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Synclinic–anticlinic phase transition in tilted organosiloxane liquid crystals†

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In this paper, we considered the case of low molecular weight bimesogenic liquid crystals containing a siloxane moiety as the central part of their molecular architecture. For some of these compounds, both ferro- and antiferroelectric mesophases are present. Two distinct smectic structures can develop as a function of temperature, the first one at high temperature corresponding to a synclinic molecular arrangement with elongated molecules, and the second one at lower temperature corresponding to an anticlinic organisation with V-shaped molecules. Numerical calculations of the energy of different conformations of these bimesogenic molecules presented here indicate that there is no difference in energy between V-shaped and linear conformations regardless of the number of silicon atoms in the siloxane moiety. Thus a microscopic model of the synclinic–anticlinic phase transition is developed where the driving force is indeed a free energy difference between the two phases, and not a difference of energy between the V-shaped and linear conformations. The model explains why the anticlinic SmC_A phase is more stable than the synclinic SmC one, why the synclinic SmC phase is generally the higher temperature one, and why in some organosiloxane materials the anticlinic SmC_A phase is not present.

Introduction

Low molecular weight organosiloxane liquid crystals form an interesting class of liquid crystal materials in which one or two mesogenic moieties are attached to a short siloxane chain. In a liquid crystal phase, siloxane groups have a tendency to microseparate and to aggregate in layers thus strongly promoting smectic phases and depressing the nematic phase.[1–3] In a certain sense the smectic layer formed by organosiloxane liquid crystals with one mesogenic group is analogous to a Langmuir–Blodgett film. In Langmuir–Blodgett films strongly anisotropic amphiphilic molecules are attached to the water surface *via* a polar head. The phase state of such a film strongly depends on the surface density, *i.e.* on the average area per polar head.[4] In particular, the film may undergo a transition into the tilted phase as the surface area increases. This tilting transition is determined by an attraction between alkyl chains and by packing effects. In a similar way, the mesogenic groups in the organosiloxane smectic liquid crystals are attached to a 'plane' formed by siloxane groups. In this plane the average area occupied by one siloxane group is significantly larger then the cross-section of a classical mesogenic moiety. As a result the mesogenic groups have a strong tendency to tilt and the system undergoes a transition into the smectic C (or smectic C_A) phase directly from the isotropic phase. One notes that the corresponding mesogenic groups without siloxane chains may form smectic A and/or nematic phases. These phases completely disappear in siloxane materials. The majority of the existing organosiloxane liquid crystals are chiral and thus they possess ferroelectric or antiferroelectric properties in the Smectic C* (SmC*) or Smectic C_A* (SmC_A*) phase, respectively. At the same time these materials maintain the mechanical stability typical of their polymer analogues. The combination of these two properties opens up interesting possibilities for display application.[5]

The main problem which we are going to address in this paper is the microscopic origin of the anticlinic ordering (*i.e.* herringbone structure) in bimesogenic organosiloxane compounds and the nature of the SmC*–SmC_A* transition in these systems. Recently one of the present authors together with Fukuda[6] has developed a model of the anticlinic SmC_A phase in conventional monomesogen liquid crystals. In that model the anticlinic ordering is stabilised by the orientational correlations between permanent transverse molecular dipoles in neighbouring smectic layers. Such correlations are particularly effective if the dipoles are located in bent chiral chains. It should be noted however that this mechanism cannot be applied to organosiloxane liquid crystals. It has already been stressed by Carboni and Coles[7] that the anticlinic structure observed in materials with bimesogen organosiloxane molecules should not be determined by any anticlinic coupling between molecules in adjacent layers but should rather be due to the V-shaped conformation of the dimer molecules. The packing of such V-shaped molecules would result in the anticlinic arrangement of mesogenic groups which, in turn, would give rise to the antiferroelectric ordering of molecular dipoles. This idea is confirmed by the fact that the corresponding monomesogen compounds (with or without the siloxane group) do not form the anticlinic phase.[8]

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It should also be noted that the anticlinic SmC_A phase is formed only if the bimesogen molecule possesses a short siloxane chain with an odd number of silicon atoms. Experimentally the anticlinic phase has not been observed for monodisperse compounds which contain more than five silicon atoms in the chain. One may assume that for longer siloxane chains the corresponding V-shaped conformation is not 'rigid' as the siloxane link between two mesogenic groups behaves more like a flexible polymer chain. In this case the specific packing effects of V-shaped molecules are not strong enough and the anticlinic ordering disappears. These experimental results support the conclusion that the anticlinic ordering in bimesogen organosiloxane compounds is not determined by an interaction between mesogenic groups but is related to a difference between V-shaped and linear conformations.

