minimize interaction between the meta chiral alkyl groups on next nearest silicon atoms (Si*−Si−Si*). The Cotton effect of **4** at around 400 nm is essentially negative in sign, although a small positive band is evident on the longer wavelength side. This observation is consistent with the results for **3** above and may be rationalized by a consideration that the screw pitches of segments of opposing screw sense are not necessarily identical. In this case, the shorter pitch segments could give rise to the major negative peak and the longer pitch segments to the smaller positive peak.

As can be seen by comparing the data in Table 1, the room-temperature spectroscopic data for **1**, **3**, and **4** are very similar. The differences in the data of **2** presumably result from the lower MW of this polymer.[19] The UV absorption maxima for **1**−**4** occur at longer wavelength values than in dialkyl (typically ca. 320 nm) or arylalkyl (ca. 345 nm) systems.[20] It has been suggested[9,10] that the origin of the red-shift in diarylpolysilane electronic spectra may result both from interaction between backbone σ and phenyl π ring orbitals and also to extension of the backbone[11] and larger dihedral angles, and although these influences cannot be separately evaluated in the present systems, we suggest that a combination of these factors is responsible for the observed red-shifts and thus that **1**−**4** exhibit extended backbone structures, as is also indicated by the force field calculation for H−(SiPh$_2$)$_{30}$−H.[15] The narrow line widths (fwhm = ca. 20 nm) indicate a regular structure with a long persistence or segment length.[12c] The fluorescence anisotropy data are consistent with a semiflexible polymer backbone, resulting from a small angle between absorption and emission chromophore transition moments (the theoretical maximum value for coaligned transition moments is 0.4, corresponding to a rigid rod[22]). The Stokes' shift is small in both cases and is also consistent with a regular backbone structure.

In summary, we have succeeded in the preparation of the first optically active diarylpolysilanes with preferential screw sense helical backbone conformations in solution and extended backbone structures. We have also shown that the direction of the screw sense (and thus sign of the Cotton effect in the CD spectrum), both positive and negative, of helical diarylpolysilanes containing (*S*)-2-methylbutylphenyl moieties is controlled by the number of chiral moieties per Si repeat unit. This side chain−main chain relationship should provide a new insight into the design of CP, CPL (CP luminescence), and CP-EL devices using only single-handed enantiopure chiral moieties.

Supporting Information Available: Synthesis of monomers; monomer data (boiling points, optical rotation, gas chromatography, ^{29}Si and ^{13}C NMR data), synthesis of polymers, and fluorescence excitation data for **1**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA991680C

(19) The lower MW of **2** is presumed to result from its lower solubility due to the greater steric requirements of the side chains and a higher chain scission rate on precipitation, since SEC during synthesis indicated a MW for **2** of 75000.

(20) The low-temperature UV spectra of **3** and **4**, in addition to the main absorption around 395 nm, also exhibit weaker bands at around 320 nm. Such blue-shifts in the electronic spectra of diarylpolysilanes have been reported[21] in the case of bis(alkoxyaryl)-substituted polymers and were attributed to significant distortion from the almost all-trans conformation due possibly to the unfavorable coalignment of the aryl ring *p*-alkoxy substituents on silicon atoms 1,3 to one another. We are currently investigating the origin of these bands.

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