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Cooperative Helical Order in Optically Active Poly(diarylsilylenes)

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ABSTRACT: Microscopic helical order in poly(diarylsilylene) copolymers containing enantiopure chiral (*S*)-2-methylbutylphenyl and achiral *n*-butylphenyl side chains results in macroscopically observable optical activity. These polymers are shown to adopt helical backbone conformations with a prevailing screw sense in solution through cooperative side chain interactions. Ultraviolet (UV) and circular dichroism (CD) spectroscopic studies over the temperature range −70 to 80 °C indicate temperature dependence of the dissymmetric ratio, g_{abs}. For copolymers of the type $(Ar^*{}_2Si)_x(Ar_2Si)_{(1-x)}$ (where Ar* = *p*-(*S*)-2-methylbutylphenyl, Ar = *p*-*n*-butylphenyl, and $x = 0.2$, 0.5, or 0.8), positive Cotton effects in the CD spectra indicate optical activity due to helical polymer backbones, optimally for the case where $x = 0.5$. This is in contrast to the copolymers with Ar* = *m*-(*S*)-2-methylbutylphenyl and $x = 0.2$, 0.5, or 0.8, for which the Cotton effects are of smaller magnitude and negative, except in the case of $x = 0.2$, for which a temperature-dependent inversion of Cotton effect sign is observed, as we communicated recently.[1] There is no optical activity, as expected, in the special case where $x = 0$, although from spectroscopic data and force field calculations, it is also concluded that even optically inactive poly(diarylsilylenes), including the above case where $x = 0$, adopt helical forms, but in an internal racemate. For the most highly chirally substituted bis-para copolymer, poly[bis(*p*-(*S*)-2-methylbutylphenyl)$_{0.8}$-*co*-bis(*p*-*n*-butylphenyl)$_{0.2}$silylene], an unusual (hypsochromic) thermochromic transition is observed at 320 nm, the origin of which is postulated in a helical backbone conformation with a concomitant phenyl ring twist to inhibit phenyl ring/Si−Si conjugation. Viscometric studies indicate that incorporation of branched side chains on the aryl rings results in polymers with stiffer, more extended structures, and this is related to the observed increase in UV absorption intensities.

Introduction

Attention has recently focused on optically active conjugating organic polymers due to their differential absorption and emission of circularly polarized (CP) light. Examples of such polymers include poly(phenylenevinylenes),[2,3] polythiophenes,[4] and polysilylenes[5] (also commonly termed "polysilanes"), which have optical band gaps in the range 2.5−4.0 eV and are candidates for use in CP light-emitting diodes (LEDs). Compared with inorganic wide gap III−V and II−VI LED materials, such organic polymers[6] have several advantages, including processability, low cost, ease of fabrication of large area thin films, and chemical tunability of emission wavelength through choice of substituents. Among poly(silylenes), the greatest reported electroluminescence (EL) efficiency has been that of a poly(diarylsilylene), poly[bis(*p*-*n*-butylphenyl)silylene] ($\Phi_{ex} = 0.01-0.10\%$), for which emission at 407 nm was observed in these labs.[7] Recently, using circular dichroism (CD) spectroscopy, we showed that poly(diarylsilylene) homopolymers bearing one or two enantiopure (*S*)-2-methylbutylphenyl groups per Si repeat unit adopted helical backbone conformations in solution, the screw sense being determined by the number of chiral groups per repeat unit.[8] We also showed that a structure-specific temperature-dependent helix−helix transition occurred for the coploymer poly[bis(*m*-(*S*)-2-methylbutylphenyl)$_{0.2}$-*co*-bis(*p*-butylphenyl)$_{0.8}$silylene].[1] Now we wish to report our findings that poly(diarylsilylene) copolymers synthesized from mixtures of achiral bis(*p*-*n*-butylphenyl)dichlorosilane and chiral bis(*p*-(*S*)-2-methylbutylphenyl)dichlorosilane at different ratios exhibit optical activity (due to the adoption of a preferential helical scew sense, through the cooperative induction of helicity in achirally substituted polymer segments by helicity in chirally substituted segments) of greater magnitude than either the related homopolymers or the *m*-phenyl-substituted series. This is important for the purposes of industrial application as it significantly reduces the need for expensive enantiopure chiral synthons, while still affording optically active materials. For the *p*-phenyl-substituted series, it is apparent that for maximum helical cooperativity there is an optimum chiral:achiral ratio of 50:50, whereas for the *m*-phenyl-substituted series the degree of helical cooperativity increases with chiral content. On the basis of a comparison of spectroscopic data of polymers with chiral and achiral side chains and force field calculations on model poly(diarylsilylenes), we also suggest that poly[bis(*p*-*n*-butylphenyl)silylene] adopts a racemic mixture of helical backbone conformations in solution. We also offer an explanation of the unusual 320 nm thermochromism which has been observed in these and other[9] poly(diarylsilylenes). Finally we indicate that incorporation of branched side chains on the aryl rings in the poly(diarylsilylenes) studied results in polymers with stiffer, more extended structures and relate this to the observed increase in UV absorption intensities.

