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Synthesis of Ferroelectric Liquid Crystalline Polysiloxanes Having a Chiral *n*-Alkyl Tolansulfinate as the Pendant Group

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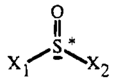
ABSTRACT: The synthesis and mesomorphic properties of a series of ferroelectric liquid crystalline polysiloxanes bearing chiral 4-[(4-((*n*-alkyloxy)sulfinyl)phenyl)ethynyl]phenyl 4-(undecyloxy)benzoate as mesogenic pendant groups are presented. In these polymers, the chirality is introduced via an asymmetric sulfur atom. The synthesis of the materials was possible through three successive polymer-analogous reactions. The last key synthetic step is the polyesterification of the poly((undecyloxy)benzoic acid−methylsiloxane) with the *n*-alkyl 4-[(4-hydroxyphenyl)ethynyl]benzenesulfinate derivatives, which could be carried out efficiently. Up to 97% overall substitution rates of the siloxane units by the mesogenic moiety could thus be obtained. In this paper are also reported the results of the preliminary investigations of the ferroelectric properties, carried out in the $\mathrm{S_C}^*$ phase of one polymer. Finally, the comparison of the mesomorphic properties of a sulfinate-based polymer and molecule with their carboxylate-based counterparts is briefly reviewed.

Introduction

Ferroelectric side chain liquid crystalline polymers (FLCP's) have attracted great interest during recent years, mainly because of their potential development in electrooptical devices.[1,2] The $\mathrm{S_C}^*$ phase is the most fluid ferroelectric mesophase and, thus, attracts much attention toward the device applications. The rapid development of FLCP's was possible because of two decades of intensive research on low molecular weight ferroelectric liquid crystals (FLC's). Most of the mesogenic side groups in FLCP's are already ferroelectric (or potentially ferroelectric) liquid crystals, when taken as single molecules.[1] They are generally composed of two or three aromatic ring cores and possess a chiral moiety of a different kind, such as 1- or 2-methylalkoxy[3,4] 1-(trifluoromethyl)alkoxy,[5,6] cyanohydrin,[7] lactate,[8] β-chlorohydrin,[9,10] oxirane,[11,12] dioxolane,[13] .... In all cases, the chirality is introduced by one to three asymmetric carbon(s), which is (are) not directly connected to the aromatic core but via a linkage, mainly a −O−, −COO−, or a −OCO− group.

Recently, a novel chiral source was investigated in FLC's with the goal of having $\mathrm{S_C}^*$ molecules with enlarged spontaneous polarization (Ps): the sulfinyl group.[14−18] The sulfinyl moiety



is a group of choice for use in FLC's, since the sulfur atom here is chiral and strongly polarized (the S=O bond bears a 4 to 5 D dipole moment).[16] In addition, it is possible to directly connect the chiral sulfinyl moiety to the aromatic core of the mesogen (X_1 = Ar).[14−18] Two main series of FLC's bearing a sulfinyl group as a new source of chirality have been reported in the literature. First is a series of chiral sulfoxides[14] (X_2 = alkyl), in which only two compounds exhibit a stable $\mathrm{S_C}^*$ phase. Measured in mixtures, the ferroelectric properties for these materials revealed very high extrapolated values of Ps, over 400 $\mathrm{nC/cm^2}$. The second series of molecules concerns a number of chiral *n*-alkyl sulfinates[15−18] (X_2 = alkoxy) connected to a 4-(4-phenylethynyl)phenyl 4-alkoxybenzoate core (for simplification, the "(4-phenylethynyl)phenyl" moiety will be named "tolan" further on in the text). Numerous compounds were synthesized and intensively characterized as pure components. For most of the materials, an enantiomerically pure $\mathrm{S_C}^*$ phase was obtained with high values of Ps (up to 300 $\mathrm{nC/cm^2}$) and response time in the few microseconds range.[18] In regard to the polymeric liquid crystalline materials, only one series of side chain liquid crystal polymer bearing a sulfur atom as asymmetric center has been reported in the literature. It concerns a series of polyacrylates with chiral sulfoxide groups, potentially usable in nonlinear optics.[19]

Our goal was to synthesize ferroelectric polysiloxanes exhibiting an extended $\mathrm{S_C}^*$ phase and endowed with large Ps. To reach this goal, the chiral alkyl tolansulfinate mesogen described above appeared as a very promising molecule, and so was used as a side group for our polymers. Due to the presence of the tolan and sulfinate moieties, the "attachment" of the mesogen directly onto the polysiloxane backbone (through a classical hydrosilylation reaction) was not possible,[20] so a new way of preparation of the side chain polysiloxanes was used. The novel procedure consists of connecting the targeted mesogen to the polysiloxane using three successive and efficient chemical modifications of the polymers. The polymer-analogous reactions have sometimes been used to prepare side chain liquid crystal polymers;[4,21−25] however, the literature reports only a very few examples of fully characterized materials involving quantitative or nearly quantitative modifications. The present report describes the synthetic pathway we developed to prepare the tolansulfinate polysiloxanes. This alternative method (or some of the reactions described here) can be extended to many other systems where direct preparation of ramified polymers (through hydrosilylation or polymerization reactions) is not usable because of sensitive or incompatible functionalities present in the starting materials.[25−28] The efficiency of the reactions carried out and the characterization of the polymers obtained are given here in

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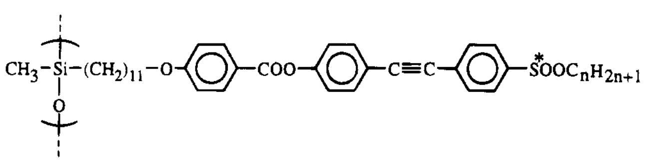
detail. The preliminary results on the investigation of the mesomorphic, structural, and ferroelectric properties for the final liquid crystalline polysiloxanes are also presented. Finally, this paper reports the effect of the substitution of a sulfur atom to a carbon one on the mesomorphic properties, by comparison of the temperature and mesophase occurrence in a sulfinate polymer and its molecule, with their carboxylate homologs.

Results and Discussion

Synthesis. Our target polymers are the following:

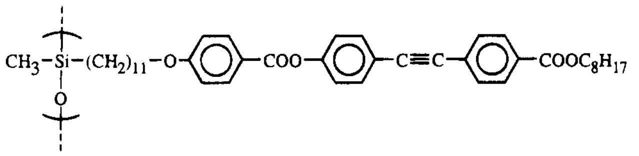


optically active polymer : **(R)-(+)-PS 11-n** with n = 8, 10, 12

racemic polymer : **(+,-)-PS 11-n** with n = 8

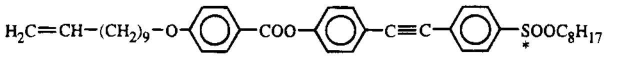
(The acronyms used for naming the polymers are fully detailed in Table 2.)

In order to compare the effect of the substitution of a sulfur atom by a carbon one on the mesomorphic properties of the polymers, we also aimed to synthesize a carboxylate polysiloxane:

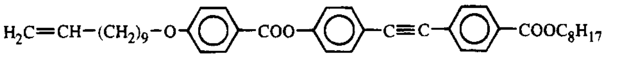


PC 11-8

Polysiloxane was chosen as a polymer backbone because of its low *Tg* and its ability to stabilize the smectic phases.[29] The preparation of the polymers was first attempted via the hydrosilylation reaction of the following vinylic mesogens:



(R)-(+)-MS 11-8

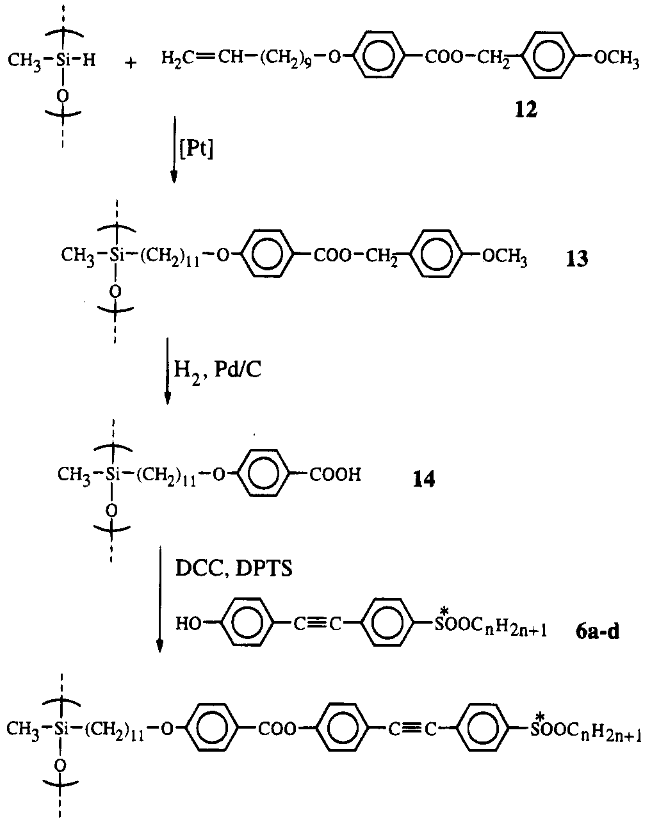


MC 11-8

with the silane functionalities of the polysiloxane backbone, using a platinum-based catalyst.[30] (The acronyms used for naming the low molecular weight sulfinate and carboxylate mesogens are fully detailed in Table 3. As we suspected, the "attachment" of both mesogens directly onto the polysiloxane backbone failed. Undoubtedly, the presence of the ethynyl group has competed with the vinylic functionalities in the hydrosilylation process.[20,31] In addition, the sulfur atom in the sulfinate mesogen might be an additional limiting factor of the reaction,[20] since elemental sulfur is well-known to act as a metal-based catalyst inhibitor, even though a few sulfurated compounds are reported as being successfully hydrosilylated.[32]

