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Cooperative Preferential Helical Ordering in Poly(alkylarylsilylene) Copolymers

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ABSTRACT: We prepared two series of poly[((*S*)-2-methylbutyl(phenyl)silylene)$_x$-*co*-(methylphenylsilylene)$_{1-x}$] ($0 \leq x \leq 0.5$) (**1**) with coiled conformations and poly[((*S*)-2-methylbutyl(phenyl)-silylene)$_x$-*co*-(*n*-hexyl(*m*-tolyl)silylene)$_{1-x}$] ($0 \leq x \leq 0.5$) (**2**) with stiffer conformations; however, we could not produce the poly[((*S*)-2-methylbutyl(phenyl)silylene)] homopolymer due to steric overcrowding. We conclude that even optically inactive **1** with $x = 0$ and **2** with $x = 0$ adopt helical conformations with an equal quantity of *P*- and *M*-screw-senses by means of UV, circular dichroism (CD), fluorescence (FL) spectra, FL anisotropy, and molecular mechanics calculations. We found that the preferential screw-sense is subject to a noticeable cooperative induction effect in both copolymer systems as the chiral silylene moiety increases. This is based on a quantative analysis of the dissymmetry ratio ($g = \Delta\epsilon/\epsilon$) as a function of chiral molar composition. However, the helical cooperative effects are markedly different between **1** and **2**, which is believed to arise from their differences regarding chain stiffness, global conformation, and persistence length.

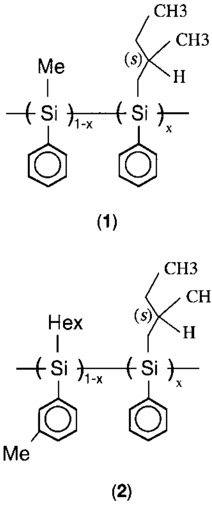
Introduction

It is important to control the handedness of helical polymers[1−10] in order to use them as chiral selectors such as for analysis columns and in chiral drugs. There are only few synthetic polymers available as chiral selectors. Functional groups are necessary to distinguish a pair of enantiomers through such chemical interactions as $\pi-\pi$ phenyl and dipole−dipole interactions.[9] Polysilylenes have attracted considerable interest as a new class of σ-conjugated polymers.[11,12] Their valence and conduction bands consist of a σ-conjugating wave function along a silicon main chain. They show sharp and strong absorption and fluorescence in the 300−400 nm region. This absorption is attributed to the transition from the valence band level to the first exciton energy level.[13−15] The optical properties are, however, strongly affected by their global and local conformations.[16] Our recent studies have shown that optically active poly(alkylalkoxyphenylsilylenes) arising from the incorporation of chiral substituents have unique optical properties.[17] Their helical conformations are controlled by the position of the chiral group, which is far from the main chain. These results suggest that it is possible to tune the chiral selectors capability by modifying the side chains of poly(alkylarylsilylenes). This paper describes the cooperative helical conformation control of poly(alkyl(aryl)silylene)s by the incorporation of chiral moieties. We prepared poly(alkyl(aryl)silylene) copolymers with an increasing incorporated chiral moiety ratio. The single-screw-sense in the main chain of these helical polymers was induced nonlinearly as regards the incorporated chiral moiety ratio, which is consistent with a cooperative response to the chiral information on the conformational properties.[18]

Experimental Section

Apparatus. We obtained the weight-average molecular weight of polymer (M_w) and the number-average molecular weight of polymer (M_n) using gel permeation chromatography (Shimadzu A10 instruments, Shodex KF-806M for the column, and HPLC-grade tetrahydrofuran (THF) as the eluent), based on a calibration with polystyrene standards. ^{13}C and ^{29}Si NMR spectra were obtained in CDCl$_3$ at 30 °C with a Varian unity 300 spectrometer using tetramethylsilane as an internal standard. We measured the UV and circular dichroism (CD) absorption spectra at room temperature (23 °C) in THF with a JASCO J-720 spectropolarimeter using a quartz cell with a path length of 10 mm at room temperature in THF. We measured fluorescence (FL) and fluorescence anisotropy (FLA) spectra at room temperature (23 °C) in spectroscopic grade THF with a Hitachi F-850 fluorescence spectrophotometer using a quartz cell with a path length of 10 mm.

