Ferrocene-Containing Optically Active Liquid-Crystalline Side-Chain Polysiloxanes with Planar Chirality**

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Optically active liquid-crystalline side-chain polysiloxanes have been prepared by grafting planar chiral ferrocene-based vinyl monomers onto commercially available polyhydrosiloxane. Two ferrocene monomers have been synthesized: a linear-type monomer, which displays a monotropic chiral smectic C (S_{C*}) phase and enantiotropic smectic A (S_A) and chiral N (N*) phases, and a laterally branched monomer, which shows an enantiotropic N* phase. X-ray diffraction analysis indicates a mono-molecular organization of the monomeric units within the smectic layers. The polymers retain the liquid-crystalline phases of their corresponding monomers. The UV-vis and circular dichroism (CD) spectra are in agreement with the structure of the monomers and polymers. The molar absorption coefficient (ε) and molar circular dichroic absorption coefficient ($\Delta\varepsilon$) values of the polymers are proportional to the number of monomeric units grafted onto them. The absolute configuration of the ferrocene carboxylic acid intermediate, used to synthesize the monomers, has been determined on the basis of CD spectra. The helical twisting power (HTP) of the nematogenic monomer and polymer have been determined in E7, and indicate that such materials could be used as chiral dopants. Finally, this study demonstrates that the nature of chiral phases can be controlled by structural engineering of the organic groups only, with ferrocene acting as the source of chirality.

1. Introduction

Planar chiral ferrocenes[1,2a] have found fascinating applications as 1) monomeric-[1d,e,3] or dendritic-type[4] catalysts in asymmetric synthesis; 2) materials with nonlinear optical properties;[5] 3) optically active dendrimers;[6] and 4) redox-active polymers.[7] Planar chirality has opened up novel opportunities for ferrocene, which can play the role of a multifunctional unit by combining a three-dimensional structure (which offers mul-

tiple possibilities for the preparation of derivatives) with unique electrochemical and chiroptical properties.

On the other hand, ferrocene-containing liquid crystals represent a well-established family of metallomesogens.[8,9] Following the first report by Malthête and Billard in 1976,[10] sustained synthetic efforts led to an interesting variety of liquid-crystalline ferrocenes, such as mono-,[10,11] di-[12,13] and trisubstituted[14] ferrocenes, ferrocenophanes,[15] ferrocene-containing main-chain[16] and side-chain[17,18] polymers, ferrocene-containing dendrimers,[19] ferrocenium derivatives,[20] polycatenar ferrocenes,[21,22] hydrogen-bonded ferrocenes,[21,23] and ferrocene-fullerene dyads.[24] These materials exhibit a rich mesomorphism that includes the nematic (N), smectic, columnar, and cubic phases.

Optically active ferrocene-containing liquid crystals are much less explored. Two optically active monosubstituted ferrocenes containing an asymmetric center located in the organic substituent have been reported. In the first example (source of chirality: (S)-ethyl lactate),[25] a chiral smectic C (S_{C*}) phase was observed and, in the second one (source of chirality: (S)-2-methylbutan-1-ol),[26] S_{C*}, smectic A (S_A), twist grain boundary A (TGBA), blue, and chiral N (N*) phases were obtained.

With the view to design new functional materials, we used a planar chiral ferrocene to elaborate ferroelectric liquid crystals.[27] Ferrocene was functionalized at positions 1 and 3 with two different organic substituents. This chemical was obtained with an enantiomeric excess of 98 %; S_{C*} and S_A phases were observed, and a spontaneous polarization of 2.8 nC cm^{-2} was determined. A weak spontaneous polarization (Ps) value was obtained due to the fact that the two arms attached to the fer-