For polymers with helical backbone conformations which are inate, such as polyisocyanates, polyisocyanides, and polysilylenes, or induced, such as poly(phenylenevinylenes), polyacetylenes, and polythiophenes, a preferential screw sense main chain may be obtained in several ways,[10,11] including (a) polymerization with unichiral catalyst[12a] or initiator,[12b] (b) chiral doping of

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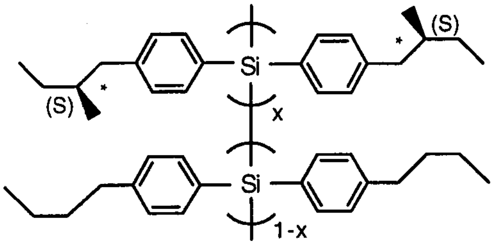
achiral (racemic) polymers with enantiopure chiral ions,[13] (c) separation of a racemic mixture of enantiomeric helices using chiral stationary phase (CSP) chromatography (for nondynamic systems),[14] (d) chiral complexation of achiral or racemic polymers with enantiopure chiral ligands/guests,[15] (e) post-polymerization functionalization with chiral moieties,[16] (f) polymerization of enantiopure chiral monomers,[8,17] (g) incorporation of enantiopure chiral end groups,[18] and (h) copolymerization of enantiopure chiral monomers with achiral monomers or with an enantiomeric excess (*ee*) of one enantiomer over the other.[5c,19,20] In the last two cases, it is the presence of the enantiopure chiral "seeds" which result in the adoption of a preferential helical screw sense in even non-enantiopure-substituted backbone regions by the preferential stereorelationship between enantiopure chiral side chains and their nearest neighbors. This cooperative phenomenon[21] has been referred to as "sergeants and soldiers" to describe the nonlinear relation between the specific optical rotation and the *ee* of chiral units in helical polythiophenes[22] and polyisocyanates[23] and has also been observed in poly(dialkylsilylene) systems.[5c]



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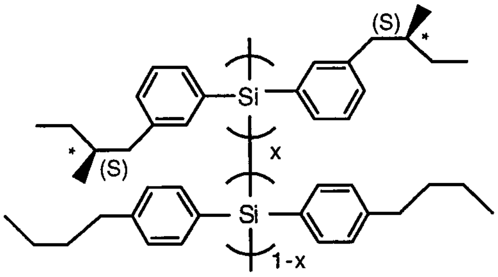
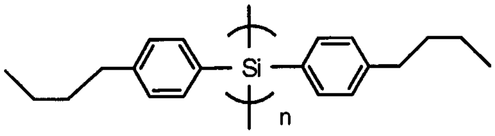
2: x = 0.5
3: x = 0.8



4: x = 0.2
5: x = 0.5
6: x = 0.8

To investigate cooperative phenomena in poly(diarylsilylenes) in greater detail, we designed a further three poly(diarylsilylene) copolymers, with chiral:achiral monomer ratios of 20:80, 50:50, and 80:20, based on the poly[{bis(*p*-(*S*)-2-methylbutylphenyl)}-*co*-{bis(*p*-*n*-butylphenyl)}silylene] system (**1**–**3**, respectively) and compare these with three based on the poly[bis(*m*-(*S*)-2-methylbutylphenyl)-*co*-bis(*p*-*n*-butylphenyl)silylene] system (**4**–**6**, respectively),[1] as shown above, and the related homopolymers **7**,[24] **8**,[8a] and **9**.[8a] We have also now performed force field calculations on model compounds of polymers **7**, **8**, and **10**[8a] and use these to support our proposal that poly(diarylsilylenes) adopt helical backbone conformations, irrespective of the phenyl ring substituent.



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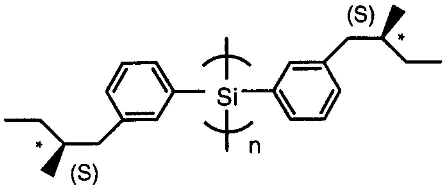

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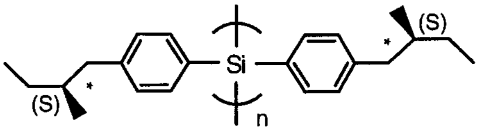

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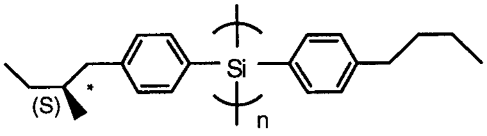

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Experimental Section

General. Molecular weights were determined by size exclusion chromatography (SEC) on a Shodex column (eluant THF) in a Shimadzu liquid chromatograph machine equipped with a diode array detector and calibrated with polystyrene standards. UV–vis spectra (room temperature, 21 °C) were recorded on a JASCO V-570 spectrometer at 1×10^{-4} mol dm^{-3} concentration. Variable temperature circular dichroism (CD) and simultaneous UV–vis spectra were recorded using a JASCO J-720 spectropolarimeter and Peltier control for temperatures from 80 to −10 °C (1 cm path length cell; sample concentration 1×10^{-4} mol dm^{-3}) and with a liquid nitrogen-cooled cryostat for temperatures down to −70 °C (0.5 cm path length cell; sample concentration 2×10^{-4} mol dm^{-3}). Fluorescence spectra[25] were recorded on a Hitachi F-850 spectrofluorimeter at room temperature. NMR spectra were recorded on a Varian Unity 300 spectrometer relative to internal TMS in toluene-d_8 for silicon at 59.591 MHz and for carbon at 75.431 MHz. Enantiopure chiral para- and meta-substituted bis(*S*)-2-methylbutylphenyl bromides were custom synthesized by Chemical Soft Co., Kyoto, Japan, and purified prior to use by distillation using a Perkin-Elmer autoannular still.