Scheme 1. Molecular Structures of 1 and 2



Materials. The molecular structures of **1** and **2** are shown in Scheme 1. Below we describe a typical method for synthesizing poly[((*S*)-2-methylbutyl(phenyl)silylene)$_{0.25}$-*co*-(methyl-(phenyl)silylene)$_{0.75}$] (**3**) and poly[((*S*)-2-methylbutyl(phenyl)-silylene)$_{0.20}$-*co*-(*n*-hexyl(*m*-tolyl)silylene)$_{0.80}$] (**4**). We used the same procedure to synthesize optically active copolymers with different chiral molar composition (**1** with $x = 0.05$, 0.10, 0.25, 0.30, and 0.50, and **2** with $x = 0.05$, 0.10, 0.20, and 0.50) and homopolymers poly(methyl(phenyl)silylene) (**5**, **1** with $x = 0$) and poly(*n*-hexyl(*m*-tolyl)silylene) (**6**, **2** with $x = 0$).

The mixture of methylphenyldichlorosilane (5.0 g) and (*S*)-2-methylbutylphenyl dichlorosilane (1.6 g) was dropped in 1

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Table 1. M_w, M_n, and the Polydispersity Index of All Samples

	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-5}$)	M_w/M_n
1 ($x = 0.0$)	3.8	1.7	2.3
1 ($x = 0.05$)	3.5	1.4	2.2
1 ($x = 0.10$)	3.2	1.2	2.7
1 ($x = 0.25$)	4.3	2.0	2.1
1 ($x = 0.30$)	3.8	1.4	2.7
1 ($x = 0.50$)	2.6	1.2	2.2
2 ($x = 0.0$)	3.2	1.3	2.5
2 ($x = 0.05$)	3.4	1.4	2.4
2 ($x = 0.10$)	2.6	1.2	2.2
2 ($x = 0.25$)	3.6	1.5	2.4
2 ($x = 0.50$)	3.2	1.3	2.5

mL increments into toluene with 1.3 g of sodium at 110 °C under an Ar gas atmosphere. We refluxed the mixture by stirring it for 5 min and then crushed the sodium into small pieces. The solution then changed to bright purple. We cooled the solution to 65 °C and then added the remaining starting materials. We added 100 mL of toluene and then filtered the solution using a 5 μm pore PTFE disk under Ar gas. We carefully added a small amount of isopropyl alcohol to the filtrate and isolated the precipitate that formed using a Kubota 5100 centrifuge apparatus at 4000 rpm for 30 min. We then dried the precipitate at 100 °C overnight in a vacuum and obtained the purified **3** (0. 22 g) as a white solid with a yield of 7%. The M_w value was 9.8×10^5 and the polydispersity index ($=M_w/M_n$) was 1.8. ^{13}C NMR in CDCl$_3$: δ −6.28, 10.90, 22.38, 25.35, 32.91, 127.19, 133.27, 135.00. ^{29}Si NMR in CDCl$_3$: δ −41.41, −39.42.

We refluxed a mixture of hexyl(*m*-tolyl)dichlorosilane (5.0 g) and (*S*)-2-methylbutylphenyl dichlorosilane (1.5 g) by stirring it for 5 min in toluene with 1.1 g of sodium at 110 °C under Ar gas. We then crushed the sodium into small pieces. The solution also changed to bright purple. After adding 100 mL of toluene, we filtrated the solution using a 5 μm-pore PTFE disk under Ar gas. A small amount of isopropyl alcohol was carefully added to the filtrate and the precipitate that formed was isolated using a Kubota 5100 centrifuge at 4000 rpm for 30 min. After drying the precipitate at 100 °C overnight in a vacuum, we obtained purified **4** (0.04 g) as a white solid with a yield of 1%. The M_w value was 2.4×10^5, and M_w/M_n was 2.2. ^{13}C NMR in CDCl$_3$: δ 14.07, 20.74, 21.19, 22.49, 31.31, 32.11, 128.26, 130.44, 132.39, 132.62, 133.90, 137.95. ^{29}Si NMR in CDCl$_3$: δ −43.41, −41.42.