It has been assumed in ref. 7 that the V-shaped conformation possesses a lower energy in comparison with the linear conformation. In this case the anticlinic SmC_A phase should be preferable to the synclinic SmC phase, and the driving force of the synclinic–anticlinic transition should be determined by a difference in energy between the V-shaped and linear conformations of bimesogen molecules. In the present paper we have made an attempt to check that assumption by performing some extensive numerical calculations of the energy of different conformations of bimesogen organosiloxane molecules. However, the results of these calculations, presented in the next section (Structure and properties of the SmC and SmC_A phases), are quite surprising as they indicate that there is practically no difference in energy between V-shaped and linear conformations of such bimesogen molecules regardless of the number of silicon atoms in the siloxane chain. This result does not confirm the phenomenological model of the SmC_A–SmC transition in organosiloxane liquid crystals proposed in ref. 7.

In this paper we propose a different microscopic model of the synclinic–anticlinic phase transition in a liquid crystal composed of bimesogen molecules. In this model the SmC–SmC_A transition is driven by a free energy difference between the two phases which is determined by a strong polar ordering (or polar packing) of V-shaped molecules in the anticlinic phase. Indeed, a V-shaped molecule apparently possesses a strong polar asymmetry of the molecular shape. This polar asymmetry may qualitatively be represented by the so-called 'steric dipole'[9,10] which is introduced using an analogy with the electric dipole. The steric dipole points to the direction of maximum shape anisotropy. The steric dipole of a V-shaped molecule is parallel to the molecular C_2 symmetry axis. In each layer of the anticlinic SmC_A phase the steric dipoles are ordered due to the optimum packing of V-shaped molecules (see Fig. 1), as for the banana-shaped molecules.[11] The corresponding electric dipoles, which are rigidly bound to the molecular skeleton, are simultaneously ordered as well. One notes that this polar ordering of V-shaped molecules is *parallel* to the tilt plane and thus it is qualitatively different from the spontaneous polarisation of a chiral tilted smectic layer which is perpendicular to the tilt plane and which is determined by molecular chirality. On the other hand, in the synclinic SmC phase a polar ordering in the tilt plane is absent due to symmetry reasons. Thus the additional polar ordering of V-shaped molecules reduces the free energy of the anticlinic SmC_A phase which may become more stable than the synclinic SmC phase.

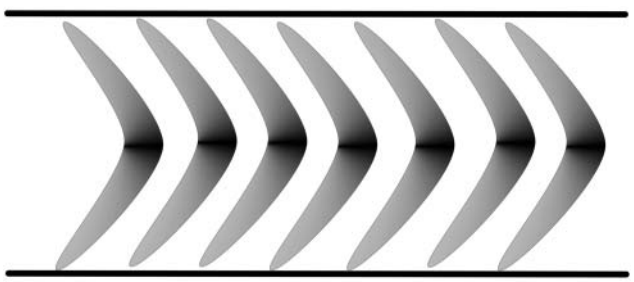


Fig. 1 Optimum packing of V-shaped molecules in a smectic layer.

The mechanism described above makes it possible to understand why the anticlinic phase, composed of V-shaped bimesogen molecules may be more stable than the synclinic phase composed of linear molecules. However, it remains unclear why several bimesogen compounds exhibit the synclinic SmC phase in preference to the anticlinic one, or even do not form the anticlinic phase at all. The model presented in this paper enables one to answer this question. It will be shown that the stability of the synclinic SmC phase at low temperature is determined by two main factors.