Monomers. These were prepared by lithiation of the aryl bromides in ether at 0 °C using *n*-butyllithium and addition of the resulting aryllithium solution to 0.5 equiv of silicon tetrachloride in hexane at 0 °C as previously described.[8] Filtration of the solution and distillation under reduced pressure afforded >95% pure (by GC) monomers in ca. 60% yield.

Polymers. Poly(diarylsilylene) random copolymers **1**–**6** were prepared according to the Wurtz-type method by coupling of a mixture of diaryldichlorosilane monomers using sodium in toluene. The synthesis of poly[bis(*p*-(*S*)-2-methylbutylphenyl)$_{0.5}$-*co*-bis(*p*-butylphenyl)$_{0.5}$silylene] (**2**) is representative:

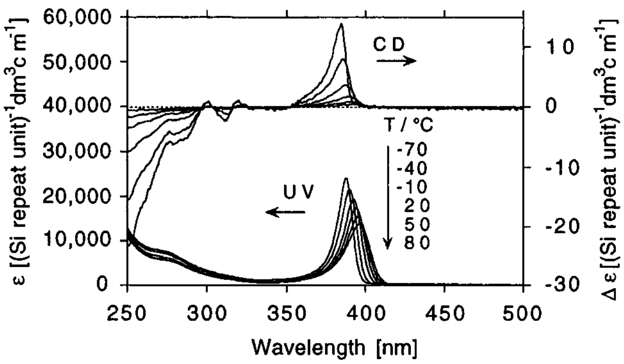

Figure 1. Variable temperature UV and CD spectra of **2** in isooctane.

Bis(p-(S)-2-methylbutylphenyl)dichlorosilane (1.52 g, 3.86 mmol) and bis(p-n-butylphenyl)dichlorosilane (1.41 g, 3.86 mmol) were combined to give a mixture in the ratio 1:1 and added in toluene (2 mL) to 2.5 equiv of sodium (0.44 g, 19.32 mmol) dispersed in toluene (11 mL) and surface-activated by diglyme (13 μL). The mixture was stirred slowly at 70 °C, shielding the vessel from light and monitoring the molecular weight periodically by SEC. After 3 h, 0.1 equiv of trimethylchlorosilane (0.08 g, 0.77 mmol) was added as terminator, and stirring continued for a further 30 min, after which the mixture was pressure filtered through two Teflon membranes (pore size 40 and 10 μm). The high molecular weight (M_w) fraction was isolated as a white powder or fibrous material by fractional precipitation in a mixed 2-propanol−toluene solution, followed by centrifugation, and vacuum-dried in an oven at 80 °C overnight. Yield: 0.24 g (10.1%). Incorporation of the monomers at the nominal addition ratio was verified by ^{1}H and ^{13}C NMR spectroscopy (see Supporting Information).

Viscometric Studies. Measurements were performed by the Toray Research Center (Shiga, Japan) using an in-line configuration of viscometer (Viscotek H502a, equipped with a capillary of dimensions 0.5 mm i.d. × 61 cm length) and SEC (Waters 150C). The solvent was THF and the measurement temperature 30 °C. Molecular weights were determined from a universal calibration plot, and the corresponding intrinsic visosities, [η], were obtained from the viscometer. Application of the Mark−Houwink−Sakurada equation (eq 1) in a plot of log[η] vs log molecular weight, M, affords the viscosity index a, and constant K, from the slope and intercept, respectively.

$$[\eta] = KM^a \tag{1}$$

The radius of gyration, R_g, at a given molecular weight, M, may be derived from eq 2, where Φ is the Flory constant (2.86 × 10^{-23} mol^{-1}).

$$[\eta]M = \Phi(6R_g^{\ 2})^{3/2} \tag{2}$$

Results and Discussion

Spectroscopy and Cooperativity. The CD spectrum of **2** (Figure 1), containing 50% p-(S)-2-methylbutylphenyl-substituted monomer units, exhibits a positively signed Cotton effect (389 nm), almost coincident with the lowest energy backbone electronic transition (σ−σ*) in the 20 °C UV spectrum (394 nm). This CD signal derives from the preferential absorption of left circularly polarized light and indicates that **2** adopts a preferential screw sense helical backbone conformation, which presumably results from the preferential stereorelationship between phenyl ring alkyl substituents on silicon atoms 1,3 to each other.

The CD spectra of **1** and **3** show similar features to that of **2**. The dissymmetry ratio, g_{abs} (defined[26] as the ratio of CD and UV molar absorptivities, $\Delta\epsilon/\epsilon$), is displayed as a function of chiral content for **1**−**9** at 20 °C in Figure 2. It is evident that the absolute magnitudes of $|g_{abs}|$ (i.e., independent of sign) for the p-phenyl-substituted copolymers **1**−**3** exceed those for enantiopure chirally substituted homopolymer **8**.[8] Since spectroscopic data (UV, fluorescence, fluorescence excitation,[25] and fluorescence anisotropy) are similar for **1**−**9** (see Table 1), it is reasonable to assume that polymer backbone dihedral angles are also similar, so that an increase in g_{abs} should thus imply greater helical screw sense selectivity. The larger g_{abs} values for **1**−**3** compared with that for **8** may therefore indicate that the cooperative effect in the p-phenyl-substituted copolymer cases is such as to induce helical backbone conformations with greater screw sense selectivity than the enantiopure-substituted poly(diarylsilylene) homopolymer, in which there is assumed to be a minor presence of segments of the less favored, opposite, chiral sense, resulting in a lower dissymmetry ratio.[8] Among **1**−**3**, it is **2**, with a chiral:achiral ratio of 0.5:0.5, which shows the greatest absolute dissymmetric ratio. At higher chiral content than this, the dissymmetric ratio decreases again, becoming negative for the bis-chiral homopolymer **8**,[8a] indicating a change of preferential screw sense. This cooperativity is unusual and contrasts with that observed in other optically active copolymer systems such as some polyisocyanates[20,23f] and poly(dialkylsilylenes).[5c] In these latter cases, the screw sense is determined by a small minority of enantiopure chiral repeat units, and the dissymmetric ratio is constant or only slightly increases at greater chiral content levels. The CD and UV spectra of all three polymers **1**−**3** exhibit a temperature dependence as is evident in Figure 1 and presented graphically in Figure 3a,b (which show plots of UV and CD λ_{max} intensities vs temperature, respectively), the UV λ_{max} shifting to slightly longer values at higher temperatures with generally a concomitant reduction in intensity and the CD intensity dropping in most cases to near zero at about 80 °C. This is consistent with the loss of helical screw sense preference due to the thermal energy exceeding that of the conformational fixing effect and consequent partial cancellation of oppositely signed CD bands.[8]