The (*S*)-2-methylbutylphenylsilylene content in **1** was almost the same as the feed ratio based on the peak ratio between Si−CH$_3$ from methylphenylsilylene and CH$_3$C*H-(C$_2$H$_5$)CH$_2$Si units from (*S*)-2-methylbutylphenyl-silylene units obtained by ^{1}H NMR (300 MHz, CDCl$_3$). The (*S*)-2-methylbutylphenylsilylene content in **2** was also almost the same as the feed ratio based on the peak ratio between C$_6$H$_{13}$Si from hexyl(m-tolyl)-silylene units and CH$_3$C*H(C$_2$H$_5$)CH$_2$Si units from (*S*)-2-methylbutylphenyl-silylene units obtained by ^{1}H NMR (300 MHz, CDCl$_3$). Table 1 shows M_w, M_n, and the polydispersity index of all the samples. All the samples had a large M_w of more than 10^5.

Results and Discussion

UV absorption, FL, and FLA spectra of optically inactive homopolymers **1** ($x = 0$) and **2** ($x = 0$) are shown in Figure 1, parts a and b, respectively. There are two bands around 280 and 320−360 nm in both absorption spectra. The latter absorption is due to their silicon backbone, while the former is due to their phenyl π−phenyl π^* transition. However, a comparison of the UV absorption, FL, and FLA spectra of **5** and **6** reveals great differences.

For **5**, the FL spectral profile with a full width at half-maximum (fwhm) of 30 nm is not a mirror image of the 340 nm absorption band, and the photoexcitation wavelength depends strongly on FLA around the 340 nm exciton band, ranging from 0.00 at 300 nm to 0.36 at 350 nm. By contrast, for **6**, the FL spectral profile with an fwhm of 15 nm is a mirror image of the 350 nm absorption band and the photoexcitation wavelength depends strongly on FLA around the 350 nm exciton band, ranging from 0.00 at 300 nm to 0.31 at 360 nm. These properties relate to the conformational structure. The polysilylene absorption spectra result from a convolution of various segmented chromophores with different excitation energies. Therefore, when segments with higher energy absorption are excited, the photoexcited $\epsilon-h$ pair migrates into segments with a lower energy absorption from which the emission occurs. Consequently, the mirror-image relation and narrower absorption show that the backbone conformation of **6** has a more regular spatial conformation than that of **5**. This may be consistent with the idea that **5** and **6** have a random-coil and stiff global conformation structures, respectively, in dilute solution from the ϵ (absorptivity)−α (viscosity index) and fwhm−α correlation revealed in our recent studies.[16]

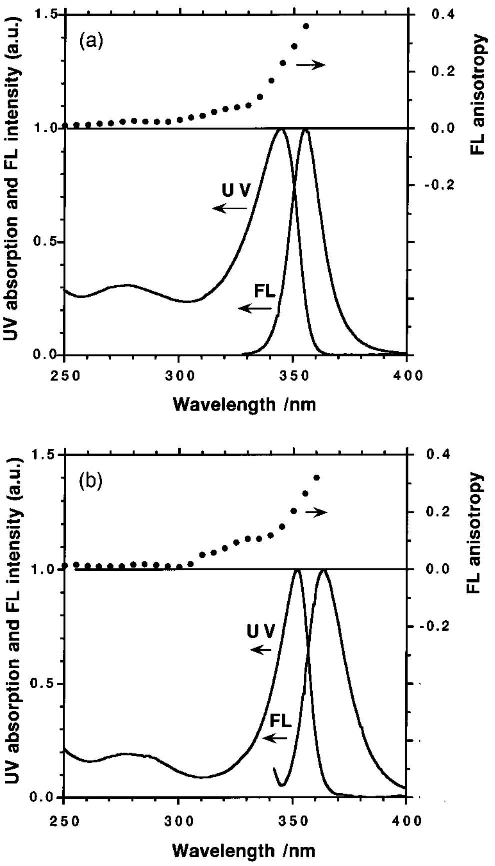

Figure 1. UV absorption, FL excited at 320 nm, and FLA spectra of (a) **5** and (b) **6** in dilute THF at 23−25 °C.