Firstly, it is important to note that the anticlinic phase formed by V-shaped molecules is usually characterised by a nearly temperature independent tilt angle which is apparently and mainly determined by the molecular conformation. In a sense the relatively 'rigid' V-shaped conformation works as a mechanical constraint. At a given temperature the corresponding fixed tilt angle may differ from the 'equilibrium' tilt which corresponds to the minimum of the free energy determined by interactions between mesogenic units. One notes that the equilibrium tilt is expected to be temperature dependent and should be nearly the same for synclinic and anticlinic configurations, *i.e.* it weakly depends on the direction of the tilt. This is related to a small free energy difference between the synclinic and anticlinic phases compared to the energy associated with the tilt. Indeed, the antiferroelectric anticlinic SmC_A* phase can easily be switched to the synclinic ferroelectric SmC* phase by a moderate electric field.[8] At the same time a small tilt in the Smectic A phase can only be induced in the vicinity of the second order Sm_A*–SmC* phase transition due to the electroclinic effect.[12] Thus, at higher temperatures directly below the transition into the tilted smectic phase the equilibrium tilt angle may be significantly smaller than the tilt determined by the V-shaped molecular conformation. In this case the free energy of the anticlinic phase with approximately fixed tilt may be too high and the synclinic configuration with the equilibrium tilt appears to be more stable. The actual transition temperature from the synclinic SmC* to the anticlinic SmC_A* phase is then determined by a balance between the negative free energy associated with the polar ordering of V-shaped molecules in the anticlinic phase and the positive free energy cost related to the deviation of the actual tilt from its equilibrium value.

Another factor which acts in the same direction is related to the intermolecular interactions which stabilise the synclinic configuration in the smectic phase composed of monomesogen molecules. These interactions make a positive contribution to the free energy of the anticlinic phase, and this contribution should also be counterbalanced by the decrease of the total free energy associated with more favourable V-shaped conformations. One notes that in the present model the liquid crystal phase is considered as a mixture of molecules adopting V-shaped or linear conformations. However, the concentration of V-shaped conformers in the synclinic phase is very low because such conformations are strongly suppressed. The same is valid for linear conformations in the anticlinic phase. As a result, the SmC*–SmC_A* transition should be accompanied by a steep change of relative concentrations of the two conformers.

The paper is arranged as follows. In the following section, the molecular organization of the SmC* and SmC_A* phases will be described, along with molecular simulation of these organosiloxane compounds. In the next two sections a theoretical approach of the transition between these two phases is developed in agreement with most of the experimental

data available and the nature of the synclinic–anticlinic phase transition in organosiloxane materials is discussed.

Structure and properties of the SmC and SmC_A phases

The organosiloxane compounds considered in the present work are described in Scheme 1.

The synthesis and thermal behaviour of Br–Si_n–Br compounds has already been reported in the literature.[13] S–Si_3–S is a new compound, and its synthesis and chemical characterization are reported in detail in the Experimental section.

Let us concentrate first on the dimesogen S–Si_3–S (containing the sulfinate moieties), for which an extensive structural study has been performed, and which represents the very interesting case of a pure compound exhibiting a transition from a synclinic SmC* (ferroelectric) to an anticlinic SmC_A* (antiferroelectric) phase. The layer spacing, d, as a function of temperature is represented in Fig. 2. On cooling from the isotropic phase, one observes the usual decrease of d in the SmC* phase in connection with an increase of the tilt angle; then after a small discontinuity at the transition it levels off to a constant value of about 33.6 Å at low temperature in the SmC_A* phase. Even if the jump in the layer spacing between the two phases is only of 1%, it is however the signature of a weakly first order nature for the corresponding transition.