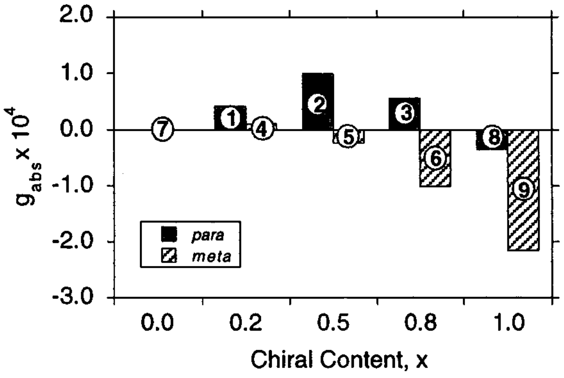

Figure 2. Plot of dissymmetry ratio, g_{abs}, at 20 °C against chiral content, x, for **1**−**9**.

In contrast, however, the CD spectrum of **5**, containing 50% bis(m-(S)-2-methylbutylphenyl)-substituted monomer units, exhibits very weak negative CD bands (dissymmetry ratio at −10 °C, $g_{abs} = -0.23 \times 10^{-4}$), lower by a factor of 4−8 than those of **1**−**3**, indicating that there is only a weak cooperative effect in the meta case, the backbone adopting the opposite screw sense to the para-substituted cases, presumably resulting

Table 1. Data[a] for Polymers 1−9

cmpd	T^a/°C	UV[b] ϵ/λ_{max}/fwhm	CD[b] $\Delta\epsilon/\lambda_{ext}$	$g_{abs}/10^{-4}$	FL[a] λ_{max}	FL−A[c]	$M_w{}^d/10^3$	PDI[e]	yield/%[f]
1	20	10 900/393/16.8	0.45/391	0.41	406.5	0.25−0.35	162	3.23	1.6
	−10	12 300/392/15.1	1.04/388	0.84					
2	20	17 400/394/15.0	1.73/389	0.99	407.0	0.27−0.33	186	2.73	10.0
	−10	19 300/392/13.6	3.67/387	1.90					
3	20	14 700/395/17.1	0.81/394	0.55	407.0	0.18−0.28	247	3.25	6.9
	−10	14 400/394/16.0	1.63/390	1.13					
4[g]	20	24 300/397/14.0	0.24/393	0.10	408.5	0.20−0.30	474	2.77	5.9
	−10	26 800/396/12.9	0.04/390	0.02					
5[g]	20	25 700/399/14.6	−0.61/400	−0.24	410.5	0.20−0.30	271	2.88	3.9
	−10	28 200/398/13.2	−0.65/397	−0.23					
6[g]	20	10 400/393/19.0	−1.06/392	−1.02	407.5	0.34−0.38	8	1.34	3.3
	−10	11 100/392/17.5	−1.37/389	−1.23					
7[h]	20	13 300/394/15.8	0.00/−	0.00	407.0	0.20−0.35	434	2.93	2.5
	−10	15 410/392/13.8	0.00/−	0.00					
8[h,i]	20	8400/395/18.7	−1.47/384	−0.35	406.0	0.20−0.30	240	2.86	3.2
	−10	3500/319/−	−	−					
		1800/391/−	−0.26/377, 0.43/392	−1.44, 2.39					
		7100/321/−	−	−					
9[h]	20	7400/386/26.5	−1.60/382	−2.16	404.0	0.30−0.38	5	1.1	3.3
	−10	7800/384/23.4	−1.86/384	−2.38					

[a] UV and CD data in isooctane at −10 and 20 °C; fluorescence (FL) data in toluene at room temperature (21 °C). [b] ϵ and $\Delta\epsilon$ units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}; λ_{max} and λ_{ext} units: nm; fwhm = full width (nm) at half-maximum of λ_{max}. [c] Fluorescence anisotropy measured over region of backbone σ−σ* transition; toluene, room temperature. [d] Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards; eluant: THF. [e] PDI = polydispersity index: M_w/M_n; given for isolated high M_w fractions. [f] Isolated yields of high M_w fraction. [g] Data from ref 1. [h] Samples described in ref 8; data newly recorded (in isooctane for **7** and **9** and in toluene for **8** due to poor solubility in isooctane). [i] See note in ref 38.