Since the polymers could not be synthesized directly, a new way of preparation was designed. This novel procedure consists of assembling the mesogen onto the polysiloxane backbone, using three successive chemical modifications of the polymer. The synthetic pathway to prepare the series of sulfinate polysiloxanes and the carboxylate one is outlined in Schemes 1 and 2, respectively. The final key step of the synthesis is the polyesterification of the carboxylic acid groups of a poly((undecyloxy)benzoic acid−methylsiloxane) (**14**) with the alkyl hydroxytolansulfinate **6a−d** or carboxylate **9** derivatives. The polyacid **14** could not be prepared directly, because the benzoic acid can react in the hydrosilylation reaction process.[20] So, this latter poly-

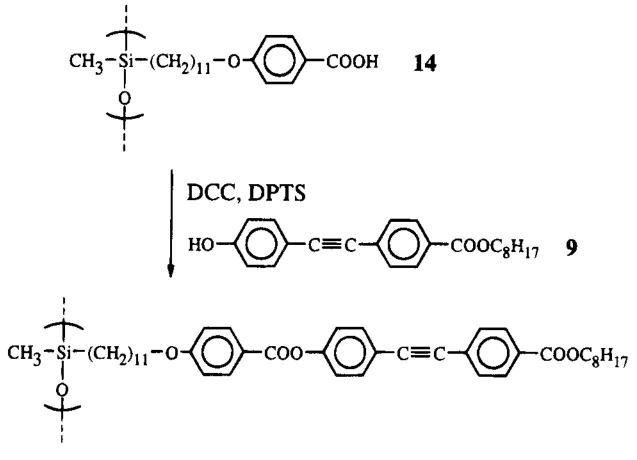
Scheme 1. Synthetic Route for the Preparation of the Liquid Crystalline Polysiloxanes Having Chiral *n*-Alkyl Tolansulfinate as Pendant Groups



n = 8, 10, 12 optically active : (R)-(+)-PS 11-8
(R)-(+)-PS 11-10
(R)-(+)-PS 11-12

n = 8 racemate : (+,-)-PS 11-8

Scheme 2. Preparation of the Liquid Crystalline Polysiloxane PC 11-8 Having *n*-Alkyl Tolancarboxylate as the Pendant Group



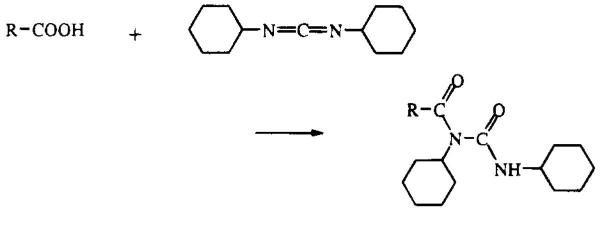
PC 11-8

mer was synthesized in two steps via a protection/deprotection procedure of the benzoic acid groups. The protection/deprotection reactions to obtain the "acidic" polysiloxane **14** were performed using a modified Kato and Fréchet procedure.[23] The reactions involved stand for the two first synthetic steps.

The starting reaction consists of hydrosilylating 4-methoxybenzyl 4-(10-undecenyloxy)benzoate (**12**) with the Si−H functionalities of a poly(methylhydrosiloxane). The 4-methoxybenzyl group was chosen as the protecting group instead of the benzyl one because it can undergo faster deprotection by hydrogenolysis.[33] The hydrosilylation reaction was carried out in toluene with a 20% excess of vinylic derivatives and with dicyclopentadienylplatinum(II) chloride as the catalyst.[30] Polysiloxane **13** was isolated from the reaction mixture by several precipitations into methanol from tetrahydrofuran solutions. The careful observation of the ^{1}H-NMR spectra of the resulting polysiloxane **13** revealed that 97% of the Si−H groups were converted into the Si−(acid protected derivative).

The second reaction is the deprotection step. The removal of the 4-methoxybenzyl group was performed by catalytic hydrogenolysis. As catalyst, 10% palladium on charcoal was used. Hydrogen donor cyclohexene, utilized in Kato and Fréchet's procedure,[23] was replaced by hydrogen gas which was found to undergo faster and more efficient deprotection. After a filtration and precipitation process, poly((undecyloxy)benzoic acid−methylsiloxane) (**14**) was obtained as a white solid. The absence of benzylic and methoxy protons near 5.2 and 3.75 ppm, respectively, in the ^{1}H-NMR spectra of the polymer, confirmed that the deprotection step was quantitative. Due to the formation of a dimeric structure of the benzoic acid moieties via hydrogen bonding,[23,34] polysiloxane **14** has a high melting point ($K \rightarrow I$:215 °C). No monotropic mesophase could be observed in this polymer because of its degradation after melting.

To prevent any racemization of the optically active sulfinate esters, the polyesterification reaction (the last step) was carried out in mild conditions. Polyacid **14** was esterified with the alkyl hydroxytolansulfinate **6a−d** or -carboxylate **9** derivatives by using dicycloxexylcarbodiimide (DCC) as the coupling agent. The first attempt to utilize the usual (dimethylamino)pyridine (DMAP) as catalyst led to over 10% contamination of our polymer with *N*-acylurea formation.[35] This side reaction resulted in the coupling of the benzoic acid pendant groups of the polymer with the DCC:



To overcome this side reaction, the p-toluenesulfonic acid salt of the (dimethylamino)pyridine (DPTS) was substituted to DMAP. DPTS was recently reported by Moore and Stupp to enable one (by reducing the basicity of the reactional medium) to suppress the *N*-acylurea formation in the carbodiimide esterification process.[35] With the use of DPTS in our polyesterifications, it was possible to totally eliminate the *N*-acylurea side reaction or at least to drastically reduce its extent. In addition, DPTS enabled the polyesterification to proceed quantitatively. So, this catalyst has proved its high effectiveness in the polyesterification of fully substituted polymer with benzoic acid pendant groups with bulky hydroxytolan derivatives. All polyesters were prepared at room temperature in dichloromethane, by using a large excess of hydroxytolan derivatives and DCC (2.0 equiv in total) and 0.5 equiv of DPTS. The best results on the polyesterification (quantitative reaction and absence of any *N*-acylurea contamination) were obtained when the two following conditions were respected: (i) solubilization of polysiloxane **14** in a minimal amount of tetrahydrofuran before adding dichloromethane (solvent of the reaction), (ii) introduction of the solution of DCC into the cooled reaction mixture (at 0 °C). The potential *N*-acylurea contamination in the final polymers could be quantified from the nitrogen trace determined by elemental analysis. The extent of the polyesterification reaction could also be accurately measured by quantitative determination of the unreacted benzoic acid moieties with the reagent tetrabutylammonium hydroxide (TBAH), using a potentiometric detection method.

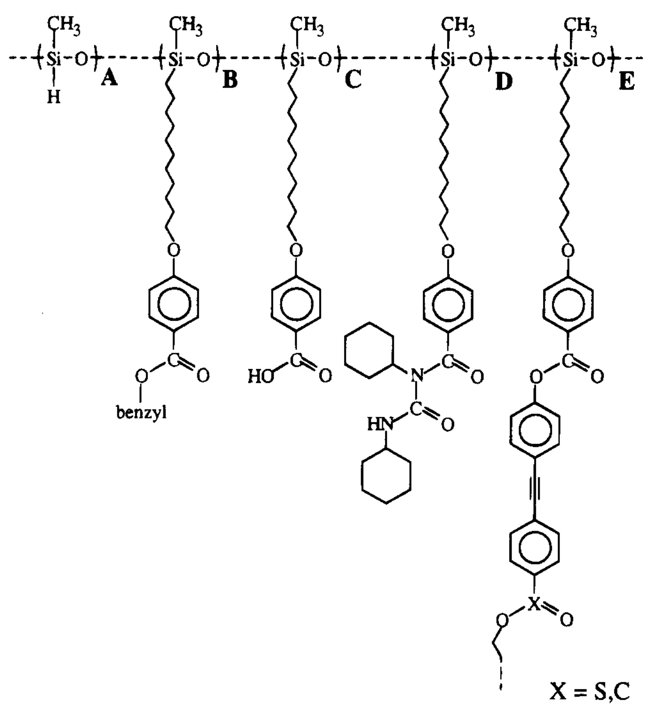
Table 1. Substitution Ratio in the Polysiloxane Backbone for Each Reactional Step

polymers	% substitution[a] A	B	C	D	E	F
(*R*)-(+)-PS 11-8	3	none	none	none	97	90
(*R*)-(+)-PS 11-10	3	none	none	none	97	97
(*R*)-(+)-PS 11-12	3	none	1.5	2.5	94	92
(+,−)-**PS 11-8**	3	none	none	none	97	90
PC 11-8	3	none	0.5	2.5	94	