UV absorption and CD spectra of chiral−achiral copolymers **3** (**1** with $x = 0.25$) and **4** (**1** with $x = 0.20$) in THF at 23−25 °C are shown in Figure 2, parts a and b. The positive-sign CD spectral profile around 340 nm almost traces the corresponding 340 nm UV absorption profile for both copolymers. This is consistent with a local helical conformation of **3** and **4**. This is because, if **3** and **4** have an achiral, trans-planar conformation, no signal or a far smaller CD signal should be observed. If **3** and **4** have partly trans-planar moieties not responsible for a CD signal in the backbone, the CD band will not completely match the apparent UV band. All the spectral profiles for all the chiral molar composition

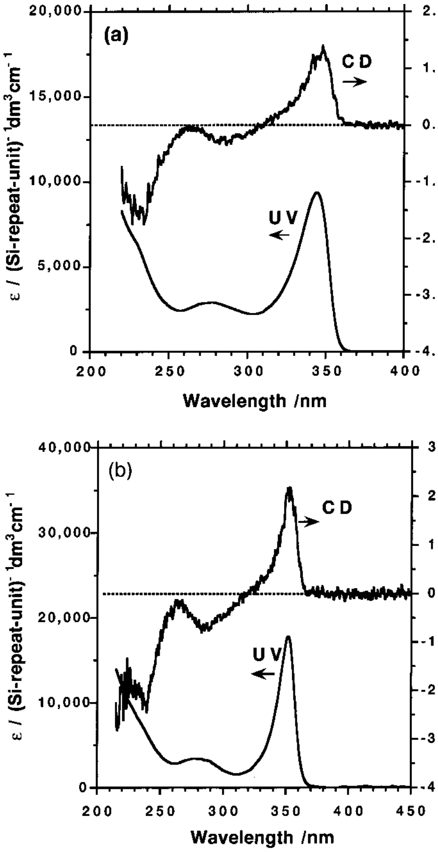

Figure 2. UV absorption and CD spectra of (a) **3** (**1** with $x = 0.25$) and (b) **4** (**1** with $x = 0.20$) in THF at 23–25 °C.

were almost identical except for the magnitude of the CD band. Therefore, this led to the idea that the local conformations of the optically active copolymers **1** and **2** have a helical structure with a preferential screw-sense for any incorporated chiral units composition, and therefore by extrapolation that even optically inactive **5** and **6** have a helical structure with no preferential screw-sense.

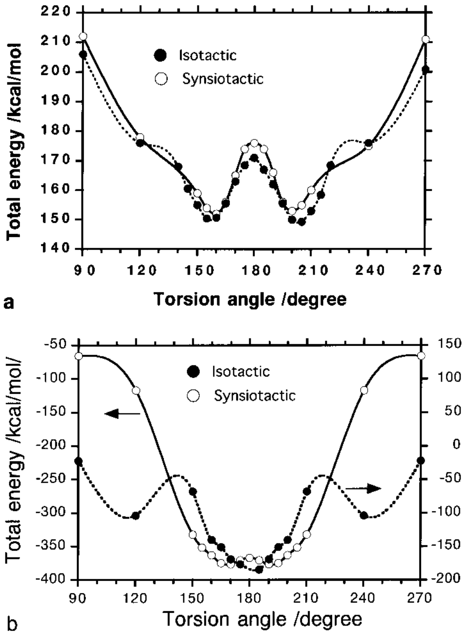

Figure 3. (a) Total energy of oligomers as a function of Si–Si–Si–Si torsion angle: **5** with 21 Si repeating units; (b) **7** with 31 Si repeating units.