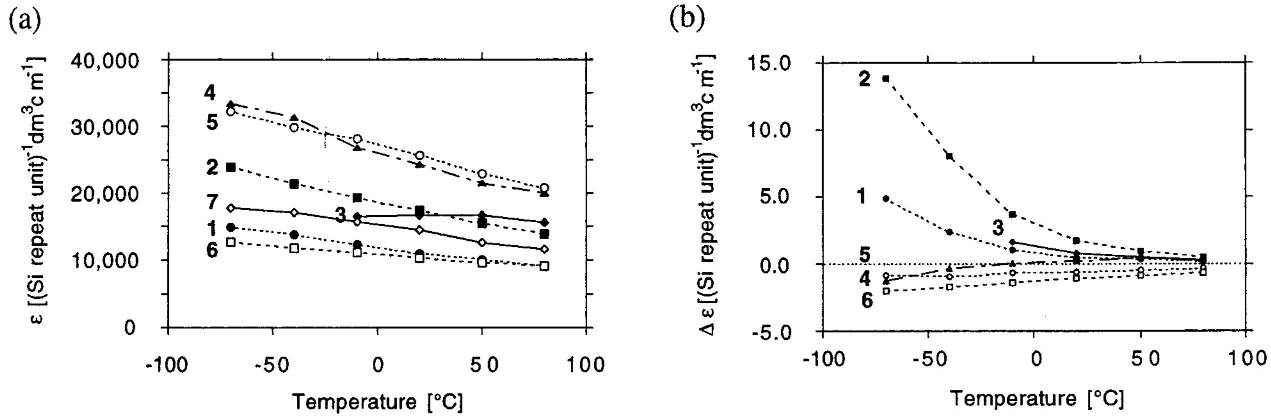

Figure 3. Plots of (a) UV (ϵ) and (b) CD ($\Delta\epsilon$) molar absorptivities per Si repeat unit vs temperature for **1**−**7** (data for **3** recorded in toluene and only available to −10 °C due to poor solubility; CD zero for **7**, so not included).

from the better alleviation of steric hindrance afforded. Two possible, nonexclusive, reasons can be considered to account for the lower dissymmetry ratio: (i) The polymer backbone dihedral angles are very close to 180°, resulting in a looser helix. (ii) Although the backbone is helical, there is less dominant screw sense selectivity, thus giving rise to weaker Cotton effects through partial cancellation of oppositely signed CD bands.[8] This may result from the greater ability of **5** to mitigate steric congestion by phenyl ring rotation, minimizing interaction between the meta chiral alkyl group and *p*-*n*-butyl or *m*-(*S*)-2-methylbutyl groups on neighboring silicon atoms. As can be seen by comparing the data in Table 1, the room temperature spectroscopic data (excluding CD) for all the polymers are similar, though **5** exhibits a longer UV absorption maximum (indicative of more open backbone dihedral angles)[27] than **1**−**3**. Although it is not possible at present to definitively state the origin of the weaker Cotton effects observed for **5**, we suggest that both factors outlined above are responsible; viz. **5** has a loose helical structure (near to all-anti) in which *P* and *M* sense helical turns coexist but in unequal proportions. For copolymer **6**, similar spectral features to **5** are evident, though with increasing negative dissymmetry ratios, and in the *m*-phenyl-substituted series, it is the homopolymer (**9**) which evidences the highest dissymmetry ratio. In the case of **4**, as we communicated recently,[1] containing 20% *m*-(*S*)-2-methylbutylphenyl-substituted monomer units, the CD spectrum shows a negative Cotton effect at −70 °C, approximately zero intensity at −10 °C, and positively signed Cotton effects at temperatures above this, with a maximum at 50 °C, exhibiting a rare example of a temperature-driven helical inversion of a polymer in dilute solution. There are only five other reports, one concerning certain poly(α-amino acid ester)s,[28a] another poly(β-phenethyl L-aspartate),[28b] the third, a poly(arylisocyanate),[28c] the fourth, poly(dialkylsilylenes),[29] and most recently, some polyisocyanate copolymers.[28d] In the present case, since we consider that *P* and *M* screw senses coexist in these polymer systems, the transition may be considered to reflect the gradual thermodynamic stabilization of one screw sense relative to the other, as the populations alter with temperature, rather than an abrupt switch. It is clear that this phenomenon is structure-dependent, since no such