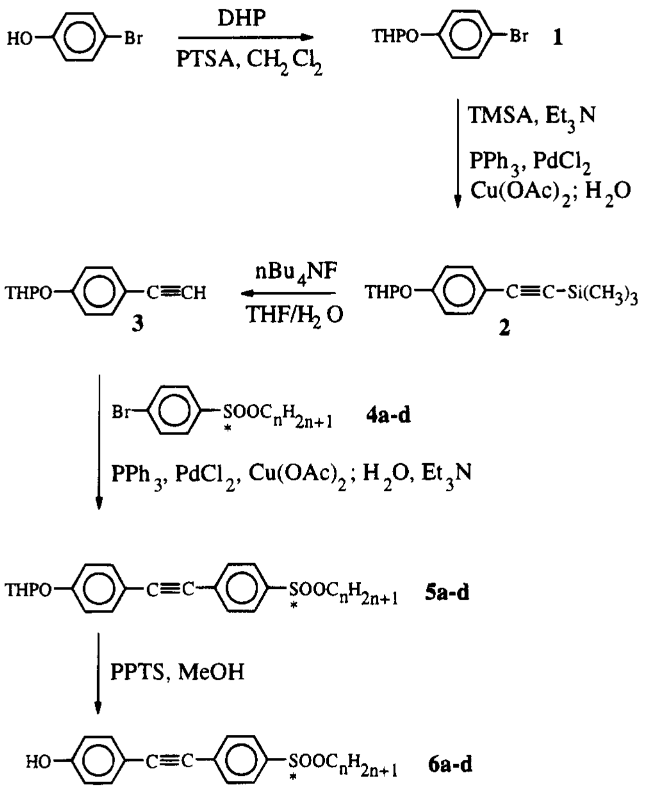
[a] Key: A, unreacted silane functionalities after hydrosilylation; B, undeprotected benzoic acid moieties after hydrogenolysis; C, unreacted benzoic acid moieties after polyesterification; D, *N*-acylurea formation in polyesterification; E and F, total substituted mesogenic pendant groups [calculated from each reactional step analysis (E), calculated from sulfur elemental analysis in the final polymers (F)].

The results of the successive chemical modifications of the polymers and their final constitution are reported in Table 1. The indexes (A, B, ...) represent the substitution percentages in the polysiloxane backbone, for each reaction step. These results clearly show that the overall substitution ratio in the final polymers is essentially limited by the extent of the hydrosilylation process (A = 3%). For three out of five polymers, this latter represents the only limiting factor for the total conversion. The removal of the benzyloxy group was performed quantitatively, no trace of protected benzoic acid group was left after hydrogenolysis (B = 0). Only two polymers, **(*R*)-(+)-PS 11-12** and **PC 11-8**, reveal an incomplete esterification reaction, with 1.5 and 0.5% of residual benzoic acid (C), respectively. These same two polymers are also affected by *N*-acylurea formation (D), which represents a total of 2.5% contamination for each of them. For the other materials, quantitative polyesterification without any *N*-acylurea contamination (C = D = 0) was observed. So, up to 97% of the siloxane units of the polymers are substituted by the desired mesogenic side group (E = 97%). The last column (F) in Table 1 represents the overall substitution ratios of the mesogenic moieties, calculated from the sulfur elemental analysis in the final polymers. These results are slightly inferior to the ones determined from each reactional step analysis (E) and may be due to a smaller amount of siloxane repetition units in the polysiloxane backbone than expected.

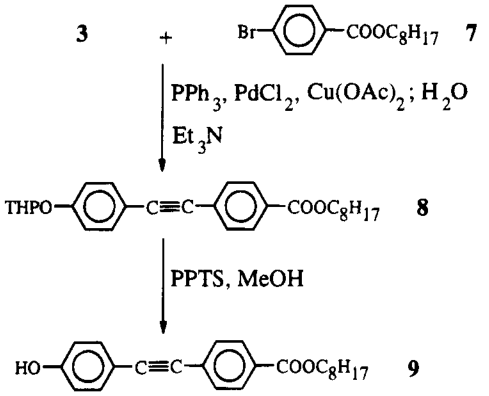
Chart 1



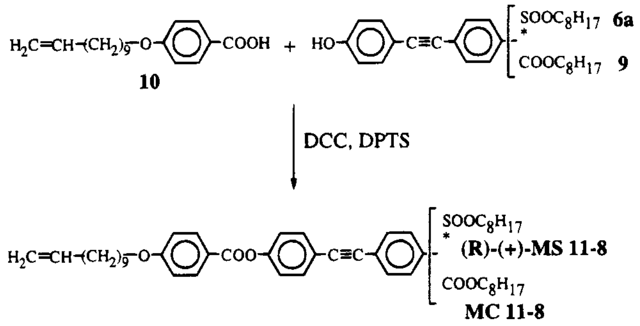
Scheme 3. Synthetic Route for the Preparation of the 4-(*n*-Alkoxysulfinyl)-4′-hydroxytolan



Scheme 4. Synthetic Route for the Preparation of the 4-[(*n*-Octyloxy)carbonyl]-4′-hydroxytolan



Scheme 5. Preparation of the Optically Active Sulfinate ((*R*)-(+)-MS 11-8) and the Carboxylate (MC 11-8) Low Molecular Weight Mesogens



The alkyl hydroxytolansulfinate derivatives **6a**−**d** used in the esterification reaction (to give the sulfinate polymers and the sulfinate mesogen) are prepared according to a synthetic pathway outlined in Scheme 3. 4-Bromophenol is protected with 3,4-dihydro-2*H*-pyran (DHP) (**1**) to allow its palladium-catalyzed coupling with (trimethylsilyl)acetylene (TMSA). The removal of the trimethylsilyl group in compound **2**, with tetra-*n*-butylammonium fluoride,[36] leads quantitatively to the intermediate 1-[(tetrahydro-2*H*-pyran-2-yl)oxy]-4-ethynylbenzene (**3**).[37] The series of optically active n-alkyl (R)-4-bromobenzenesulfinates **4a**−**c** are synthesized in a two-step procedure via the passage to a sulfinamide diastereomer intermediate. This asymmetric synthesis procedure, which proceeds with 80% overall yield and gives up to 95% enantiomeric excess (ee), will be reported in detail in a forthcoming paper.[18] *n*-Octyl 4-bromobenzenesulfinate (**4d**) (racemate) is prepared from the classical esterification reaction of 4-bromobenzenesulfinic acid with 1-octanol, in the presence of DCC. The palladium-catalyzed coupling of the ethynyl derivative **3** with the 4-bromobenzenesulfinate compounds **4a**−**d** yields the series of (pyranyloxy)-tolansulfinates **5a**−**d**. The removal of the pyranyl ether protecting group in **5a**−**d** is performed in very mild acidic conditions, in the presence of pyridinium *p*-toluenesulfinate (PPTS) as catalyst,[38] in methanol. PPTS is used instead of the usual PTSA in order to prevent any racemization side effect of the particularly acid sensitive optically active sulfinate esters. With the use of PPTS, the deprotection proceeds quantitatively to yield the alkyl hydroxytolansulfinates **6a**−**c**, with no effect on their enantiomeric purity.

Octyl hydroxytolancarboxylate (**9**), precursor for the preparation of the polymer **PC 11-8** and the mesogen **MC 11-8**, is synthesized in the same way as for the alkyl hydroxytolansulfinate derivatives. Its synthesis is presented in Scheme 4.

The sulfinate and carboxylate mesogens **(*R*)-(+) MS 11-8** and **MC 11-8**, respectively, are prepared by the esterification reaction in the presence of DCC and DPTS (Scheme 5). As shown by ^{1}H-NMR analysis using a chiral shift reagent,[17] no loss of enantiomeric excess was observed in the sulfinate mesogen **(*R*)-(+)-MS 11-8** during this reaction, which confirms the mildness and the effectiveness of the esterification reaction. This observation let us conclude that the polyesterification

Table 2. Temperatures and Mesophases of the Liquid Crystalline Polymers Bearing as Pendant Group an Optically Active Sulfinate ((*R*)-(+)-PS 11-*n*, with *n* = 8, 10, 12), a Racemate Sulfinate ((+,−)-PS 11-8), and a Carboxylate Ester (PC 11-8)

		temperature (°C)								
polymers[a]	% ee[b]	g		K		$S_C^{(*)}$		S_A		I
(*R*)-(+)-PS 11-8	90	·	19	·	96	·	150	·	197	·
(*R*)-(+)-PS 11-10	91	·	13	·	104	·	142	·	185	·
(*R*)-(+)-PS 11-12	91	·	13	·	105	·	122	·	172	·
(+,−)-PS 11-8		·	19	·	80	·	148	·	198	·
PC 11-8		·	*c*	·	73	·	219			·

[a] The acronyms used for naming the polymers are built as follows: PS stands for sulfinate-based polymer, while PC is for carboxylate-based polymer. 11 and *n* (with *n* = 8, 10, or 12) stand for the number of methylene segments in the spacer and the terminal alkyl chain, respectively. (+,−) is used to express the sulfinate polymer in its racemic form. (*R*)-(+) means optically active sulfinate polymer, where *R* stands for the configuration at the sulfur atom and + for the sign of the optical rotation. [b] Enantiomeric excess. [c] Not found.