Dilatometry experiments have been performed as a function of temperature in the whole stability range of the mesophases. The molecular volume thus determined varies linearly from 2190 $Å^3$ at 50 °C to 2260 $Å^3$ at 95 °C with no significant jump at the SmC*–SmC_A* transition. Combining these results with those of the layer spacing, it is straightforward to deduce the variation of the molecular area, S, *i.e.* the area occupied by one dimer molecule in the plane of the smectic layers, as a function of temperature. Such a behaviour is represented in Fig. 3. The important point to notice is the high value of S which ranges between 63.5 and 65.5 $Å^2$. The calculated S is more than twice the molecular area of the aromatic cores[14] ($\sigma_{ar} \approx 22$–24 $Å^2$). These results suggest a monolayered arrangement of tilted aromatic groups with a tilt angle of $\cos^{-1}(\sigma_{ar}/S) \approx 40$–$45°$, which is consistent with previous values of similar organosiloxane mesogens and with the optically measured tilt angles. Regarding the aliphatic chains, the molecular area (σ_{par}) may vary between 20 and 40 $Å^2$ depending on the chain conformation, again consistent with the monolayered arrangement of the

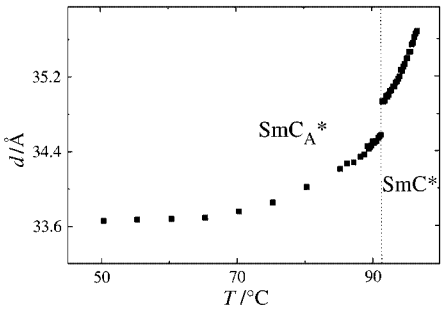


Fig. 2 Layer spacing as a function of temperature in the synclinic SmC* and anticlinic SmC_A* phases of S–Si_3–S.

aromatic cores. The molecular area of a dimethylsiloxane polymer chain (σ_{sil})[15] is approximately 43 $Å^2$. The ratio of S to σ_{sil} is such that the orthogonal siloxane cross-section is considerably smaller than the molecular area. This indicates that the siloxane part does not lie fully extended, but instead should slightly bend back on itself, running in part parallel to the smectic layer, thus increasing the transverse area occupied. Such a behaviour is in agreement on one hand with the diffuse band observed in the X-ray pattern corresponding to an average distance of 11 Å between siloxane moieties, and on the other with molecular simulations presented further in the paper. The structural model of molecular organisation is represented in Fig. 4 for both the SmC* and SmC_A* phases. It consists essentially of tilted mesogenic moieties separated by

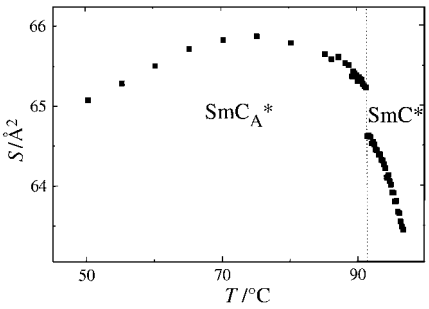
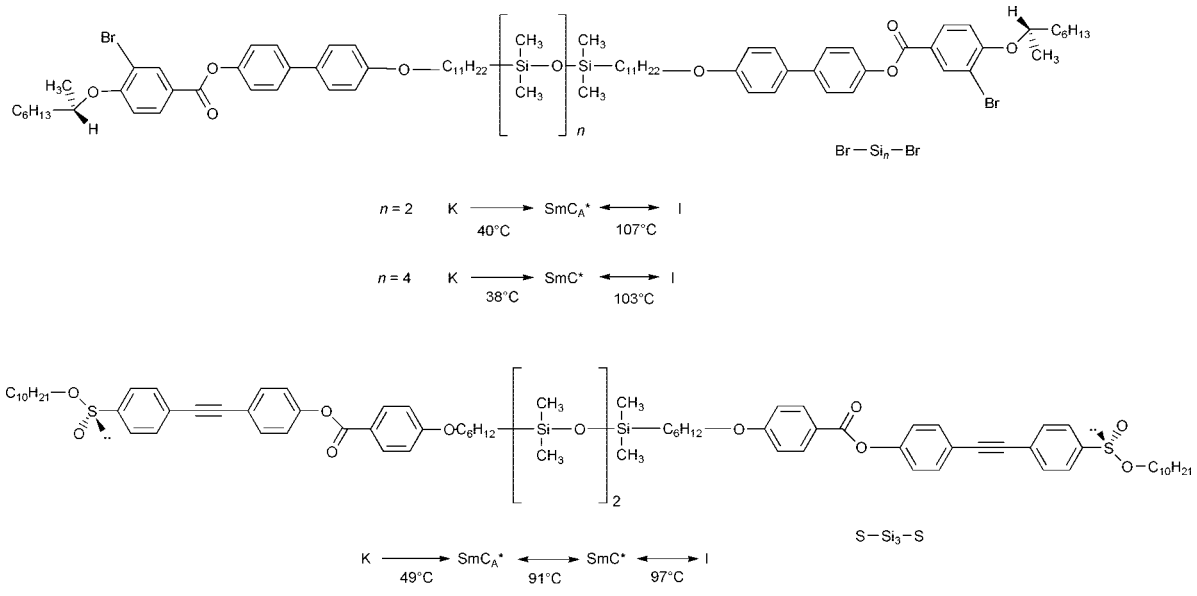