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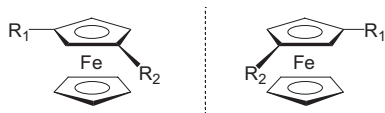E-mail: guillon@ipcms.u-strasbg.fr
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rocene were not greatly different in length or polarity. It is important to note that planar chirality was rarely used to prepare optically active liquid-crystalline materials: only butadiene-tricarbonyliron complexes (S_{C*} and N* phases)[28] and [2.2]paracyclophane derivatives (S_{C*}, S_A, and N* phases)[29] were reported in addition to our ferrocene compound.
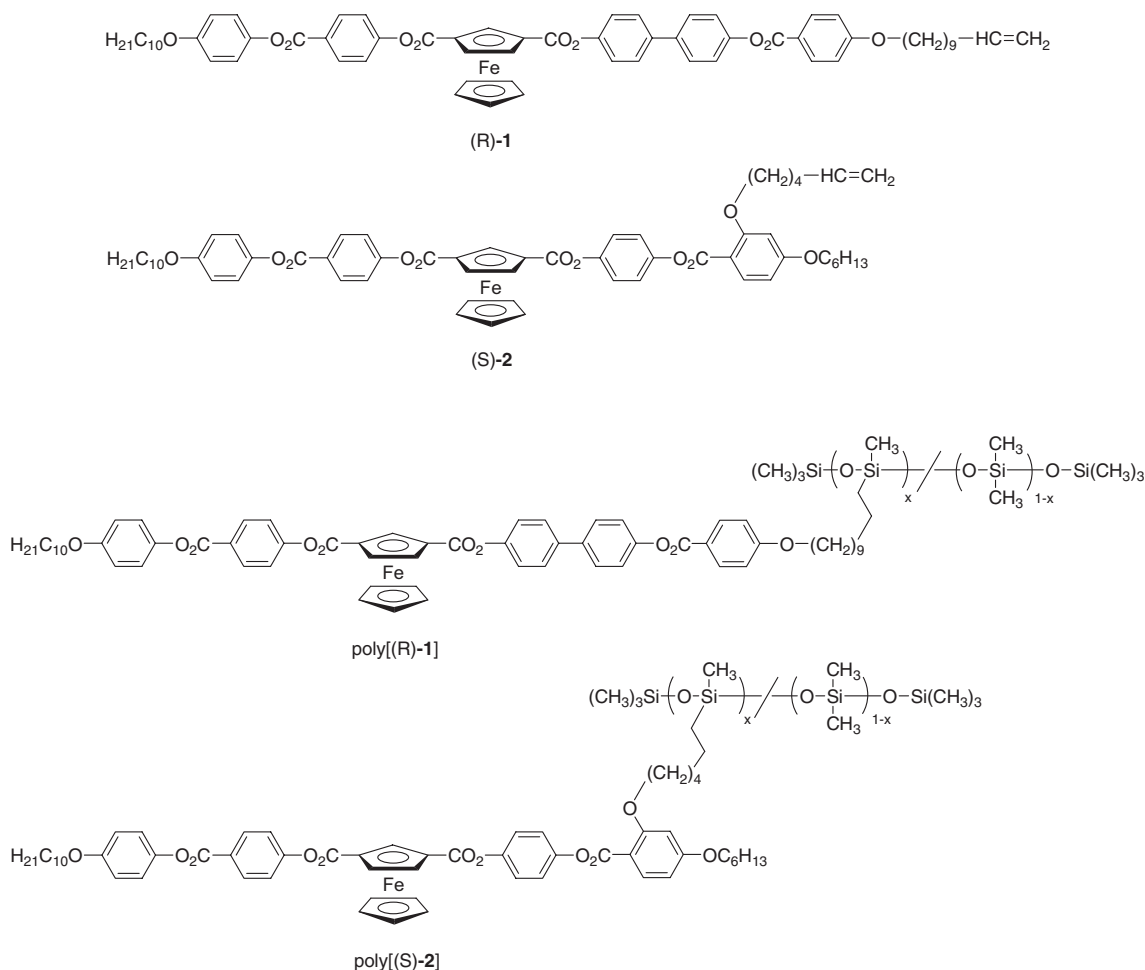
Planar chiral 1,3-disubstituted ferrocenes (Fig. 1) appear as valuable building blocks for the preparation of optically active polymers. The chirality would be located on the ferrocene unit, and the polymerizable group would be located in one (for side-chain polymers) or both (for main-chain polymers) organic fragments connected to ferrocene. Tuning of the liquid-crystalline

properties of the monomers and polymers could be achieved by structural modifications of the organic part only. This concept is appealing since the modification of the organic motifs would not alter the chirality at the ferrocene. Finally, among the disubstituted ferrocene derivatives, the 1,3-substitution pattern led to the materials having the highest molecular anisotropy and, consequently, to the highest liquid crystal tendency.[8,9]

In this paper, we report the synthesis, characterization, and liquid-crystalline properties of optically active planar chiral ferrocene-containing vinyl monomers (R)-**1** and (S)-**2** and of their corresponding side-chain polysiloxanes, poly[(R)-**1**] and poly[(S)-**2**]. The polymers were obtained by grafting the monomers onto commercially available polyhydrosiloxane. The structures of the monomers were chosen in order to generate either S_{C*} (from the linear-type monomer) or N* (from the laterally branched monomer) phases. A polyhydrosiloxane with a low content of SiH units (15–18 %) was used to avoid decomposition of the polymers at elevated temperatures. Indeed, we observed that the clearing temperature increased with the content of the ferrocenyl monomers.[18] The absolute configuration of acid intermediate (R)-**3** was established on the basis of circular dichroism (CD) spectra.

Figure 1. Planar chiral 1,3-disubstituted ferrocene derivatives ($R_1 \neq R_2$). Planar chirality: chirality resulting from the arrangement of out-of-plane groups with respect to a reference plane, called the "chiral plane" [30]. The configuration of the 1,3-disubstituted ferrocenes described in this paper is assigned by applying the planar nomenclature; see [26].


(R)-**1**

(S)-**2**

poly[(R)-**1**]

poly[(S)-**2**]

2. Results and Discussion

2.1. Synthesis of the Monomers

The synthesis of the monomers (R)-**1** and (S)-**2** is described in Scheme 1. Treatment of acid derivative (R)-**3** with oxalyl chloride in the presence of pyridine led to the corresponding acid chloride, which was reacted with phenol derivative **4** to give monomer (R)-**1**. Reaction of (R)-**3** with phenol intermediate **5** in the presence of N,N′-dicyclohexylcarbodiimide (DCC), 4-di-methylaminopyridinium p-toluenesulfonate (DPTS), and 4-pyr-rolidinopyridine (4-PPy) gave monomer (S)-**2**. The monomers were purified by column chromatography. Their purity and structure were confirmed by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. We have already reported the preparation of (R)-**3** (enantiomeric excess: 98 %), but its absolute configuration was not known.[27] The latter was established during this study on the basis of CD spectra (see Sec. 2.4), as crystals suitable for X-ray crystallography were not obtained. The syntheses of **4** and **5** are described in the Supporting Information.