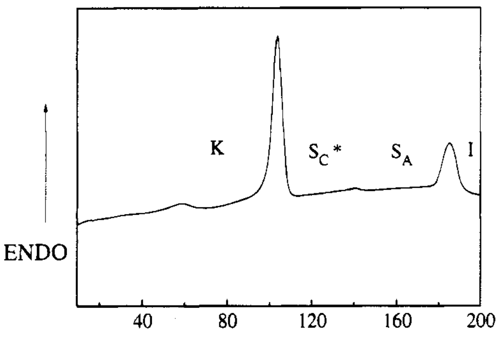


Figure 1. DSC thermogram of the polymer **(*R*)-(+)-PS 11-10**.

has no effect on the enantiomeric purity of our polymers (**(*R*)-(+)-PS 11-8**, **(*R*)-(+)-PS 11-10**, and **(*R*)-(+)-PS 11-12**) which are prepared according to the same procedure.

Mesomorphic, Structural, and Ferroelectric Properties. The transition temperatures of the liquid crystal polysiloxanes are presented in Table 2. The reported clearing temperatures and the S_A−$S_C^{(*)}$ transition temperatures are observed by microscopy, while T_g and the transition temperatures corresponding to the high ordered phases are obtained by DSC, with a heating rate of 10 °C/min.

Optically, the sulfinate polymers exhibit a fan-shaped texture in the S_A phase with additional breaks and strias in the S_C* phase (absence of strias in the S_C of the racemate ((+,−)-**PS 11-8**). By cooling further from the $S_C^{(*)}$ phase, no textural change could be distinctly observed by microscopy. A DSC trace for a typical sulfinate polymer is shown in Figure 1, it corresponds to the first heating of the previously melted polymer **(*R*)-(+)-PS 11-10**. The DSC thermograms could confirm the existence of the S_A−$S_C^{(*)}$ transition. This transition corresponds for each sulfinate polymer to a small enthalpy variation of about 0.2−0.5 J/g. Two additional peaks can be seen at low temperatures on the thermograms. The one at lower temperature corresponds to a relatively weak heat of transition (1.0−1.5 J/g) and can be observed only by heating. The second one is characterized by a high enthalpy variation of about 15−18 J/g. Both peaks indicate the existence of a partial crystallization of the side groups. All sulfinate polymers exhibit a T_g at about room temperature.

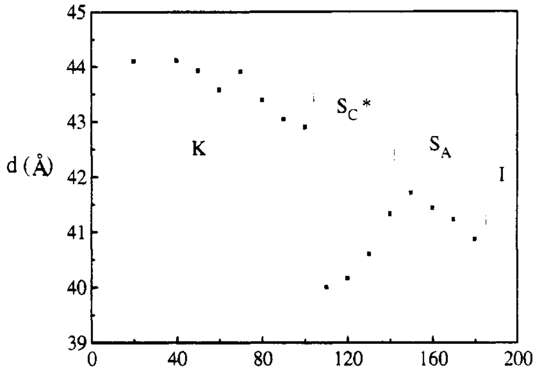


Figure 2. Temperature dependence of the layer spacing for the polymer **(*R*)-(+)-PS 11-10**.

An X-ray diffraction experiment was carried out for the sulfinate polymer **(*R*)-(+)-PS 11-10**. The length, *l*, of the mesogenic side chain (including the siloxane unit) measured by molecular modeling (Sybyl 5.2 molecular modeling software from Tripos) is 43.5 Å and corresponds to the molecular length of the compound of minimized energy. Figure 2 presents the thermal variation of the layer spacing for **(*R*)-(+)-PS 11-10**, recorded as a function of decreasing temperature. One observes a linear dependence of the layer spacing in the S_A phase, the values being in agreement with a monolayer arrangement of the side groups. At the S_A−S_C* transition, a strong and continuous decrease of the layer spacing occurs, reflecting the usual increasing tilt angle of the molecule in the S_C phase. At low temperatures, an increase of the layer spacing occurs, and the values tend to saturate at about 44 Å at room temperature. These distance values, in agreement with the length *l*, indicate the nontilted arrangement of the mesogens in the low-temperature phase of **(*R*)-(+)-PS 11-10**. This latter could be attributed either to a crystalline phase or to a high ordered smectic phase. It has to be noted that the dip observable in Figure 2 at about 60 °C is not indicative of a phase transition. We believe in fact, that it is within experimental error, since the X-ray reflections indicative of a lamellar structure observed in the small angle region of the X-ray patterns are not perfectly sharp.

Let us examine now the change of the transition temperatures in the series of optically active sulfinate polymers. Lengthening the terminal alkyl chain from 8 to 12 methylene segments produces a decrease of both the clearing and the S_A−S_C* transition temperatures, as is the general case in side chain liquid crystal polymers. However, the increase of the chain length has no significant effect on the melting and glass temperatures of the polymers. It is worth noticing that the chirality seems to have no effect on the values of the transition temperatures in our systems, since identical temperatures (except for the melting temperature) are obtained for the optically active sulfinate polymer **(*R*)-(+)-PS 11-8** (90% ee) and for its racemate homolog (+,−)-**PS 11-8**.

The temperatures of the alkyl tolancarboxylate polymer **PC 11-8** are also given in Table 2. In contrast with the sulfinate polymers, the polymer **PC 11-8** exhibits a single mesophase. This mesophase, present on a wide temperature range (about 150 °C) and appearing optically as a schlieren texture, is a S_C phase. The existence

Table 3. Temperatures and Mesophases of the Liquid Crystalline Sulfinate (*R*)-(+)-MS 11-8 and carboxylate MC 11-8 Derivatives

		temperature (°C)										
molecules[a]	% ee[b]	K		S_B		S_C*		S_A		N		I
(*R*)-(+)-MS 11-8	90	•	78.7			•	88.8	•	109.6			•
MC 11-8		•	74.0	•	76.6			•	160.1	•	161.2	•

[a] In the acronyms used for naming the low molecular weight mesogens, MS and MC stand for the sulfinate and carboxylate molecules, respectively. The prefix (*R*)-(+) is to express the optically active sulfinate molecule, in which *R* stands for the configuration at the sulfur atom and + for the sign of the optical rotation. [b] Enantiomeric excess.

of the S_C phase has been confirmed by X-ray diffraction experiments. The layer spacings measured at 140 and 100 °C are 37.1 and 37.4 Å, respectively, while the calculated molecular length is 46.0 Å. The layer spacing measured at low temperatures (crystalline state) is about 40 Å and is in agreement with a tilted arrangement of the mesogenic side groups.

Investigation of the electrooptical properties in the S_C* phase was performed on the sulfinate polymer **(*R*)-(+)-PS 11-10**. The polymer was placed between two ITO-coated glass plates which were rubbed with Teflon.[39,40] After shearing the sample in the S_A phase, a relatively good alignment could be obtained. By applying a triangular wave voltage, clear optical bistability, typical for ferroelectricity, was observed at a low frequency in the S_C* phase. The preliminary investigations of the spontaneous polarization at 5 deg below the AC* transition, on a 30 μm thick cell and using a 300-V amplitude triangular wave voltage gave a value on the order of 30 nC/cm^2. Due to a nonperfect alignment of the sample, this value is surely underestimated. Further investigations of the electrooptical properties are underway, especially in order to improve the macroscopic alignment of these polymers.