Fig. 3 Molecular area as a function of temperature in the synclinic SmC* and anticlinic SmC_A* phases of S–Si_3–S.



Scheme 1

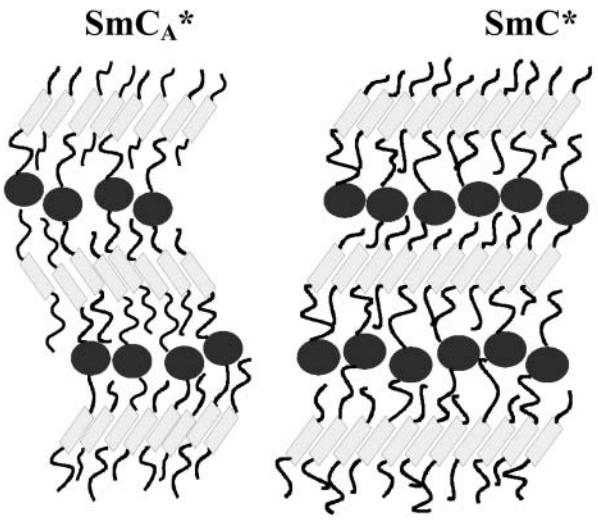


Fig. 4 Schematics of molecular organisation of dimesogenic organosiloxane liquid crystal molecules within the synclinic SmC* and anticlinic SmC$_A$* phases. The yellow rectangles stand for the rigid aromatic mesogenic moieties, the blue ellipses for the siloxane moieties and the wavy lines for the aliphatic chains.

siloxane groups, the total layer being formed by the superposition of three distinct sublayers, one made of the aromatic cores, the other one with the aliphatic chains and the third one with the siloxane moieties. These three sublayers microseparate in order to respect the amphiphatic character of such mesogenic molecules. This structure is similar to that already reported by us for the Br–Si$_n$–Br compounds.[16]

The variation of the tilt angle of the aromatic parts can directly be deduced from the values of S reported above (Fig. 5). It is important to notice a small but sharp increase of the tilt angle at the transition when cooling down in temperature. From a molecular point of view, the transition can be seen as illustrated in Fig. 4. The molecule changes its conformation from an elongated one to a V-shaped one through essentially a conformational change of the siloxane part itself. It is important to note that the angle between the two arms of the V is about 90°, since the tilt angle of the mesogenic groups with respect to the layer normal is 44–45° in the whole range of the antiferroelectric phase. Such an angle is rather small and is in favour of a contribution of a polar ordering due to steric constraints.

As discussed in the Introduction, it is interesting to know whether there is a significant difference in energy between linear and V-shaped conformations of the same molecule because it may be responsible for the transition under consideration. Molecular simulations have been performed using the semi-empirical AM1 method from the MOPAC 6 program.[17] First we have considered the dimethylsiloxane moieties containing 3

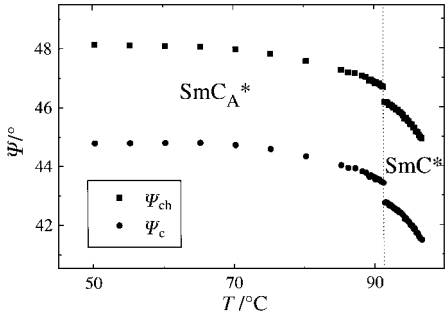


Fig. 5 Tilt angle of the rigid aromatic moieties (ψ_c) and average tilt angle of the disorganised aliphatic chains (ψ_{ch}) in the synclinic SmC* and anticlinic SmC$_A$* phases of S–Si$_3$–S.