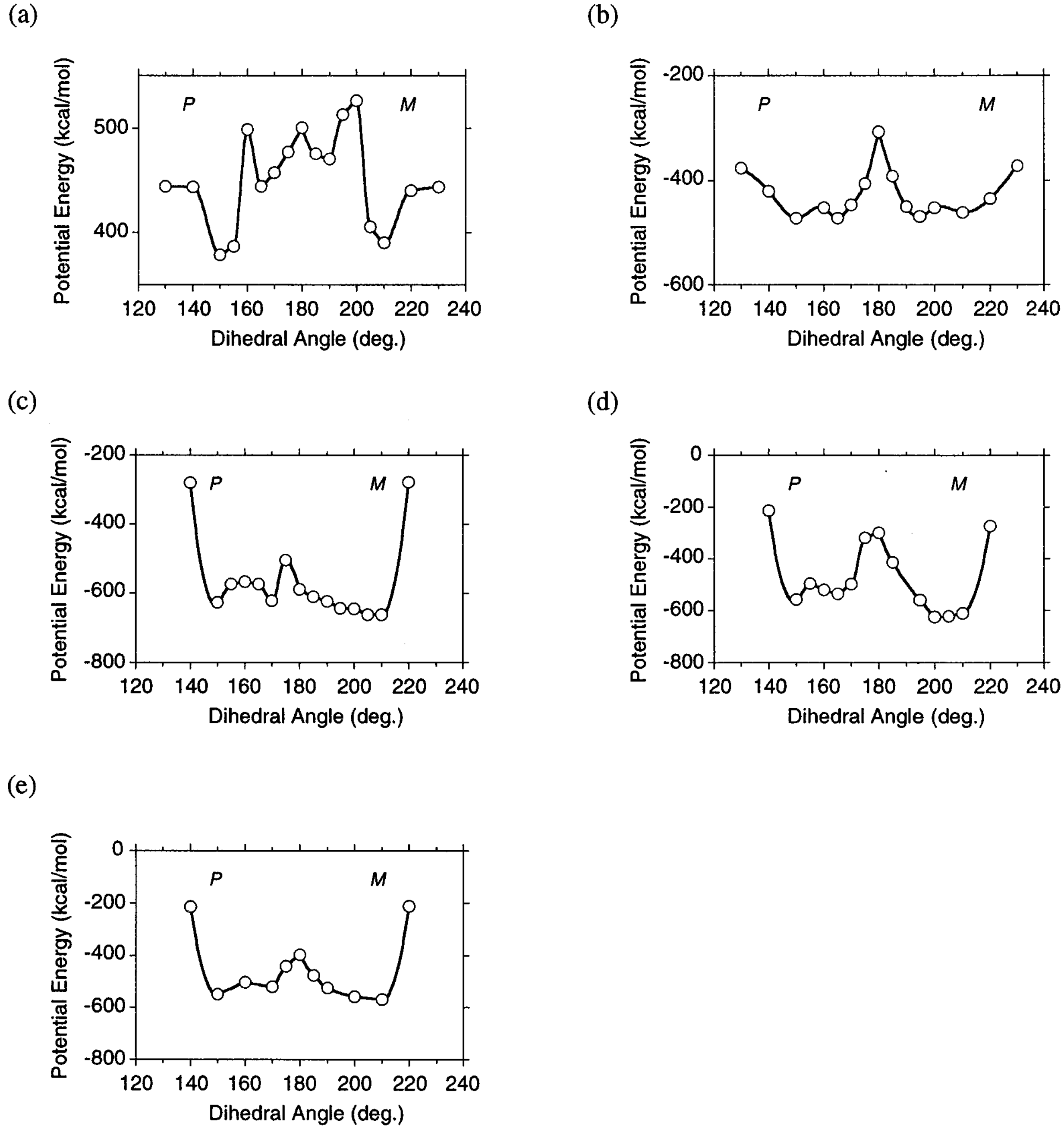

Figure 4. Force-field-calculated potential energy as a function of backbone dihedral angle for (a) H−$(Ph_2Si)_{30}$−H, (b) H−$(Ar_2Si)_{30}$−H, (c) H−$(Ar^*_2Si)_{30}$−H, (d) syndiotactic H−$(ArAr^*Si)_{30}$−H, and (e) isotactic H−$(ArAr^*Si)_{30}$−H (where Ar = 4-*n*-butylphenyl and Ar* = 4-(*S*)-2-methylbutylphenyl).

transition is observed for any of the other polymers studied.

Calculated Structures of Achirally and Chirally Substituted Poly(diarylsilylenes). To investigate theoretically whether poly(diarylsilylenes) might be expected to adopt either a helical or a planar all-anti backbone structure, we performed force field calculations[30a] for various model compounds to determine the dependence of potential energy on backbone dihedral angle. Figure 4a−e shows these results graphically for H−$(Ph_2Si)_{30}$−H,[8a] H−$(Ar_2Si)_{30}$−H (model for **7**), H−$(Ar^*_2Si)_{30}$−H (model for **8**), H−$(ArAr^*Si)_{30}$−H (syndiotactic model for **10**), and H−$(ArAr^*Si)_{30}$−H (isotactic model for **10**) (where Ar = 4-*n*-butylphenyl and Ar* = 4-(*S*)-2-methylbutylphenyl), respectively. (We did not calculate any meta-substituted polymers due to the additional complexity resulting from the ring positional isomerism.) It is clear in all cases that a backbone dihedral angle of 180° does not correspond to an energy minimum. For the achirally substituted model polymers in Figure 4a,b, symmetrical potential curves are obtained with nonminimum 180° energies, indicating that helical backbone structures should be preferred. In fact, minima are evident for dihedral angles corresponding approximately to 15_7 and 7_3 helical conformations in both cases. The experimental analogues of these models compounds would, however, be expected to be optically inactive due to the formation of intramolecular racemates. As expected for the experimental compound, poly[bis(*p*-*n*-butylphenyl)silylene], **7**, no Cotton effect is observed in the CD spectrum. By similar reasoning to that for **5** above (similarity of spectroscopic properties), supported by these calculation results, it may be inferred that **7** also adopts a helical backbone conformation in solution (with equal *P* and *M* turns), in contrast to earlier reports which suggested an all-anti planar backbone conformation for this polymer.[24] On the other hand, calculations for the model compounds of **8** and **10** with enantiopure chiral substituents afforded asymmetric potential curves, as shown in Figure 4c–e. Experimentally, this imbalance of energies of *P* and *M* screw senses should manifest itself in a preference for one screw sense over the other, resulting in optically active polymers, as is indeed the case, as we reported recently.[8a] For **10**, we calculated both syndiotactic and isotactic sequences in which the alkyl chains were initially oriented orthogonally to the phenyl rings (Figure 4d,e) and also an isotactic sequence with the alkyl chains coplanar with the phenyl rings (see Supporting Information). While small local energy differences were observed, the overall dependence of potential energy on dihedral angle was similar, with nonminimum 180° values and asymmmetric plots, indicating greater stability for the *M* screw sense helices.