2.2. Synthesis of the Polymers

Polymers poly[(R)-**1**] and poly[(S)-**2**] were prepared by grafting either (R)-**1** or (S)-**2** onto commercially available polyhydrosiloxane **6** (Hüls America Inc.; x = 15–18 %, 1 − x = 82–85 %, molecular weight = 2000–2500 g mol^{-1}) in the presence of [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane] adapting a literature procedure[31] (Scheme 2). The reaction was followed by ^{1}H NMR spectroscopy. Disappearance of the Si-H signal at 4.7 ppm indicated that the reaction occurred to completion, i.e., four (molecular weight = 2000 g mol^{-1}, x = 15 %) to six (molecular weight = 2500 g mol^{-1}, x = 18 %) monomers were
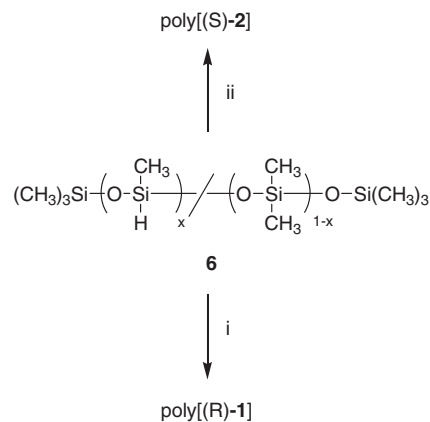
Scheme 2. i) [Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane], toluene, 70 °C, 72 h, 48 %; ii) [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane], toluene, 70 °C, 48 h, 66 %.

grafted onto the polymer. The crude polymers were purified by size-exclusion chromatography (SEC). The structure and purity of poly[(R)-**1**] and poly[(S)-**2**] were confirmed by ^{1}H NMR spectroscopy and gel-permeation chromatography (GPC). In agreement with previous studies,[18d] the calculated molecular weights are smaller than those determined by GPC (Table 1). The discrepancy arises from the fact that polystyrene standards were used to calibrate the GPC columns.

UV-vis spectra with absorption bands at 360 and 460 nm were obtained for both monomers and polymers (Figs. 2,3). CD spectra (Figs. 4,5) exhibit absorption bands in agreement with the UV-vis spectra (compare Figs. 2,4 with Figs. 3,5). The molar absorption coefficient (ε) and molar circular dichroic absorption coefficient (Δε) values of the polymers are proportional to the number of monomeric units grafted onto the polymer.
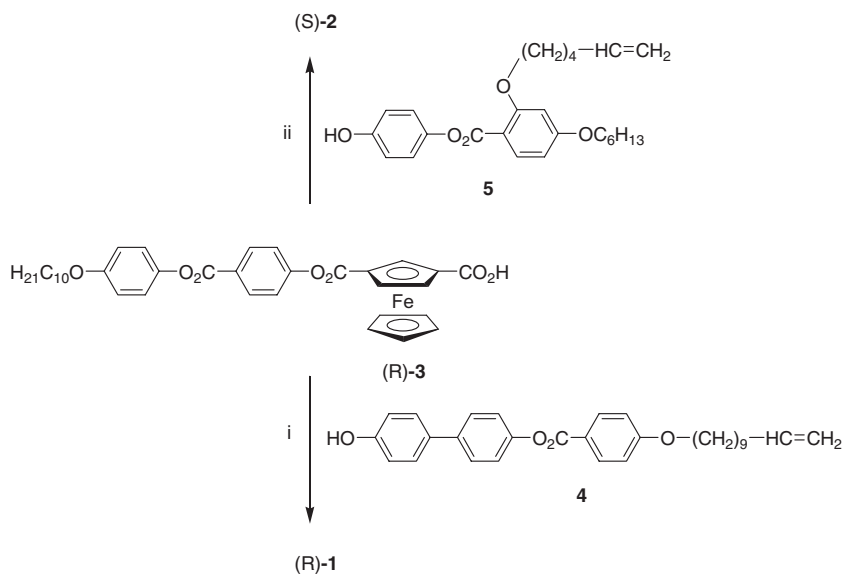

Scheme 1. i) Oxalyl chloride, pyridine, CH$_2$Cl$_2$, reflux, 7 h; Et$_3$N, CH$_2$Cl$_2$, reflux, 18 h, 50 %; ii) N,N′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridinium toluene-p-sulfonate (DPTS), 4-pyrrolidinopyridine (4-PPy), CH$_2$Cl$_2$, room temperature, 18 h, 90 %.

Table 1. Molecular weights and molecular-weight distributions of poly[(*R*)-**1**] and poly[(*S*)-**2**]. M_w: weight-average molecular weight; M_n: number-average molecular weight.

| Polymer	Molecular weight of starting polysiloxane [a] [g mol^{-1}]	Calculated molecular weight [g mol^{-1}]	M_w [b] [g mol^{-1}]	M_n [b] [g mol^{-1}]	M_w/M_n
Poly[(*R*)-**1**]	2000–2500	6300–8900	27 700	20 300	1.4
			27 800	20 600	1.3
Poly[(*S*)-**2**]	2000–2500	6100–8600	19 100	12 100	1.6
			19 000	12 100	1.6