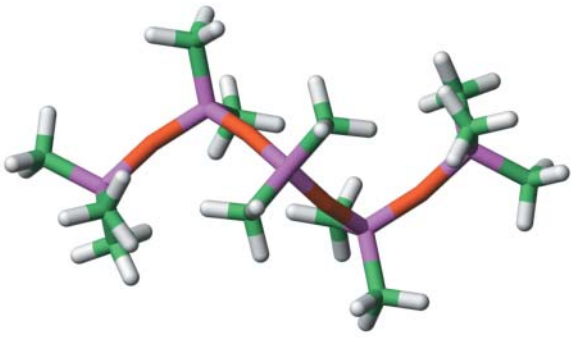


Fig. 6 Molecular simulation of the central siloxane moiety of bimesogenic molecules, showing the quasi-helical conformation of the siloxane backbone. The conformer represented here is a dodecamethylpentasiloxane.

and 5 silicon atoms and substituted by a methyl group at both extremities. Only one conformer with a minimum energy has been chosen which is the best candidate to obtain elongated and V-shaped molecules when the mesogenic group is attached to the siloxane part. It can be seen in Fig. 6 that this conformer is rather compact and close to a helical shape.

The next step was to substitute the terminal methyl groups of the siloxane chain as a function of the orientation wanted for the substituent to obtain elongated or V-shaped molecules. As a matter of fact, the direction of the substituent was found to be mainly determined by the rotation around the two terminal O–Si bonds of the siloxane part. Then the aliphatic spacers have been attached and the resulting molecules minimized again, thus leading to one elongated and two V-shaped conformers. It should be noted that the potential barrier between the two conformations appears to be very small. This has been evaluated from a molecular mechanics calculation on the siloxane moiety containing 5 silicon atoms, using the Discover3 software (Molecular Simulations Inc.) with the cvff forcefield.[18] The energy of the molecule has been minimized with a fixed value of the torsion angle around one specific Si–O bond. This angle is then increased stepwise from 0 to 360°. In that way, we can calculate the energy of the molecule as a function of the rotation angle around one single bond in the siloxane part. It turns out that in this case the potential barrier is only 4 kcal mol^{-1}, representing a fraction of kT. Even if one assumes that several bonds are involved in the process of conformational change of the siloxane part at the SmC*–SmC$_A$* transition, the potential barrier between the two conformations still remains only a small fraction of kT, which is indeed negligible.

The previously optimized mesogenic groups are bonded to the spacers on each conformer of the central moiety and the energy of the whole molecule is then calculated. The results appear to be quite surprising. The energy for each individual molecule is the same (within a fraction of kcal) for the three conformers (elongated, V-shaped conformers with 90 and 150°), *i.e.* 570 kcal for S–Si$_3$–S, 848 kcal for Br–Si$_5$–Br and 605 kcal for Br–Si$_3$–Br respectively. As an example, three conformations of Br–Si$_5$–Br (elongated, V-shaped with large and smaller angle) are represented in Fig. 7 and all of them have the same internal energy. In other words, this indicates clearly that the transition from the synclinic SmC* phase to the anticlinic SmC$_A$* one is not driven by an energy difference between the conformations adopted by the molecule. Moreover, the particular chemical structure of the chiral part and of the mesogenic group itself appears to have no effect at all.

Finally, let us remark that the organosiloxane compounds present in general rather high values of spontaneous polarisation,[19] of the order of some hundreds of nC cm^{-2}. An example of such a behaviour is given in Fig. 8 for S–Si$_3$–S.