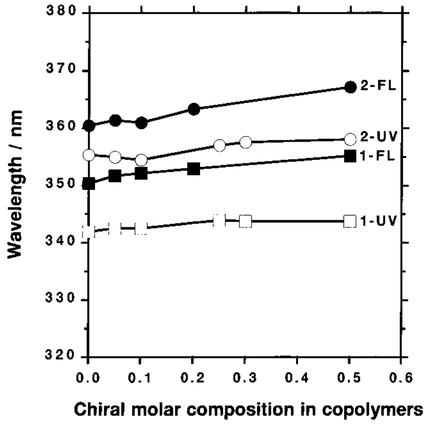

Figure 4. Peak wavelengths of UV absorption and FL spectra as a function of chiral molar composition in copolymers **1** and **2** with the UV peak absorption wavelengths due to the main chain of **1** (open squares) and **2** (closed squares) and FL peak wavelengths due to the main chain of **1** (open circles) and **2** (closed circles).

The idea that the most stable conformation of homopolymers **5** and **6** is helical is supported by a force-field calculation using Discover III with a PCFF force-field (MSI, ver 3.00). Figure 3a shows the total energy of **5** oligomer with 21 Si repeating units as a function of the Si–Si–Si–Si torsion angle. The respective *P* (plus, right-handed)- and *M* (minus, left-handed)-helical conformations of **5** near torsion angles of 160 and 200° are more stable than a trans-planar conformation of 180° regardless of the *it*- and *st*- configuration. The thermodynamic excess energy of the kinetic barrier between the *P*- and *M*-helical states reached 20–25 kcal/mol. We also calculated the total energy of the *n*-hexyl(phenyl)silylene (**7**) oligomer with 31 Si repeating units instead of **6** for simplicity. The conformations of **6** and **7** are almost the same because the UV-absorption and FL spectral profiles of **6** trace those of **7**. Figure 3b shows the total energy of **7** oligomer with 20-one Si repeating units as a function of the torsion angle. The respective *P*- and *M*-helical conformations of the *it*-configuration of **7** near 170 and 190° are more stable than a trans-planar conformation at 180° although the conformations of the *st*-configuration of **7** are stable near 180° for a trans-planar conformation. If we are aware that the total energy of the *st*-configuration is about 300 kcal/mol more unstable than that of the *it*-conformation at any torsion angle, actual **6** is likely to contain mainly *it* sequence rather than *st* sequence. These calculation results and considerations led to the idea that helical **5** and **6** are the most stable conformational structures regardless of optical inactivity.

To discuss the preferential screw sense capability qualitatively in a series of chiral–achiral helical **1** and **2** copolymers, we compared the UV and CD spectral characteristics of **1** and **2** as a function of the chiral molar composition in detail.

The chiral molar composition dependences of the peak wavelengths in the UV and FL spectra in **1** and **2** are shown in Figure 4. As the chiral molar composition changes from 0.00 to 0.50, these peak wavelengths are only slightly red-shifted: the UV and FL peak wavelengths of **1** change from 342 to 344 nm and from 350 to 355 nm, respectively, while the UV and FL peak wavelengths of **2** change from 356 to 358 nm and from 360 to 367 nm, respectively. As for the overall chiral

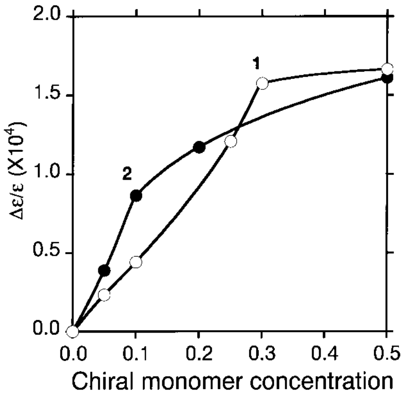

Figure 5. Dissymmetry ratio (g value) as a function of chiral molar composition in copolymers **1** (open circles) and **2** (closed circles).

compositions, there were no significant changes in either the UV and FL peak wavelengths or intensities. This means that the introduction of the chiral moiety causes an imbalance between the P- and M-screw-senses populations only in their helical main-chain but does not have a great effect on their global conformation and local main-chain helical structures.