The effect of the substitution of a sulfur atom by a carbon one can be observed in comparing the transition temperatures of the sulfinate polymer **(+,−)-PS 11-8** and molecule **(*R*)-(+)-MS 11-8** with their carboxylate counterparts **PC 11-8** and **MC 11-8**, respectively (Table 2 and Table 3). From a pure configuration point of view, one of the main differences between the sulfinate and the carboxylate groups is that in the sulfinate, the sulfur atom is pyramidal, while the carbon atom in the carboxylate is trigonal planar. In our systems, this configuration aspect leads to a major structural effect because of the resulting difference of the deviation of the alkyl chain from the long axis of the mesogen. We showed by molecular modeling that in the alkyl benzoate molecule, the angle between the phenyl ring and the C-alkoxy is about 145°, while it is as narrow as 100° betwen the phenyl ring and the S-alkoxy in the alkyl phenylsulfinate molecule. The stronger deviation of the alkyl chain observed in the case of the sulfinate as compared to the carboxylate one must lead to an important impact in the mesomorphic properties, as we are going to present now. First let us observe the polymers (Table 2). In the sulfinate polymer **(+,−)-PS 11-8**, the clearing point is 20 deg lower than for the carboxylate polymer **PC 11-8**. This thermal destabilization in **(+,−)-PS 11-8** is also accompanied with the appearance of a S_A phase above the S_C phase, when **PC 11-8** exhibits only a S_C phase. The effect of the sulfinate group as compared to the carboxylate one can be analyzed with the low molecular weight molecules, also. Table 3 reports the transition temperatures and the mesophases of the sulfinate **(*R*)-(+)-MS 11-8** and the carboxylate **MC 11-8** molecules. The sulfinate molecule **(*R*)-(+)-MS 11-8** is optically active (*R* configuration, 90% ee) but we expect its transition temperatures to be the same as for the racemate form, as was established for the polymers (**(*R*)-(+)-PS 11-8** and **(+,−)-PS 11-8**). As was observed for the polymers, the molecule **(*R*)-(+)-MS 11-8** presents a clearing point 50 deg lower than for the carboxylate molecule **MC 11-8**. Again, the larger deviation of the terminal alkyl chain from the long molecular axis in **(*R*)-(+)-MS 11-8** has a major impact in the isotropization temperature. The phase sequence for **(*R*)-(+)-MS 11-8** is S_C*−S_A−I, while for **MC 11-8** it is S_B−S_A−N−I. The S_C phase is thus stabilized in the sulfinate molecule, in contrast with the carboxylate molecule which exhibits only a high ordered S_B phase below the S_A phase. Finally, it is worthwhile to point out that the strong decrease of the clearing point was already observed in a series of sulfinate molecules of the same structure but bearing a chiral ramified alkyl chain.[15,16,41,42] In addition, the newly discovered TGBA phase was observed in these materials, which was found to be strongly stabilized in regard to their carboxylate homologs reported elsewere.[42,43]

Conclusions

The present paper reports, to our knowledge, the first example of ferroelectric liquid crystalline polymers in which the chirality is introduced by a heteroatom. The synthesis of the targeted side chain polysiloxanes was possible by using a three successive polymer-analogous reactions procedure. The efficiency of the reactions used was such that up to a 97% overall substitution rate of the siloxane units of the polymer by the mesogenic moieties could be obtained. All polysiloxanes having an optically active sulfinate group exhibit a S_C* phase, its stability depending upon the length of the terminal alkyl chain. By comparison of the mesomorphic properties of a sulfinate-based polymer and its molecule, with their carboxylate counterparts, we showed the sulfinate materials exhibit a much lower clearing point. Also, it seems that this effect is accompanied in the polymers by a slight destabilization of the S_C phase in favor of the S_A phase. These thermal behaviors might be explained in terms of the deviation of the terminal alkyl chain from the long molecular axis, much stronger in the case of the alkyl sulfinate materials. Other systems should be synthesized and investigated in order to confirm this assumption. The future directions are to synthesize ferroelectric sulfinate-based polymers having much lower viscosities and transition temperatures. This work, currently under progress, consists of preparing a series of copolysiloxanes with “dilute” mesogenic pendants on the polymer backbone and of modifying the chemical structure of the mesogenic core.

Experimental Section

Material. Dichloromethane was distilled over anhydrous $CaCl_2$ and stored over 4-Å molecular sieves. Tetrahydrofuran (THF) was freshly distilled over CaH_2 prior to use. Toluene used in the hydrosilylation reaction and 1,4-dioxane used in the pyranylation reaction were of analytical reagent grade and were stored as received over 4-Å freshly regenerated molecular sieves. High-quality triethylamine was stored over KOH pellets and used without further treatment. Poly(methylhydrosiloxane) was purchased from Petrarch Systems Inc. (PS 120, M_n = 2270) and was used as received.

Techniques. ^{1}H-NMR spectra (200 MHz) were recorded on a Bruker NR/200 AF spectrometer. The gas chromatograph was a Hewlett Packard 5890 Series II instrument fitted with a HP-5 capillary column. The determination of the enantiomeric excess (ee) of all the optically active sulfinyl compounds (except for the final polymers) was performed by ^{1}H-NMR using tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) [$Eu(hfc)_3$, Aldrich, 98%] as chiral shift reagent.[17] The optical rotations were measured by using a Perkin-Elmer 241 MC polarimeter. The molecular parameters of the materials were measured by molecular modeling, by using Sybyl software from Tripos Associates Inc. The energy was calculated by Tripos Force Field 5.2 and was minimized by the MM2 program. The transition temperatures were measured by using both a polarized optical microscope equipped with a Mettler FP82 hot stage and a differential scanning calorimeter Perkin-Elmer DSC-7. X-ray diffraction patterns were recorded photographically using a Guinier focusing camera equipped with a bent quartz monochromator (Cu-Kα_1 radiation from a Philips PW-1009 generator) and an electric oven.

Synthesis of the Materials. A. Synthesis of the Molecules. 4-Bromo-1-[(tetrahydro-2*H*-pyran-2-yl)oxy]benzene (1). To a stirred solution of 4-bromophenol (14.0 g, 81 mmol) and *p*-toluenesulfonic acid monohydrate (250 mg, 1.2 mmol) in dry dioxane kept at 0 °C was introduced dropwise dihydro-4*H*-pyran (22 mL, 240 mmol). After completion of the reaction checked by TLC (about 30 min), 2 g of solid $NaHCO_3$ was directly poured into the mixture. The solution was diluted with ether (100 mL) and then washed with a $NaHCO_3$ solution and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated on a rotatory evaporator under vacuum. The pyranyl derivative was further purified by column chromatography on silica gel (dichloromethane/pentane: 1/1 as eluent) to give 19.1 g of product as white crystals. Yield: 92%. Mp = 55 °C. ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.37 (d, J^3 9.0 Hz, 2H, Ar–H), 6.95 (d, J^3 9.0 Hz, 2H, Ar–H), 5.38 (t, 1H, –O–CH–O–), 3.55–3.95 (m, 2H, $-CH_2-O-$), 1.55–2.05 (m, 6H, $-CH_2-$).

1-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-4-[(trimethylsilyl)ethynyl]benzene (2). A deaerated solution of compound **1** (12.0 g, 46.7 mmol) in dry triethylamine (80 mL) was stirred at 50 °C under an argon atmosphere. This solution was charged with the following catalytic mixture: copper(II) acetate monohydrate (90 mg, 0.47 mmol), palladium(II) chloride (165 mg, 0.93 mmol), and triphenylphosphine (1.22 g, 4.67 mmol) and was kept at the same temperature for 0.5 h. Then, (trimethylsilyl)acetylene (TMSA) (8.5 mL, 60 mmol) was quickly introduced into the mixture which was further heated to 80 °C for 6 h. After cooling to room temperature, the precipitate of triethylammonium bromide was filtered off and washed with pentane. The filtrate was kept and the solvent evaporated to leave a residue which was purified by column chromatography on silica gel (dichloromethane/pentane: 1/1 as eluent) to give 9.0 g of slightly yellowish oil. Yield: 70%. Purity: 96% as checked by gas chromatography. ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.35 (d, J^3 9.0 Hz, 2H, Ar–H), 6.95 (d, J^3 9.0 Hz, 2H, Ar–H), 5.35 (t, 1H, –O–CH–O–), 3.55–3.95 (m, 2H, $-CH_2-O-$), 1.55–2.05 (m, 6H, $-CH_2-$), 0.24 (s, 9H, $-Si(CH_3)_3$).

1-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-4-ethynylbenzene (3). The (trimethylsilyl)acetylene derivative (**2**) (9.0 g, 32.8 mmol) was solubilized in a mixture of tetrahydrofuran (50 mL) and water (8 mL). Then, a solution of tetra-*n*-butylammonium fluoride 1.1 M in tetrahydrofuran (7.5 mL, 8.25 mmol) was added and the mixture was kept while stirring at room temperature for 6 h. After filtration over silica and concentration of the solution, the residue was chromatographed on a column of silica gel (dichloromethane/pentane: 1/1 as eluent) from which 5.8 g of slightly yellowish crystals were obtained. Yield: 87%. Purity: 98% as checked by gas chromatography. Mp = 66 °C (lit. mp = 65.5 °C[37]). ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.43 (d, J^3 8.9 Hz, 2H, Ar–H), 7.00 (d, 2H, Ar–H), 5.44 (t, 1H, –O–CH–O–), 3.55–3.95 (m, 2H, $-CH_2-O$), 3.00 (s, 1H, $-C{\equiv}C-H$), 1.55–2.05 (m, 6H, $-CH_2-$).

***n*-Alkyl 4-Bromobenzenesulfinates (4a–d).** The series of optically active 4-bromobenzenesulfinates (**4a–c**) were synthesized in a two-step procedure and will be presented in a forthcoming paper.[18] The racemic *n*-octyl 4-bromobenzenesulfinate (**4d**) was synthesized by a classical esterification reaction of 4-bromobenzenesulfinic acid with 1-octanol, in the presence of DCC. All the prepared *n*-alkyl 4-bromobenzenesulfinates (**4a–d**) gave satisfactory ^{1}H-NMR and elemental analyses. These analysis data are given only for compound **4a**, representative of the series. Enantiomeric excess and rotatory power data are given for the three optically active sulfinate materials.