The complexity of these plots, showing several stable helical conformations for any one compound, may explain the complexity of the cooperative response in these systems. The energy differences between the different conformations are not large, and it is likely that the observed spectra result from a conformation or conformations depending on environment (substituent, solvent, and temperature). Because of this complexity and the fact that the calculations refer to models under nonreal conditions,[30a] we cannot correlate the sign of the experimental Cotton effect in the CD spectrum with the direction of preferential screw sense. However, while the choice of initial ground state structure affects the relative minimum energies of the dihedral angle potential curves, the most important feature remains unchanged: that the energy at a dihedral angle of 180° (all-anti, or all-trans, as it has been commonly termed) is not a minimum. This is corroborated by the single-crystal X-ray structure of 1,7-dichlorotetradecaphenylheptasilane, which revealed a helical conformation with SiSiSiSi torsion angles in the range of 154–162°.[30b] We therefore suggest that all poly(diarylsilylenes) are in fact helical, even if the dihedral angles are small. In view of the developing consensus within the polysilylene community with respect to definitions of conformations, the description of "transoid" for these polymers seems appropriate.

Thermochromism: Band at 320 nm. It is evident from Figure 3a that in the case of **3** the UV molar extinction coefficient per Si repeat unit, ϵ, at −10 °C is actually slightly less than at 20 °C, in contrast to all other temperatures and copolymers. The reason for this may be seen in Figure 5, which includes the UV absorption spectrum of **3** at −10 °C, in which, in addition to the main UV absorption at 394 nm, there is a new low-intensity (ϵ = 3100 per Si repeat unit) absorption at ca. 320 nm, into which intensity is transferred from the lower energy absorption. Such thermochromism is unusual in polysilylenes and has been reported only once, in a class of poly[bis(*p*-alkoxyphenyl)silylene]s.[9] It was proposed that the bands at ca. 325 nm derived from backbone segments significantly distorted from the planar all-anti arrangement and conjectured that the origin of the distortion might lie in the unfavorable coalignment of C–O dipole moments which would occur between next-nearest silicon atom substituents in an all-anti scenario. In our case, however, this band is observed despite the absence of such potential dipole interactions. It is widely accepted in polysilylene chemistry that both backbone planarity[27] and conjugation with aryl side chains[31] result in bathochromic shifts in the UV main-chain absorption. Raman investigations have also shown that σ–π conjugation between Si–C and C=C bonds in allylic silanes is negligible when the Si–C bond lies in the C=C plane.[32] We therefore suggest that steric hindrance between bulky substituted phenyl rings results in a combination of a helical backbone and concomitant phenyl ring rotation out of maximum conjugation with the silicon chain, which both result in higher transition energies and could thus account for the observed large bathochromic shifts. Although a bisigned CD signal is evident with positive and negative extrema at ca. 295 and 315 nm, respectively, this is shifted somewhat with respect to the UV signal at 320 nm, and its origin is not clear. We are currently investigating the origin of the CD and UV bands near 320 nm and also the solid-state morphology of **3** (by Raman and X-ray spectroscopies).

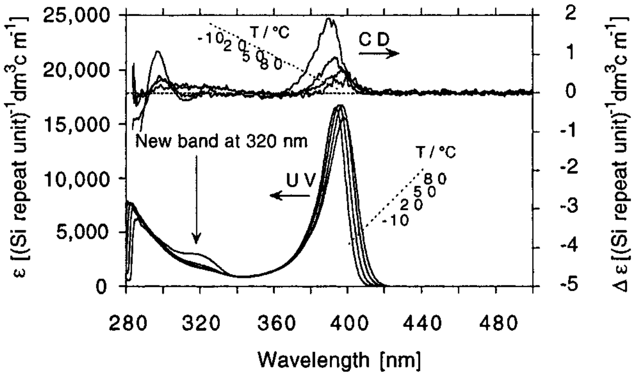

Figure 5. Variable temperature UV and CD spectra of **3** in toluene.

Viscometric Properties. To investigate the macroscopic effect of incorporating enantiopure chiral monomer units of greater steric bulk than bis(4-butylphenylsilylene) (by copolymerization) upon viscosity, the viscometric properties of **4** and **7** (data for **7** already reported,[33] but measured here again for control purposes) were determined. The viscosity index, *a*, for **4**, **7,** and reported **7** are the same (ca. 1.0–1.1) within experimental error (and variation expected due to differing experimental conditions between those described here and those in ref 33). The major difference, however, lies in the data for the radius of gyration (R_g) of **4** and **7**, which are plotted in Figure 6 on a log/log scale, as a function of molecular weight (together with data for their idealized rigid-rod analogues)[34] and are greater by about 30% for **4** compared to **7**. This is consistent with a stiffer, more extended structure of the copolymer **4** due to the greater steric demand of the bulkier branched alkyl phenyl side chains incorporated compared to **7**, the side chains of which contain straight chain alkyl phenyl ring substituents. The R_g values for **4** also lie closer to those for the idealized rigid-rod plot than do those of **7**. From the data represented in Figure 6, a greater persistence length for **4** compared to **7** could also be expected and is indeed found (75 vs 45 Å, respectively; estimates are derived in ref 34). This result would also be consistent with the proposal that polysilylene UV absorption intensities are a function of viscosity index[35] and thus also of persistence length (as