Figure 5 shows Kuhn's dissymmetry ratios ($g = \Delta\epsilon/\epsilon$) in a series of **1** and **2** at CD−UV peak absorption wavelengths as a function of the chiral molar composition. It is already established that the g value in numbers of optically active polysilylenes[16,17,19−25] is very sensitive to changes in both helical pitch and a P- and M-helix population and the g value is more convenient for quantatively discussing the conformational changes than the $\Delta\epsilon$ value. This is because our recent studies have shown that both the ϵ and $\Delta\epsilon$ values depend greatly on the M_w of rigid rodlike helical polysilane homopolymers and copolymers with (S)-2-methylbutyl and long n-alkyl substituents.[24,25] Although the g value for either **1** or **2** increases nonlinearly as the molar composition of the chiral units increases, there is a significant difference in the relation between the g value and the chiral composition. The g value of **1** increases almost linearly as the chiral composition increases from zero to 30 mol %, and eventually converges at a chiral composition of 30 mol %. In contrast, the g value of **2** increases nonlinearly with a convex curveture as the chiral composition increases from zero to 50 mol %. Although poly[((S)-2-methylbutyl(phenyl)silylene] homopolymer (**8**) was not produced, probably because of a great steric demanding effect of (S)-2-methylbutyl moieties attached to main-chain, we consider these differences to originate from the chain stiffness and/or persistence length between **5** and **6**.

However, the introduction of (S)-2-methylbutyl substituents does not cause any great change in their global or local main chain conformations including the torsion angles, as discussed above. The population of P- and M-motifs, therefore, changes nonlinearly as regards the chiral unit composition. We may call these relations between g value and the chiral composition a positive cooperative effect ("a good sergeant − good soldiers effect") for preferential screw-sense helix induction, as already established in chiral−achiral poly(alkylisocyanate) copolymers.[8]

The g value in a series of rigid rodlike poly(dialkylsilylene)s with a single-screw-sense helix reaches about $+2.1 \times 10^{-4}$ at the UV peak absorption wavelength,[19,25] while that of poly[((S)-2-methylbutyl(phenyl)silylene)$_{0.30}$-*co*-(methyl(phenyl)silylene)$_{0.70}$] (**9**, **1** with $x = 0.30$) is slightly weak, 1.7×10^{-4} at the UV peak absorption. If we assume that the maximum value of poly(alkyl(aryl)-silylene) derivatives (**1**, **2**, and **8**) with a single-screw-sense (100% enantiopure P- or M-helix) is $+1.8 \times 10^{-4}$ by extrapolation, the introduction of a 30% chiral unit composition can strongly induce an approximately 90% helix giving a CD band with a positive sign and a 10% helix showing a CD band with a negative sign, which corresponds to an 80% diastereomeric excess for a helix with a positive CD band, into the overall main-chain structure of **8**.

We believe that if we were to obtain ideal, optically active poly(alkyl(aryl)silylene) homo- and copolymer systems that had stiffer main chain structures and longer persistence lengths, we would be able to clarify the relationship between the g value and the chiral molar composition.

The amplification magnitude of the polyisocyanate chirality allowed precise correlations with the cooperative models, which in turn has offered insight into how to manipulate the chiral amplification.[26] In the theory[26] of the cooperative helical order in polyisocyanates, the polymers are characterized by the chiral order parameter M, which is the fraction of the backbone twisting in one helical sense minus the fraction of the backbone twisting in the opposing sense. This order parameter is equal to the optical activity normalized by the value for an entirely one-handed helical polymer. This theory predicts

$$M = \tanh(\Delta G_h Lr/RT) \tag{1}$$

where ΔG_h, L, r, T are the helical reversal energy, the helical domain size, the polymer composition, and the temperature, respectively. Figure 6 shows the degree of preferential helical order as a function of chiral molar composition in (a) copolymers **1** and (b) copolymers **2**. The closed circles show the estimated % ee (enantiomeric excess) of the helix and the open circles are the % ee calculated using eq 1. Here, we normalized the g value in Figure 5, assuming the saturated value to be 1.8×10^{-4} by extrapolation. The data fit the function $a \tanh br$, where a is the saturated value and b is $\Delta G_h/RT$. The results are $b = 3.9$ and 3.6 for polymers **1** and **2**, respectively. Here, we were unable to estimate ΔG_h because we do not know the L value, which may be related to the persistence of the helical conformation against defects allowing change of handedness. The b value is much smaller than that of polyisocyanates, which show a sharp response to a small enantiometric excess.[27] Polysilylenes with larger L and ΔG_h values, obtained by modifying their substituents, may exhibit a sharp response to a small enantiometric excess.