***n*-Octyl (*R*)-(+)-4-Bromobenzenesulfinate (4a).** Colorless oil. ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (d, 2H, Ar–H), 7.56 (d, 2H, Ar–H), 4.03 (dt, -ABX_2-, J^2 9.7 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 3.62 (dt, -ABX_2-, J^2 9.7 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 1.63 (mc, 2H, $-SOO-CH_2-CH_2-$), 1.40–1.20 (m, 10H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{14}H_{21}BrO_2S$: C, 50.46 (50.63); H, 6.35 (6.49); O, 9.60 (9.74); S, 9.61 (9.37). ee = 94%. $[\alpha]_D^{25}$ +103.3 (*c* 1.03, ethanol).

***n*-Decyl (*R*)-(+)-4-Bromobenzenesulfinate (4b).** Colorless oil. ee = 91%. $[\alpha]_D^{25}$ +97.6 (*c* 0.98, ethanol).

***n*-Dodecyl (*R*)-(+)-4-Bromobenzenesulfinate (4c).** White crystals. Mp = 32 °C. ee = 93%. $[\alpha]_D^{25}$ +89.2 (*c* 1.02, ethanol).

***n*-Alkyl 4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzenesulfinates (5a–d).** A deaerated solution of the ethynyl derivative **3** (1.21 g, 6.0 mmol) and *n*-alkyl 4-bromobenzenesulfinate **4a–d** (6.0 mmol) in dry triethylamine (40 mL) was stirred under an argon atmosphere. Copper(II) acetate monohydrate (6 mg, 0.03 mmol), palladium(II) chloride (21 mg, 0.12 mmol), and triphenylphosphine (157 mg, 0.6 mmol) were added to the solution, and the mixture was heated at 70 °C for 5 h. After cooling, the precipitate of triethylammonium bromide was filtered off and washed with 100 mL of a dichloromethane/pentane (1/2) mixture. The filtrate was concentrated under reduced pressure and the crude product chromatographed on a column of silica gel (dichloromethane/pentane: 5/2) to give the pure pyranyl derivative (**5a–d**) as white crystals. Yield: 70–80%.

***n*-Octyl (*R*)-(+)-4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzenesulfinate (5a).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar–H), 7.48 (d, J^3 8.8 Hz, 2H, Ar–H), 7.05 (d, J^3 8.8 Hz, 2H, Ar–H), 5.48 (t, 1H, –O–CH–O–), 3.55–4.10 (m, 4H, $-CH_2-O$ and $SOO-CH_2-$), 1.55–2.10 (m, 6H, $-CH_2-$ pyranyl), 1.40–1.15 (m, 10H, $-CH_2-$ aliphatic), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{27}H_{34}O_4S$: C, 71.33 (71.27); H, 7.54 (7.52); O, 14.08 (13.86); S, 7.05 (7.36). ee = 94%.

***n*-Decyl (*R*)-(+)-4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzenesulfinate (5b).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar–H), 7.48 (d, J^3 8.7 Hz, 2H, Ar–H), 7.05 (d, J^3 8.7 Hz, 2H, Ar–H), 5.47 (t, 1H, –O–CH–O–), 3.55–4.10 (m, 4H, $-CH_2-O$ and $SOO-CH_2-$), 1.55–2.10 (m, 6H, $-CH_2-$ pyranyl), 1.40–1.15 (m, 14H, $-CH_2-$ aliphatic), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{29}H_{38}O_4S$: C, 72.16 (72.18); H, 7.94 (8.04); O, 13.26 (13.06); S, 6.64 (6.50). ee = 91%.

***n*-Dodecyl (*R*)-(+)-4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzenesulfinate (5c).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar–H), 7.48 (d, J^3 8.8 Hz, 2H, Ar–H), 7.04 (d, J^3 8.8 Hz, 2H, Ar–H), 5.47 (t, 1H, –O–CH–O–), 3.55–4.10 (m, 4H, $-CH_2-O$ and $SOO-CH_2-$), 1.55–2.10 (m, 6H, $-CH_2-$ pyranyl), 1.40–1.15 (m, 18H, $-CH_2-$ aliphatic), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{31}H_{42}O_4S$: C, 72.90 (72.72); H, 8.29 (8.31); O, 12.53 (12.46); S, 6.28 (6.46). ee = 93%.

***n*-Octyl 4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzenesulfinate (Racemate) (5d).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar–H), 7.48 (d, J^3 8.8 Hz, 2H, Ar–H), 7.05 (d, J^3 8.8 Hz, 2H, Ar–H), 5.48 (t, 1H, –O–CH–O–), 3.55–4.10 (m, 4H, $-CH_2-O$ and $SOO-CH_2-$), 1.55–2.10 (m, 6H, $-CH_2-$ pyranyl), 1.40–1.15 (m, 10H, $-CH_2-$ aliphatic), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{27}H_{34}O_4S$: C, 71.33 (71.29); H, 7.54 (7.46); O, 14.08 (14.04); S, 7.05 (7.13).

***n*-Alkyl 4-[(4-Hydroxyphenyl)ethynyl]benzenesulfinates (6a–d).** The tetrahydropyranyl derivatives (**5a–d**) were deprotected in very mild acidic conditions using pyridinium *p*-toluenesulfonate (PPTS)[38] as catalyst, in methanol. The general deprotection procedure is the following.

Into a stirred solution of pyranyl ether (**5a–d**) (5 mmol) was poured 30 mL of methanol. Then, PPTS (0.5 mmol) was added and the mixture was heated at 50 °C (bath temperature) for 1 h under stirring. With the introduction of methanol, a precipitation of the pyranyl derivative may occur which disappears rapidly with the progress of the deprotection reaction. After cooling, the solution was diluted with dichloromethane (200 mL) and washed twice with half-saturated brine (200 mL) and once with water (200 mL) to remove the catalyst. Drying (Na_2SO_4) and concentration of the solution under vacuo (evaporator) gave a residue which was purified using short column chromatography on silica gel (ethyl acetate/pentane: 1/4 as eluent). The slightly colored crystals of the alkyl hydroxytolan derivatives (**6a–d**) were finally stored at −30 °C. Yield: 90–95%.

***n*-Octyl (*R*)-(+)-4-[(4-Hydroxyphenyl)ethynyl]benzenesulfinate (6a).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar−H), 7.45 (d, J^3 8.7 Hz, 2H, Ar−H), 6.85 (d, J^3 8.7 Hz, 2H, Ar−H), 5.63 (s, 1H, −OH), 4.05 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 3.63 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 1.65 (mc, 2H, $-SOO-CH_2-CH_2-$), 1.40–1.15 (m, 10H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{22}H_{26}O_3S$: C, 71.32 (71.48); H, 7.07 (7.09); O, 12.95 (12.81); S, 8.65 (8.77). ee = 90%. $[\alpha]_D{}^{25}$ +123.9 (*c* 1.01, ethanol).

***n*-Decyl (*R*)-(+)-4-[(4-Hydroxyphenyl)ethynyl]benzenesulfinate (6b).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar−H), 7.45 (d, J^3 8.5 Hz, 2H, Ar−H), 6.85 (d, J^3 8.5 Hz, 2H, Ar−H), 6.03 (s, 1H, −OH), 4.05 (dt, -ABX_2-, J^2 9.7 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 3.65 (dt, -ABX_2-, J^2 9.7 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 1.64 (mc, 2H, $-SOO-CH_2-CH_2-$), 1.40–1.15 (m, 14H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{24}H_{30}O_3S$: C, 72.33(72.42); H, 7.59 (7.66); O, 12.04 (12.04); S, 8.04 (7.97). ee = 91%. $[\alpha]_D{}^{25}$ +118.2 (*c* 0.97, ethanol).

***n*-Dodecyl (*R*)-(+)-4-[(4-Hydroxyphenyl)ethynyl]benzenesulfinate (6c).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 2H, Ar−H), 7.43 (d, J^3 8.6 Hz, 2H, Ar−H), 6.86 (d, J^3 8.6 Hz, 2H, Ar−H), 6.22 (s, 1H, −OH), 4.07 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 3.64 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 1.64 (mc, 2H, $-SOO-CH_2-CH_2-$), 1.40–1.15 (m, 18H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{26}H_{34}O_3S$: C, 73.20 (73.17); H, 8.03 (8.08); O, 11.25 (11.34); S, 7.52 (7.43). ee = 91%. $[\alpha]_D{}^{25}$ +110.5 (*c* 0.93, ethanol).

***n*-Octyl 4-[(4-Hydroxyphenyl)ethynyl]benzenesulfinate (racemate) (6d).** ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.67 (s, 4H, Ar−H), 7.44 (d, J^3 8.8 Hz, 2H, Ar−H), 6.84 (d, J^3 8.8 Hz, 2H, Ar−H), 5.63 (s, 1H, −OH), 4.06 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 3.64 (dt, -ABX_2-, J^2 9.8 Hz, J^3 6.6 Hz, 1H, $-SOO-CH_2-$), 1.64 (mc, 2H, $-SOO-CH_2-CH_2-$), 1.40–1.15 (m, 10H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{22}H_{26}O_3S$: C, 71.32 (71.45); H, 7.07 (7.10); O, 12.95 (12.84); S, 8.65 (8.63).