[a] Given by the supplier. [b] Data obtained by GPC (top line: UV detector; bottom line: differential refractive index detector).
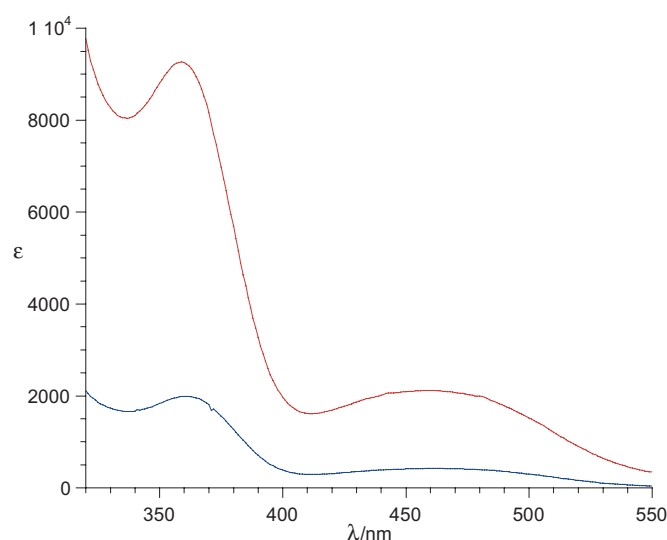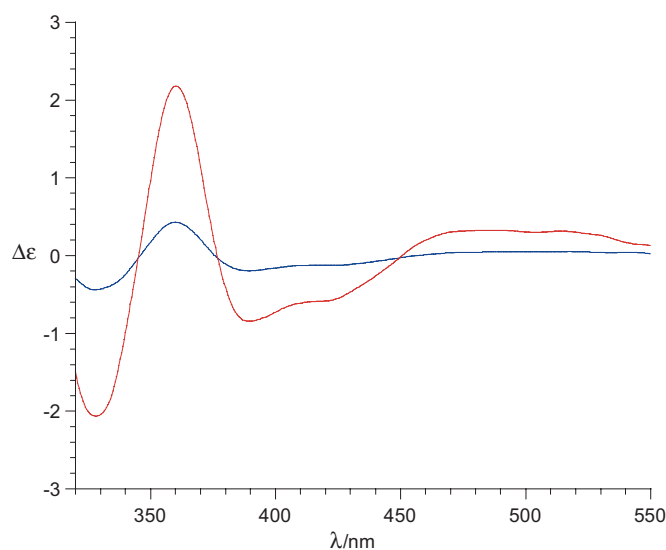

Figure 2. UV-vis spectra of (*R*)-**1** (blue) and poly[(*R*)-**1**] (red) in CH$_2$Cl$_2$; λ: wavelength.
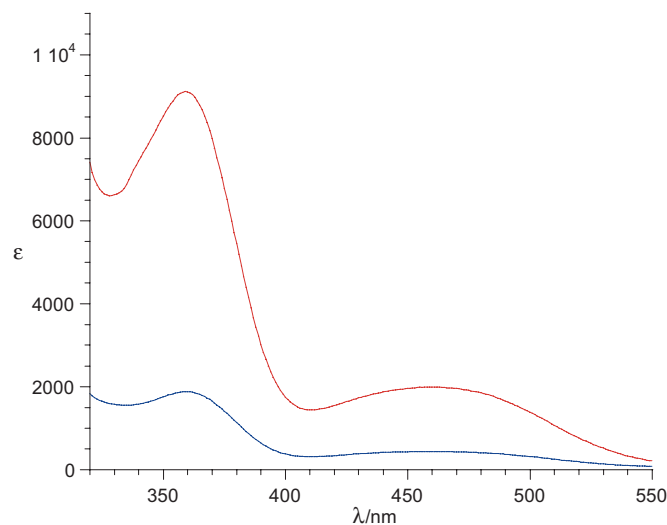
Figure 3. UV-vis spectra of (*S*)-**2** (blue) and poly[(*S*)-**2**] (red) in CH$_2$Cl$_2$.
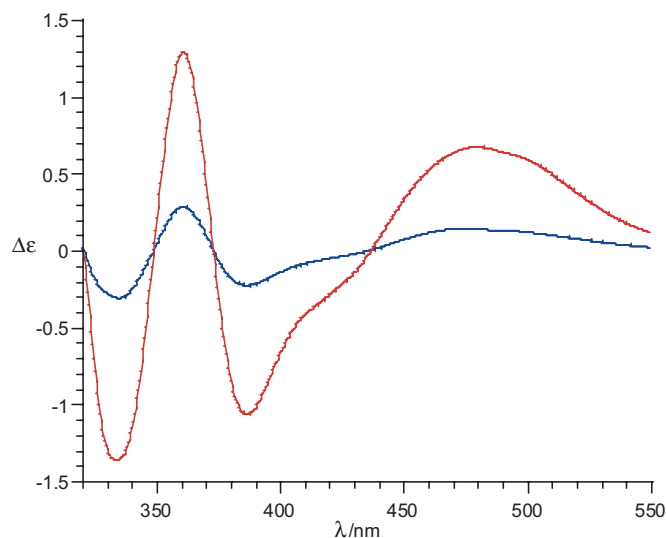
Figure 4. CD spectra of (*R*)-**1** (blue) and poly[(*R*)-**1**] (red) in CH$_2$Cl$_2$.

Figure 5. CD spectra of (*S*)-**2** (blue) and poly[(*S*)-**2**] (red) in CH$_2$Cl$_2$.

2.3. Mesomorphic Properties

Monomer (*R*)-**1** showed enantiotropic S$_A$ and N* phases and a monotropic S$_{C*}$ phase (Table 2). The S$_{C*}$-to-S$_A$ phase transition was not detected by differential scanning calorimetry (DSC) but was clearly identified by polarized optical microscopy (POM). This behavior was in agreement with a second-order phase transition. Monomer (*S*)-**2** displayed an N* phase (Table 2). The mesomorphic properties of (*R*)-**1** and (*S*)-**2** are in agreement with their structure: linear-type mesogens give rise to smectic phases, whereas laterally branched mesogens tend to exhibit nematogenic behavior.[32]

Table 2. Phase-transition temperatures and enthalpies (ΔH) of (*R*)-**1** and (*S*)-**2**.