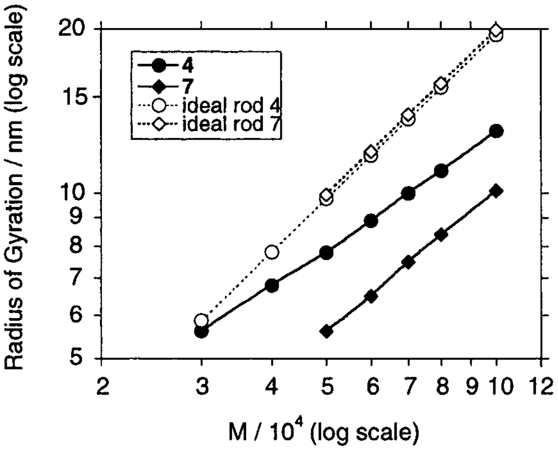

Figure 6. Plots of polymer radius of gyration R_g against M for **4** and **7** in THF at 30 °C and their idealized analogues.

the latter two parameters are related[36,37] through their dependence on R_g), since **4** has a much greater UV molar absorption coefficient (ϵ) than **7** (24 300 vs 13 300 (Si repeat unit)$^{-1}$ dm^3 cm^{-1} at 20 °C).

In summary, we have demonstrated (i) cooperative helical ordering in poly(diarylsilylene) copolymers containing both chiral and achiral monomer units. Dissymmetry ratios (CD intensity/UV intensity) depend on temperature and the chiral:achiral monomer ratio and, for the *p*-phenyl-substituted series, are greater than those of the related *m*-phenyl-substituted copolymers and the homopolymers, indicating greater screw sense selectivity in the copolymers. This may provide a new insight into the design of CP, CPL (CP luminescence), and CP-EL devices, as it significantly reduces the need for expensive enantiopure chiral synthons, while still affording optically active materials. (ii) Further, we have shown that the temperature-dependent helix−helix transition for the meta-substituted copolymer with $x =$ 0.2, **4**, is indeed structure-specific and that the no such transition is evident in the *p*-phenyl-substituted series. In the *m*-phenyl-substituted polymers the cooperative helical ordering effect is weaker, owing, we suggest, to the weaker steric interaction between the substituents attached to next-nearest silicon atoms. (iii) On the basis of a comparison of spectroscopic data of polymers with chiral and achiral side chains and the results of force field calculations, we further suggest that poly[bis(*p*-*n*-butylphenyl)silylene] also adopts a helical backbone conformation comprising equal *P* and *M* sense turns in solution (hence its optical inactivity) and that poly(diarylsilylenes) generally should be considered to adopt transoid, rather than all-anti, conformations in solution. (iv) We postulate the origin of the unusual thermochromism and UV 320 nm absorption of poly(diarylsilylenes) in a helical backbone conformation in which the phenyl ring/Si−Si conjugation is significantly inhibited. (v) We finally show that incorporation of branched side chain monomer units results in a macroscopically stiffer, more extended polymer chain and provide further evidence for the dependence of polysilylene UV absorption intensities on viscosity index and persistence length.

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Supporting Information Available: Fluorescence excitation and NMR data for **1**−**6** and force field calculation for isotactic H−(ArAr*Si)$_{30}$−H with coplanar alkyl and phenyl moieties. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) Estimation of persistence length, q. Using values for Si−Si bond lengths (2.414 Å) and Si−Si−Si bond angles (114.4°) derived from the single-crystal X-ray diffraction study of poly(dichlorosilylene) (see: Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441) and the viscometric data obtained, an estimate of q may be obtained (see ref 33; the polymer is treated as Gaussian and expansion factors are not included). For **4**: given the average formula weight per backbone repeat unit of 300.124, the mass per unit length, M_L, is 147.9 Å^{-1}. Considering data for a molecular weight, M, of 1×10^5, the contour length, $L = M/M_L$, is 676 Å. Given also $L = n_k l_k$ (where n_k and l_k are the number of Kuhn segments and the Kuhn segment length, respectively) and the mean-square end-to-end distance $\langle r^2 \rangle = n_k l_k^2$, a value for the Kuhn segment length of the polymer at the chosen molecular weight is given by $l_k = \langle r^2 \rangle / L = 148.65$ Å. Since $l_k = 2q$, the persistence length, q, therefore approximates to 75 Å. Likewise, the persistence length of **7** may be approximated to 45 Å. Considering the approximations made and that the estimate for **7** is shorter than that in ref 33 (the reported value for **7** is about 100 Å), use of the values derived here for **4** and **7** should be restricted to a qualitative comparison between them. Idealized rigid-rod values of R_g for **4** and **7** were obtained by use of calculated L values in the relation for rigid rods: $\langle r^2 \rangle = 12\langle s^2 \rangle = L^2$, where $\langle s^2 \rangle$ is the mean-square radius of gyration.

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(38) As noted in ref 20 of our previous work,[8a] at 20 °C, the CD band of **8** approximately coincident with the UV absorption at 395 nm is essentially negative, although a small, positive, longer wavelength band was apparent. At lower temperature, a new band in the UV spectrum was noted at about 320 nm. Further variable temperature CD/UV experiments down to −70 °C on this sample indicate a relative decrease of the intensity of the negative Cotton effect compared with that of the positive Cotton effect. Thus, at −10 °C, two CD bands, one positive and one negative, are apparent, values for both of which are given in Table 1. The half-height line widths in the UV spectrum at −10 °C are not determinable due to the shape of the peaks.

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