***n*-Octyl 4-[[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethynyl]benzoate (8).** This compound was prepared by palladium-catalyzed coupling between the ethynyl derivative **3** and *n*-octyl 4-bromobenzoate (**7**), using the same procedure as for the synthesis of the pyranyl-protected sulfinate materials **5a–d**. Yield: 75%, white crystals. ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.96 (d, J^3 8.4 Hz, 2H, Ar−H), 7.56 (d, J^3 8.4 Hz, 2H, Ar−H), 7.48 (d, J^3 8.7 Hz, 2H, Ar−H), 7.05 (d, J^3 8.7 Hz, 2H, Ar−H), 5.47 (t, 1H, −O−CH−O−), 4.32 (t, 2H, $COO-CH_2-$), 3.95–3.60 (m, 2H, $-CH_2-O-$ pyranyl), 2.05–1.20 (m, 18H, $-CH_2-$), 0.90 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{28}H_{34}O_4$: C, 77.39 (77.30); H, 7.88 (7.90); O, 14.73 (14.80).

***n*-Octyl 4-[(4-Hydroxyphenyl)ethynyl]benzoate (9).** The removal of the tetrahydropyranyl protecting group in compound **8** was performed using the same procedure as for the sulfinate pyranyl derivatives **6a–d**. This compound was stored at −30 °C. Yield: 93%, slightly greenish crystals. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.03 (d, J^3 8.1 Hz, 2H, Ar−H), 7.56 (d, J^3 8.1 Hz, 2H, Ar−H), 7.45 (d, J^3 8.3 Hz, 2H, Ar−H), 6.85 (d, J^3 8.3 Hz, 2H, Ar−H), 5.35 (s, 1H, −OH), 4.33 (t, 2H, $COO-CH_2-$), 1.85–1.20 (m, 12H, $-CH_2-$), 0.84 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{23}H_{26}O_3$: C, 78.83 (78.81); H, 7.48 (7.51); O, 13.69 (13.76).

Liquid Crystalline Tolansulfinate Molecule (*R*)-(+)-MS 11-8. 4-[[4-[(*n*-octyloxy)-(*R*)-(+)-sulfinyl]phenyl]ethynyl]phenyl 4-(10-Undecenyloxy)benzoate. A 25 mL roundbottom flask containing a stirring bar and equipped with a $CaCl_2$ drying tube was charged with 4-(10-undecenyloxy)benzoic acid (**10**) (157 mg, 0.54 mmol), *n*-(*R*)-octyl 4-[(4-hydroxyphenyl)ethynyl]benzenesulfinate (**6a**) (200 mg, 0.54 mmol), the catalyst 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (80 mg, 0.27 mmol), and 4 mL of dry dichloromethane. The suspension was gently stirred for 15 min, and a solution of DCC (165 mg, 80 mmol) was poured into the mixture. The suspension was allowed to stir for 24 h at room temperature. The precipitate of dicyclohexylurea was filtered off and rinsed with toluene, and the resulting filtrate was washed successively with a brine solution and water. After evaporation of the solvent, the residue was then subjected to column chromatography on silica gel (dichloromethane/pentane: 1/2 as eluent) to give 300 mg of pure sulfinate mesogen as white crystals. Yield: 85%. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.14 (d, J^3 8.6 Hz, 2H, Ar−H), 7.70 (s, 4H, Ar−H), 7.60 (d, J^3 8.4 Hz, 2H, Ar−H), 7.24 (d, J^3 9.2 Hz, 2H, Ar−H), 6.98 (d, J^3 8.6 Hz, 2H, Ar−H), 5.80 (m, 1H, $-CH{=}CH_2$), 4.96 (m, 2H, $-CH{=}CH_2$), 4.10–3.60 (m, 4H, $-CH_2-O-$), 2.04 (m, 2H, $-CH2-CH{=}CH_2$), 1.80 (mc, 2H, $-CH_2-CH_2-O-$), 1.70–1.20 (m, 24H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{40}H_{50}O_5S$: C, 74.73 (74.96); H, 7.84 (7.85); O, 12.44 (12.42); S, 4.99 (5.03). ee = 90%. $[\alpha]_D{}^{25}$ +68.9 (*c* 1.01, dichloromethane).

Liquid Crystalline Tolancarboxylate Molecule MC 11-8. 4-[[4-[(*n*-(octyloxy)carbonyl]phenyl]ethynyl]phenyl 4-(10-Undecenyloxy)benzoate. The synthesis of the carboxylate mesogen **MC 11-8** was carried out by esterification of 4-(10-undecenyloxy)benzoic acid (**10**) with *n*-octyl 4-[(4-hydroxyphenyl)ethynyl]benzoate (**9**), using the same procedure as for the sulfinate mesogen **(*R*)-(+)-MS 11-8**. Yield: 87%, white crystals. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.15 (d, J^3 8.8 Hz, 2H, Ar−H), 8.04 (d, J^3 8.3 Hz, 2H, Ar−H), 7.61 (d, J^3 8.5 Hz, 2H, Ar−H), 7.60 (d, J^3 8.4 Hz, 2H, Ar−H), 7.24 (d, J^3 8.8 Hz, 2H, Ar−H), 6.99 (d, J^3 8.8 Hz, 2H, Ar−H), 5.85 (m, 1H, $-CH{=}CH_2$), 4.97 (m, 2H, $-CH{=}CH_2$), 4.33 (t, 2H, $-COO-CH2-$), 4.06 (t, 2H, $-CH_2-O-Ar$), 2.06 (m, 2H, $-CH2-CH{=}CH_2$), 1.80 (mc, 4H, $-CH_2-CH_2-O-$), 1.60–1.20 (m, 22H, $-CH_2-$), 0.90 (t, 3H, $-CH_3$). Anal. Calcd (found) for $C_{41}H_{50}O_5$: C, 79.06 (79.06); H, 8.09 (8.11); O, 12.84 (12.92).

B. Synthesis of Polymers. 4-Methoxybenzyl 4-(10-Undecenyloxy)benzoate (12). This compound was prepared by a classical esterification reaction of 4-(10-undecenyloxy)benzoic acid (**10**) with 4-methoxybenzenemethanol. Yield: 75%, white crystals. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.00 (d, J^3 8.9 Hz, 2H, Ar−H), 7.39 (d, J^3 8.7 Hz, 2H, Ar−H), 6.92 (d, J^3 8.7 Hz, 2H, Ar−H), 6.88 (d, J^3 8.9 Hz, 2H, Ar−H), 5.82 (m, 1H, $-CH{=}CH_2$), 5.27 (s, 2H, $ArCH_2-$), 4.96 (m, 2H, $-CH{=}CH_2$), 4.00 (t, 2H, $-CH_2-CH_2-O-$), 3.82 (s, 3H, $-OCH_3$), 2.04 (m, 2H, $-CH2-CH{=}CH_2$), 1.78 (mc, 2H, $-CH_2-CH_2-O-$), 1.55–1.20 (m, 10H, $-CH_2-$). Anal. Calcd (found) for $C_{26}H_{34}O_4$: C, 76.06 (75.89); H, 8.35 (8.20); O, 15.59 (15.46).

Polysiloxane 13. Hydrosilylation Step. The polysiloxane substituted with the protected (undecyloxy)benzoic acid pendant group was synthesized by hydrosilylation of the vinylic derivative **12** with poly(methylhydrosiloxane) (M_n = 2270, 35 methylhydrosiloxane units per chain in average), in toluene. The dicyclopentadienylplatinum(II) chloride used as catalyst was synthesized according to Apfel and co-workers' procedure.[30] The vinylic derivative **12** (4.10 g, 10 mmol) and poly(methylhydrosiloxane) (520 mg, 8 mmol corresponding to the Si−H functions) were added to 30 mL of dry toluene. The reaction mixture was heated at 80–90 °C under argon, and 400 μL of dicyclopentadienylplatinum(II) chloride catalyst was injected with a syringe as a solution in dichloromethane (3 mg/mL, 400 ppm as refered to Si−H functions). More catalyst solution (100 μL; 100 ppm) was injected again after 24 h. After 60 h reaction time, a 4-fold molar excess of 1-octene was added to the solution to convert the potentially unreacted Si−H in the polysiloxane, and the solution was heated at 80−90 °C for 12 h more. The reaction mixture was cooled down and filtered through a 0.45 μm pore size filter, and the filtrate was directly poured into 250 mL of methanol to precipitate the polymer. To facilitate the recuperation of the gel-like polymer, the mixture was centrifugated for 20 min and the supernatant liquid removed. The crude polymer obtained was then subjected to three successive precipitations into methanol from a dichloromethane solution followed by a centrifugation. After the final addition of dichloromethane, the resulting solution was filtered through a 0.45 μm pore size filter and the solvent removed to leave a viscous material which was dried for 2 days at 60 °C. Yield: 80%. As checked by TLC and ^{1}H-NMR, the polymer obtained was free from any residual vinylic derivatives. ^{1}H-NMR, $CDCl_3$, δ (ppm): 7.95 (d, J^3 8.7 Hz, 2H, Ar−H), 7.33 (d, J^3 8.5 Hz, 2H, Ar−H), 6.86 (d, J^3 8.7 Hz, 2H, Ar−H), 6.82 (d, J^3 8.9 Hz, 2H, Ar−H), 5.22 (s, 2H, $ArCH_2-$), 3.89 (t, 2H, $-CH_2-CH_2-O-$), 3.76 (s, 3H, $-OCH_3$), 1.58 (mc, 2H, $-CH_2-CH_2-O-$), 1.50−1.20 (m, 16H, aliphatic protons), 0.49 (m, 2H, $-Si-CH_2-$), 0.04 (m, 3.6H, $-Si-CH_3$). Careful observation of the ^{1}H-NMR spectra of polysiloxane **13** revealed no addition of 1-octene unless there were 3% of unreacted Si−H functions left (when compared to the $-Si(CH_3)O-$ polymer unit).