Monomer	Transition [a]	Temperature [°C]	ΔH [kJ·mol^{-1}]
(*R*)-**1**	Cr → S$_A$	175 [b]	29.2
	(S$_{C*}$ → S$_A$) [c,d]	171	–
	S$_A$ → N*	274 [b]	2.1
	N* → I	278 [b]	2.3
(*S*)-**2**	Cr → N*	115 [b]	3.0
	N* → I	120	0.7

[a] Cr: crystalline phase; S$_{C*}$: chiral smectic C phase; S$_A$: smectic A phase; N*: chiral nematic phase; I: isotropic liquid. [b] Determined during the first heating run. [c] Determined by polarized optical microscopy (POM). [d] Monotropic transition.

Polymers poly[(*R*)-**1**] and poly[(*S*)-**2**] displayed liquid-crystalline behavior (Table 3). For poly[(*R*)-**1**], melting and clearing points were clearly identified by POM and DSC. On heating, poly[(*S*)-**2**] gave a series of broad transitions between

Table 3. Phase-transition temperatures and enthalpies of poly[(*R*)-**1**] and poly[(*S*)-**2**].

| Polymer	Transition [a]	Temperature [°C]	ΔH [kJ·mol^{-1}]
Poly[(*R*)-**1**]	T_m	171 [b]	9.8
	T_c	302 [b]	6.7
Poly[(*S*)-**2**]	T_m	82 [c]	11.6
	T_c	94 [c]	0.22

[a] T_m = melting point; T_c = clearing point. [b] Determined during the first heating run. [c] Monotropic transition determined during the first cooling run.

100 and 115 °C, which corresponded to melting and cold crystallization processes; poly[(*S*)-**2**] displayed a monotropic mesomorphic behavior. When poly[(*R*)-**1**] and poly[(*S*)-**2**] were cooled very slowly from the isotropic liquid, small focal conics and fingerprints were observed for poly[(*R*)-**1**] and poly[(*S*)-**2**], respectively. Those textures indicated the formation of smectic phases for poly[(*R*)-**1**] and an N* phase for poly[(*S*)-**2**]. Therefore, the polymers retained the type of liquid-crystalline phases displayed by their respective monomers, and their thermal and liquid-crystalline properties are in agreement with the structure of their pendant motifs (poly[(*R*)-**1**]: linear-type mesogens; poly[(*S*)-**2**]: laterally branched mesogens).[32]

Racemic monomer (*R*,*S*)-**1** (Cr → S$_C$: 169 °C; S$_C$ → S$_A$: 171 °C; S$_A$ → N: 274 °C; N → I: 278 °C; from first heating run) and polymer poly[(*R*,*S*)-**1**] (T_m: 150 °C, T_c: 290 °C from first heating run) were synthesized (see Experimental) for comparison purposes. Racemic and optically active monomers gave identical S$_C$(or S$_{C*}$)-to-S$_A$, S$_A$-to-N(or N*) and N(or N*)-to-isotropic-liquid transition temperatures. A difference was observed for their melting point resulting in the formation of an enantiotropic S$_C$ and a monotropic S$_{C*}$ phase for (*R*,*S*)-**1** and (*R*)-**1**, respectively. In the case of the polymers, poly[(*R*)-**1**] showed a higher clearing point (T_c = 302 °C) than poly[(*R*,*S*)-**1**] (T_c = 290 °C). This result could be due to the fact that different molecular-weight distributions were obtained for both poly-

mers (M_w/M_n = 1.3–1.4 for poly[(*R*)-**1**]; M_w/M_n = 1.6–1.7 for poly[(*R*,*S*)-**1**]). However, we cannot exclude that, in the optically active polymer, the presence of only one enantiomer led to stronger intermolecular interactions than in the racemic polymer.

Further information of the structure of the liquid-crystalline phases exhibited by (*R*,*S*)-**1** and poly[(*R*,*S*)-**1**] were obtained by X-ray diffraction (XRD). For the monomer, a *d*-layer spacing of 56 Å was obtained at 200 °C, i.e., in the S$_A$ phase. This value was compared to the molecular length, *L*, in the fully extended conformation (60 Å). A *d/L* ratio of 0.93 was calculated, suggesting a monomolecular organization of the monomeric units within the smectic layers. For the polymer, the *d*-layer spacing was determined as a function of temperature (Fig. 6). The variation of the layer thickness showed two regimes typical of smectic C and smectic A phases. A *d*-spacing value of about 71 Å was obtained at 240 °C. The increase of the *d*-spacing value on going from the monomer to the polymer
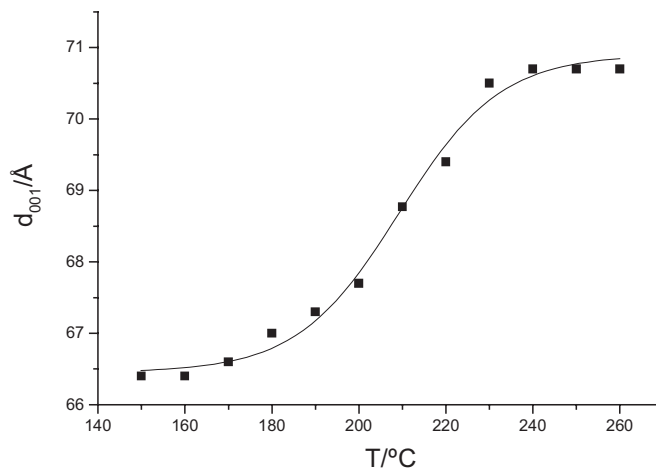
Figure 6. Variation of the *d*-layer spacing as a function of temperature (*T*) for poly[(*R*,*S*)-**1**].

is due to the polymer chain, the presence of which at the interface between the smectic lamellae makes the layer thickness larger. Similar supramolecular organization should be obtained for optically-active (*R*)-**1** and poly[(*R*)-**1**]. The XRD data supported the POM observations. Because of lack of materials, no XRD experiments were carried out with the optically active monomer and polymer.