Conclusions

We prepared two series of poly[((S)-2-methylbutyl-(phenyl)silylene)$_x$-*co*-(methyl(phenyl)silylene)$_{1-x}$] ($0 \le x \le 0.5$) (**1**) with a coiled main-chain structure and poly-[((S)-2-methylbutyl(phenyl)-silylene)$_x$-*co*-(n-hexyl(m-tolyl)-silylene)$_{1-x}$] ($0 \le x \le 0.5$) (**2**) with a stiffer main-chain conformation. Their UV and chiroptical properties in dilute THF at 23−25 °C were studied to clarify the relation between the conformation and optical activity. Unfortunately, poly[((S)-2-methylbutyl(phenyl)silylene)] homopolymer could not be formed, presumably due to steric overcrowding.

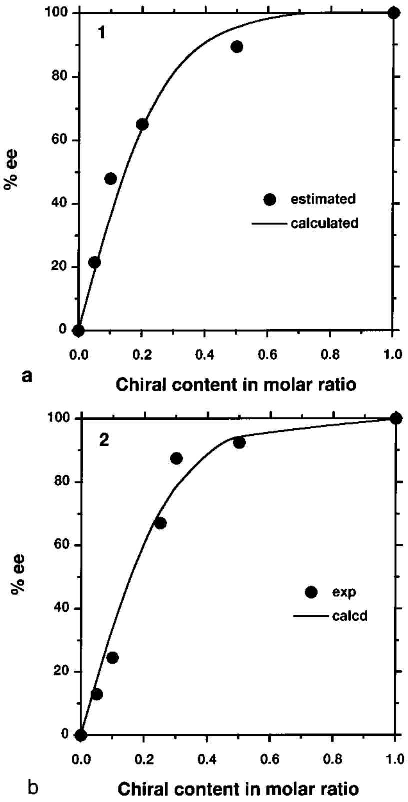

Figure 6. Degree of preferential helical order as a function of chiral molar composition in (a) copolymers **1** and (b) copolymers **2**. The closed circles are the estimated % ee (enantiomeric excess) of the helix and the open circles show the calculated % ee.

We concluded that either optically inactive ***1*** ($x = 0$) or ***2*** ($x = 0$) adopts a helical confomation with an equal quantity of P- and M-screw-senses. We proved this by means of UV, circular dichroism (CD), fluorescence (FL) spectral measurements, as well as force field calculation. We found that there was a marked "positive" cooperative induction effect of the preferential screw-sense in **1** and **2** copolymer systems, as the (S)-2-methylbutyl(phenyl)–silylene silylene moieties increased, on the basis of an analysis of the dissymmetry ratio ($g = \Delta\epsilon/\epsilon$), rather than the $\Delta\epsilon$ value or optical rotation. The "positive" cooperative effect refers to the fact that a preferential screw-sense is positively biased by chiral moieties incorporated in the copolymer main-chain. However, there is a marked difference in the helical cooperation between **1** and **2**, probably because of the differences in their global and local conformations. For **1**, the g value of **1** changed linearly up to 30 mol % chiral and became constant at the chiral composition, inducing an approximately 80% diastereomeric (pseudo-enantiomeric) purity of a single-screw-sense helix. In contrast, the g value of **2** was positively biased by the chiral moiety with a concave curvature, leading to a similar diastereomeric purity at a chiral composition of 50 mol %. This difference can be related to the persistence of the helical conformation against defects allowing change of handedness as seen originally in the work of the Italian school on isotactic vinyl polymers and later in the polyisocyanates.[17]

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