"Acidic" Polysiloxane 14. Deprotection Step. The removal of the 4-methoxybenzyl protecting group in polymer **13** was carried out by hydrogenolysis, catalyzed with 10% palladium on charcoal (10% Pd−C). The procedure used was the following: A suspension of 10% Pd−C (1.20 g) in 35 mL of tetrahydrofuran was charged with polysiloxane **13** (3.60 g, 55 mmol benzyl group). Slight hydrogen bubbling was allowed into the stirred mixture for 48 h at room temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated and precipitated into pentane. The precipitate was removed with a minimum volume of tetrahydrofuran, filtered through a 0.45 μm pore size filter, and precipitated again into pentane. The resulting white solid was dried under vacuum at room temperature for 2 days. Yield: 86%. ^{1}H-NMR, tetrahydrofuran-d_8, δ (ppm): 7.92 (d, J^3 8.8 Hz, 2H, Ar−H), 6.89 (d, J^3 8.8 Hz, 2H, Ar−H), 3.96 (t, 2H, $-CH_2-CH_2-O-$), 1.20−1.60 (m, 18H, aliphatic protons), 0.59 (m, 2H, $-Si-CH_2-$), 0.12 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{653}H_{1042}O_{138}$: Si, 9.22 (8.56); C, 63.48 (64.60); H, 8.65 (8.61). The absence of a trace of a peak at 5.2 ppm (corresponding to the benzylic protons) on the ^{1}H-NMR spectra of polysiloxane **14** revealed the deprotection step was complete; thus 100% of the benzyloxycarbonyl groups were converted into carboxylic acid ones.

Liquid Crystalline Polysiloxanes. General Procedure. The liquid crystalline polymers having an alkyl tolansulfinate or tolancarboxylate group as part of the side chain were prepared using the same following procedure: A single-neck round-bottom flask, fitted with a calcium chloride drying tube and containing a stir bar, was charged with polyacid **14** (220 mg, 0.62 mmol of carboxylic acid functions), the alkyl hydroxytolan derivative (**6a**−**d** or **9**) (1.24 mmol), and DPTS (90 mg, 0.31 mmol). The mixture was first solubilized with 1 mL of dry tetrahydrofuran, and 2 mL of dry dichloromethane were added to the solution. The reaction mixture was cooled down to 0 °C with an ice-water bath, and DCC (255 mg, 1.24 mmol) in solution in 4 mL of dry dichloromethane was then introduced. After 1 h, the ice-water bath was removed and the mixture was kept stirring for 3 days at room temperature. All over the reaction period, the internal glassware was rinsed a few times with a minimum volume of dry dichloromethane (in overall 10 mL of solvent added). The reaction time expired, the precipitate of dicyclohexylurea was filtered off and the filtrate was concentrated and poured into 250 mL of methanol. The polymer which precipitated was filtered, taken off with a minimum volume of tetrahydrofuran, and filtered through a 0.45 μm pore size filter. Two more steps of the precipitation/redissolution procedure in methanol from a tetrahydrofuran solution were enough to obtain the polymer free from any residual low molecular weight derivatives, as checked by TLC and ^{1}H-NMR. The polymer was finally dried for 2 days at 50 °C and appeared as a white solid. Yield: 70−90%.

(*R*)-(+)-PS 11-8. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.08 (d, J^3 8.1 Hz, 2H, Ar−H), 7.65 (s, 4H, Ar−H), 7.54 (d, J^3 7.8 Hz, 2H, Ar−H), 7.17 (d, J^3 7.7 Hz, 2H, Ar−H), 6.90 (d, J^3 8.1 Hz, 2H, Ar−H), 4.10−3.90 (m, 2H, $-CH_2-O-Ar$, and 1H, $SOO-CH_2-$), 3.62 (m, 1H, $SOO-CH_2-$), 1.90−1.15 (m, 30H, aliphatic protons), 0.85 (t, 3H, $-CH_3$); 0.54 (m, 2H, $-Si-CH_2-$), 0.09 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{1399}H_{1845}O_{206}S_{34}$: Si, 4.31 (4.68); C, 69.74 (69.19); H, 7.76 (7.77); S, 4.52 (4.20); residual N, 0.00 (0.00). Residual −COOH functions: 0.00%. $[\alpha]_D^{25}$ +60.4 (*c* 0.89, dichloromethane).

(*R*)-(+)-PS 11-10. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.08 (d, J^3 8.1 Hz, 2H, Ar−H), 7.68 (s, 4H, Ar−H), 7.56 (d, J^3 8.1 Hz, 2H, Ar−H), 7.16 (d, J^3 7.5 Hz, 2H, Ar−H), 6.90 (d, J^3 8.1 Hz, 2H, Ar−H), 4.15−3.90 (m, 2H, $-CH_2-O-Ar$, and 1H, $SOO-CH_2-$), 3.64 (m, 1H, $SOO-CH_2-$), 1.90−1.10 (m, 34H, aliphatic protons), 0.87 (t, 3H, $-CH_3$), 0.54 (m, 2H, $-Si-CH_2-$), 0.08 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{1467}H_{1991}O_{206}S_{34}$: Si, 4.15 (4.48); C, 70.35 (69.55); H, 8.01 (8.05); S, 4.35 (4.35); residual N, 0.00 (0.00). Residual −COOH functions: 0.00%. $[\alpha]_D^{25}$ +59.3 (*c* 0.79, dichloromethane).

(*R*)-(+)-PS 11-12. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.08 (d, J^3 8.2 Hz, 2H, Ar−H), 7.65 (s, 4H, Ar−H), 7.54 (d, J^3 7.8 Hz, 2H, Ar−H), 7.17 (d, J^3 8.2 Hz, 2H, Ar−H), 6.91 (d, J^3 8.1 Hz, 2H, Ar−H), 4.10−3.90 (m, 2H, $-CH_2-O-Ar$, and 1H, $SOO-CH_2-$), 3.62 (m, 1H, $SOO-CH_2-$), 1.90−1.15 (m, 38H, aliphatic protons), 0.87 (t, 3H, $-CH_3$), 0.55 (m, 2H, $-SiN-CH_2-$), 0.08 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{1535}H_{2127}O_{206}S_{34}$: Si, 4.02 (4.35); C, 71.28 (70.12); H, 7.76 (8.31); S, 4.21 (4.11); residual N, 0.00 (0.09). Residual −COOH functions: 0.08%. $[\alpha]_D^{25}$ +56.0 (*c* 0.83, dichloromethane).

(+,−)-PS 11-8. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.08 (d, J^3 8.1 Hz, 2H, Ar−), 7.65 (s, 4 aromatic protons), 7.54 (d, J^3 8.0 Hz, 2H, Ar−H), 7.17 (d, J^3 8.2 Hz, 2H, Ar−H), 6.90 (d, J^3 8.1 Hz, 2H, Ar−H), 4.10−3.90 (m, 2H, $-CH_2-O-Ar$, and 1H, $SOO-CH_2-$), 3.62 (m, 1H, $SOO-CH_2-$), 1.90−1.15 (m, 30H, aliphatic protons), 0.87 (t, 3H, $-CH_3$), 0.55 (m, 2H, $-Si-CH_2-$), 0.09 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{1399}H_{1845}O_{206}S_{34}$: Si, 4.31 (4.52); C, 69.74 (69.04); H, 7.76 (7.79); S, 4.52 (4.18); residual N, 0.00 (0.00). Residual −COOH functions: 0.00%.

PC 11-8. ^{1}H-NMR, $CDCl_3$, δ (ppm): 8.07 (d, J^3 8.6 Hz, 2H, Ar−H), 7.98 (d, J^3 7.9 Hz, 2H, Ar−H), 7.55 (d, 2H, Ar−H), 7.52 (d, 2H, Ar−H), 7.15 (d, J^3 7.8 Hz, 2H, Ar−H), 6.89 (d, J^3 7.5 Hz, 2H, Ar−H), 4.30 (t, 2H, $-COO-CH_2-$), 3.96 (t, 2H, $-CH_2-O-Ar$), 1.90−1.10 (m, 30H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$), 0.54 (m, 2H, $-Si-CH_2-$), 0.08 (m, 3.6H, $-Si-CH_3$). Anal. Calcd (found) for $Si_{37}C_{1433}H_{1855}O_{206}$: Si, 4.44 (4.79); C, 73.51 (72.67); H, 7.99 (8.01); residual N, 0.00 (0.12). Residual −COOH functions: 0.032%.

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