2.4. Absolute Configuration of (*R*)-3

The absolute configuration of **3** was determined using CD spectroscopy. A CD spectrum of an enantio-enriched sample (enantiomeric excess = 98 %) was measured at room temperature (298 K) in dichloromethane (concentration, $c = 1.46 \times 10^{-3}$ mol L^{-1}, $\Delta\varepsilon$ = +0.99 L mol^{-1} cm^{-1} at 360 nm). A transmission cell equipped with quartz windows and a path length of 1 cm was used. CD spectra of **3** were calculated

using time-dependent density functional theory (TD-DFT).[33] Calculations were performed using the GAUSSIAN03[34] suite of programs with the b3pw91 hybrid density functional.[35] For H, C, and O, a split valence basis set was used,[36] whereas for Fe the Hay–Wadt pseudopotential was applied.[37] Spin-restricted DFT calculations were performed for **3**. A similar strategy was recently reported to yield good predictions of the properties of ferrocene-containing molecules.[38]

Compound **3** can adopt several conformations. In particular, we considered the conformation at the carboxylic acid group, the conformation at the two ester groups, and the conformation at the ether group. The conformation of the alkyl moiety was assumed to be all-trans, which is, however, expected to be of minor importance, since it is far away from the chiral chromophore. Considering the degrees of freedom mentioned above results in a total of $4^2 = 16$ conformers. The structures of all these conformers were first optimized without any restriction. The resulting structures are shown in the Supporting Information. Rotational strengths were then calculated for all conformers using TD-DFT. In order to compare with experiment, a synthetic spectrum was generated using Gaussians with a full width at half maximum of 35 nm centered at the excitation energies and scaled with the calculated rotational strengths.[39] The calculated spectrum was blue-shifted by 0.15 eV in order to compare with experiment.[33] The reliability of the method was checked by comparison with reported experimental and calculated CD spectra of pentahelicene[33] and $[Ru(bipy)_3]^{2+}$ (bipy: 2,2′-bipyridine).[40]

The calculations revealed that all 16 considered conformers of **3** were within about only 0.8 kcal mol⁻¹. Inclusion of solvent effects by applying a polarizable continuum model[41] for dichloromethane had only a little effect on the relative stability of the conformers, which changed by 0.3 kcal mol⁻¹ at most (the relative energies are given in the Supporting Information). Therefore, several conformers contribute to the experimental spectrum. In order to compare with experiment, the calculated spectra of the 16 conformers were averaged. Three different methods were applied, and the results are shown in Figure 7. First, the arithmetic average of all the spectra corresponding to the 16 conformers was calculated. Second, the spectra were weighted by their respective gas-phase Boltzmann factors ($T = 298$ K). Third, the Boltzmann factors derived from the solvent calculations were used ($T = 298$ K). Figure 7 shows that the choice of the average changes the general appearance of the CD spectrum only slightly.

The calculated and experimental CD spectra compared sufficiently well for an assignment of the absolute configuration. Since the calculations were performed on (*R*)-**3**, the results in Figure 7 show that the absolute configuration of the enantiomer used for the experiment was *R*.

2.5. Helical Twisting Power of Monomer (*S*)-2 and Polymer Poly[(*S*)-2]

With respect to possible applications as new types of chiral dopants for display applications, the helical twisting power
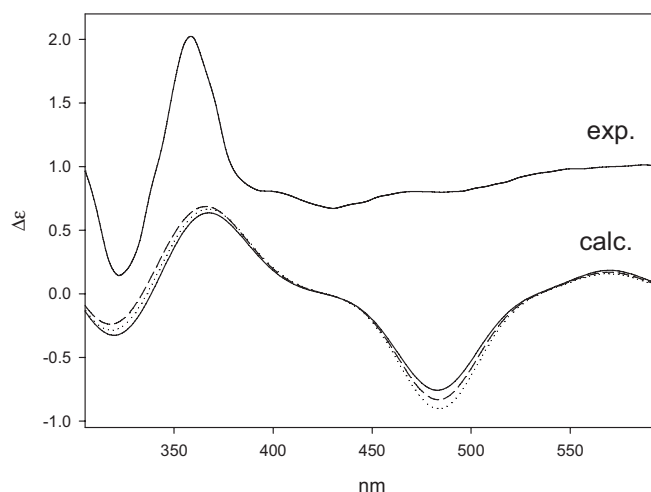
Figure 7. Experimental (top) and calculated (bottom) CD spectra of acid **3**. The three calculated spectra represent different averages of the CD spectra of the individual conformers (see text for details). Dotted line: arithmetic average; solid line: Boltzmann average; dashed line: Boltzmann average including solvent effect. The experimental spectrum has been shifted for clarity.

(HTP) of (*S*)-**2** and poly[(*S*)-**2**] were investigated in a Grandjean–Cano wedge.[42] As a nematic host, E7 (Merck) was used. The protocol followed to determine the HTP values is described in the Supporting Information.

The solubility of both materials in E7 was poor, and the prepared mixtures contained about 1 % of either (*S*)-**2** or poly[(*S*)-**2**]. Both materials induced a helix in nematic E7. Regular disclination lines became visible shortly after filling the Grandjean–Cano cells and after relaxation of the texture. Disclination lines separated regions with a different number of half pitches according to the local thickness in the Grandjean–Cano wedge. For (*S*)-**2** (1.06 % mixture, 40 μm pitch) and poly[(*S*)-**2**] (1.06 % mixture, 60 μm pitch), HTP values of 2.4 and 1.6 μm⁻¹, respectively, were obtained. These values are rather small in comparison with commercially available chiral dopants that reach values of –11 μm⁻¹ (S811 from Merck), but are in agreement with the structures of (*S*)-**2** and poly[(*S*)-**2**], in which the ferrocene unit is functionalized by two substituents with similar length and polarity. Improvement of the solubility and attachment of very different arms to ferrocene should lead to higher HTP values.

3. Conclusion

A planar chiral ferrocene synthon was used to synthesize mesomorphic monomers and side-chain polymers, which showed chiral liquid-crystalline phases. The S_{C*} (linear-type monomer) and N* (laterally branched monomer) phases were generated by derivatizing the ferrocene unit with appropriate organic motifs. The polymers were found to be thermally stable and soluble in common organic solvents. Despite the small number of monomeric units grafted onto the polymers, the latter dis-

played clear mesomorphism. This result is the consequence of the structural anisotropy of 1,3-disubstituted ferrocene derivatives. Finally, planar chirality was shown to be a valuable means for the development of optically active liquid-crystalline materials based on ferrocene, such as ferroelectric materials[27] or chiral dopants (this work).

4. Experimental

General: See Supporting Information.

Abbreviations: N,N'-dicyclohexylcarbodiimide = DCC; 4-pyrrolidino-pyridine = 4-PPy; 4-(dimethylamino)pyridinium toluene-p-sulfonate = DPTS; column chromatography = CC; size exclusion chromatography = SEC; circular dichroism = CD; electrospray ionization = ESI; atmospheric pressure chemical ionization = APCI; broad = br.

Monomer (R)-1: To a solution of (R)-3 (442 mg, 0.71 mmol) in CH$_2$Cl$_2$ (70 mL) were added oxalyl chloride (1.43 g, 11.3 mmol) and pyridine (111 mg, 1.40 mmol). The mixture was stirred under reflux for 7 h and evaporated to dryness. The black residue was extracted with petroleum ether and dried to give the acid chloride which was used without further purification. To a solution of the latter (0.71 mmol, based on (R)-3) in CH$_2$Cl$_2$ (100 mL) were added 4 (356 mg, 0.78 mmol) and triethylamine (71 mg, 0.70 mmol). The mixture was stirred under reflux for 18 h and evaporated to dryness. Purification of the residue by CC (CH$_2$Cl$_2$, then CH$_2$Cl$_2$/AcOEt 95:5) gave pure (R)-1 (380 mg, 50 %). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 8.28 (d, 2 arom. H), 8.15 (d, 2 arom. H), 7.70 (d, 2 arom. H), 7.68 (d, 2 arom. H), 7.38 (d, 2 arom. H), 7.31 (d, 4 arom. H), 7.13 (d, 2 arom. H), 7.01 (d, 2 arom. H), 6.95 (d, 2 arom. H), 5.88–5.78 (m, 1H, C*H*=CH$_2$), 5.79 (t, 1H, Cp), 5.30–5.27 (m, 2H, Cp), 5.03–4.91 (m, 2H, CH=C*H*$_2$), 4.51 (s, 5H, Cp), 4.07 (t, 2H, CH$_2$O), 3.98 (t, 2H, CH$_2$O), 2.08–2.03 (m, 2H, C*H*$_2$CH=CH$_2$), 1.86–1.76 (m, 4H, C*H*$_2$CH$_2$O), 1.48–1.30 (m, 26H, CH$_2$), 0.89 (t, 3H, CH$_3$). UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}), CH$_2$Cl$_2$): 360 (1990), 460 (420). CD (λ_{max} in nm ($\Delta\varepsilon$ in L mol^{-1} cm^{-1}), CH$_2$Cl$_2$): 360 (+0.28). Anal. calcd. for C$_{65}$H$_{70}$O$_{10}$Fe (1067.11): C, 73.16; H, 6.61 %. Found: C, 73.27; H, 6.82 %.

Monomer (R,S)-1: Monomer (R,S)-1 was prepared by following the above synthetic procedure from (R,S)-3 [14] (yield: 78 %). Selected analytical data: ESI mass spectrometry (MS): m/z: 1090 $[M+Na]^+$. UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}), CH$_2$Cl$_2$): 360 (1900), 460 (410). Anal. calcd. for C$_{65}$H$_{70}$O$_{10}$Fe (1067.11): C, 73.16; H, 6.61 %. Found: C, 73.21; H, 6.72 %.

Polymer Poly[(R)-1]: A solution of (R)-1 (204 mg, 0.191 mmol), 6 (57 mg, 0.025 mmol, calculated with an average molecular weight of 2250), and [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane] (4 mg, 0.001 mmol, in xylenes) in toluene (20 mL) was stirred at 70 °C for 3 days, cooled to room temperature, and evaporated to dryness. Purification of the solid residue by SEC (CH$_2$Cl$_2$) gave poly[(R)-1] (92 mg, 48 %, calculated with an average molecular weight of 7600). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.29 (d, 2 arom. H), 8.16 (d, 2 arom. H), 7.63 (br, 4 arom. H), 7.35 (d, 2 arom. H), 7.26 (br, 4 arom. H), 7.13 (d, 2 arom. H), 6.95–6.93 (br, 4 arom. H), 5.82 (br, 1H, Cp), 5.30–5.27 (br, 2H, Cp), 4.50 (s, 5H, Cp), 4.04 (br, 2H, CH$_2$O), 3.97 (t, 2H, CH$_2$O), 1.81–1.80 (m, 4H, C*H*$_2$CH$_2$O), 1.47–1.29 (m, 30H, CH$_2$), 0.89 (br, 3H, CH$_3$), 0.52 (br, 2H, SiCH$_2$), 0.08 (s, SiCH$_3$). UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}, calculated with an average molecular weight of 7600 g mol^{-1}), CH$_2$Cl$_2$): 360 (9600), 460 (2190). CD (λ_{max} in nm ($\Delta\varepsilon$ in L mol^{-1} cm^{-1}, calculated with an average molecular weight of 7600), CH$_2$Cl$_2$): 360 (+1.3).

Polymer Poly[(R,S)-1]: This polymer was prepared by following the above synthetic procedure from (R,S)-1 (yield: 45 %). Selected analytical data: GPC: M_w = 39 000 g mol^{-1}, M_n = 23 600 g mol^{-1}, M_w/M_n: 1.7 (UV detector); M_w: 37 000 g mol^{-1}, M_n = 23 600 g mol^{-1}, M_w/M_n: 1.6 (differential refractive index detector). UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}, calculated with an average molecular weight of 7600 g mol^{-1}), CH$_2$Cl$_2$): 360 (8700), 460 (1900).

Monomer (S)-2: To a mixture of (R)-3 (372 mg, 0.58 mmol) in CH$_2$Cl$_2$ (100 mL) were added DCC (243 mg, 1.18 mmol), DPTS (173 mg, 0.59 mmol), 4-PPy (spatula tip), and 5 (294 mg, 0.71 mmol). The mixture was stirred at room temperature for 18 h and evaporated to dryness. Purification of the solid residue by CC (CH$_2$Cl$_2$/heptane 90:10, then 95:5) gave pure (S)-2 (535 mg, 90 %). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 8.27 (d, 2 arom. H), 8.00 (d, 1 arom. H), 7.38 (d, 2 arom. H), 7.25 (s, 4 arom. H), 7.13 (d, 2 arom. H), 6.95 (d, 2 arom. H), 6.58–6.53 (m, 2 arom. H), 5.87–5.77 (m, 1H, C*H*=CH$_2$), 5.78 (t, 1H, Cp), 5.29–5.26 (m, 2H, Cp), 5.04–4.93 (m, 2H, CH=C*H*$_2$), 4.49 (s, 5H, Cp), 4.07 (t, 2H, OCH$_2$), 4.04 (t, 2H, OCH$_2$), 3.98 (t, 2H, OCH$_2$), 2.15–2.09 (m, 2H, C*H*$_2$CH=CH$_2$), 1.89–1.76 (m, 6H, C*H*$_2$CH$_2$O), 1.66–1.30 (m, 22H, CH$_2$), 0.92 (t, 3H, CH$_3$), 0.89 (t, 3H, CH$_3$). MS (APCI): m/z: 1022 $[M+H]^+$. UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}), CH$_2$Cl$_2$): 360 (1880), 460 (440). CD (λ_{max} in nm ($\Delta\varepsilon$ in L mol^{-1} cm^{-1}), CH$_2$Cl$_2$): 360 (+0.43). Anal. calcd. for C$_{60}$H$_{68}$O$_{11}$Fe (1021.04): C, 70.58; H, 6.71 %. Found: C, 70.35; H, 6.85 %.

Polymer Poly[(S)-2]: A solution of (S)-2 (200 mg, 0.196 mmol), 6 (61 mg, 0.027 mmol, calculated with an average molecular weight of 2250 g mol^{-1}), and [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane] (3.9 mg, 0.001 mmol, in xylenes) in toluene (20 mL) was heated at 70 °C for 48 h, cooled to room temperature, and evaporated to dryness. Purification of the solid residue by SEC (CH$_2$Cl$_2$) gave poly[(S)-2] (131 mg, 66 %, calculated with an average molecular weight of 7350 g mol^{-1}). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.28 (d, 2 arom. H), 8.03 (d, 1 arom. H), 7.34 (d, 2 arom. H), 7.23 (s, 4 arom. H), 7.12 (d, 2 arom. H), 6.93 (d, 2 arom. H), 6.50 (br, 2 arom. H), 5.77 (br, 1H, Cp), 5.24 (br, 2H, Cp), 4.45 (s, 5H, Cp), 4.01 (br, 4H, OCH$_2$), 3.96 (t, 2H, OCH$_2$), 1.81–1.77 (m, 6H, C*H*$_2$CH$_2$O), 1.58–1.26 (m, 26H, CH$_2$), 0.89 (t, 6H, CH$_3$), 0.49 (br, 2H, SiCH$_2$), 0.06 (s, SiCH$_3$). UV-vis (λ_{max} in nm (ε in L mol^{-1} cm^{-1}, calculated with an average molecular weight of 7350 g mol^{-1}), CH$_2$Cl$_2$): 360 (9100), 460 (2000). CD (λ_{max} in nm ($\Delta\varepsilon$ in L mol^{-1} cm^{-1}, calculated with an average molecular weight of 7350 g mol^{-1}), CH$_2$Cl$_2$): 360 (+2.2).

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