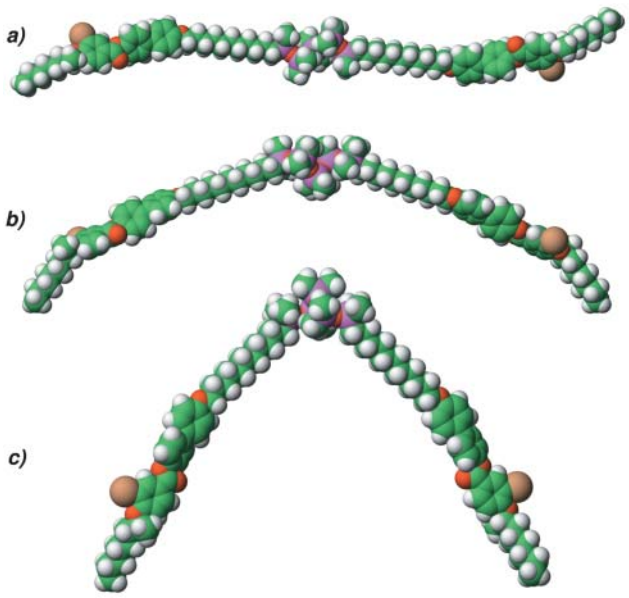


Fig. 7 Molecular simulation of three optimised conformations (one elongated (a) and two V-shaped (b, c) of Br–Si_5–Br. The angles between the mesogenic moieties in the V-shaped conformations are 150° (b) and 90° (c) respectively.

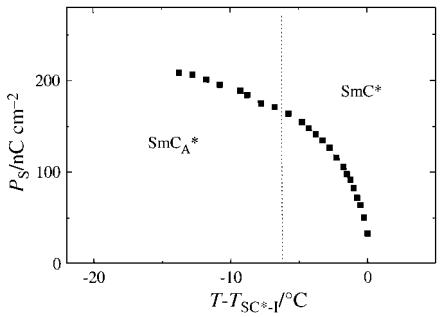


Fig. 8 Spontaneous polarisation as a function of temperature in the synclinic SmC* and anticlinic SmC_A* phases of S–Si_3–S.

Theoretical model

The siloxane bimesogen liquid crystal materials under consideration undergo a strong first order transition from the isotropic to the SmC* phase. In our model of the synclinic–anticlinic transition we assume for simplicity that both nematic and smectic order are perfect. In this case the free energy of the system can be written as eqn. (1):

$$\frac{F}{\rho kT} = x_V \log x_V + x_L \log x_L - x_V W_0 + \frac{1}{2} x_V^2 U_{VV} + x_V x_L U_{VL} + \frac{1}{2} x_L^2 U_{LL} \quad (1)$$

where ρ is the total number density of molecules, x_V and x_L are the molar fractions of V-shaped and linear conformations respectively, $x_V + x_L = 1$, and the dimensionless constants $U_{\alpha\beta}$, (α, β = V, L) are the average interaction energies between the conformers α and β multiplied by the number of nearest neighbours and divided by temperature.

The interaction constants can further be expressed as eqn. (2):

$$U_{\alpha\beta} = \gamma\sigma U_{\alpha\beta}^{\perp} + \gamma(1-\sigma) U_{\alpha\beta}^{\parallel} \quad (2)$$

where γ is the total number of nearest neighbours and σ is a fraction of nearest neighbours located in the same smectic layer and where $U_{\alpha\beta}^{\perp}$ and $U_{\alpha\beta}^{\parallel}$ are the energies of interaction between molecules located in the same smectic layer and in adjacent layers, respectively.

In the first approximation one may also neglect an interaction between mesogenic groups located in adjacent layers. This interaction is expected to be much weaker than the one between the groups which belong to the same layer. It should be noted, however, that this does not mean that we neglect the total interaction between dimer molecules located in adjacent layers. In fact, for any two molecules with siloxane groups located in neighbouring 'siloxane' layers, there are two neighbouring mesogenic groups which interact strongly within the same mesogenic layer (see Fig. 4). In eqn. (2) the constants U_{VV} and U_{LL} are determined by an interaction between parallel mesogenic groups plus an interaction between siloxane chains. At the same time the constant U_{VL} is determined by an interaction between a V-shaped and a linear molecule. In this case all interacting mesogenic groups cannot be parallel. We assume that a V-shaped molecule in the synclinic phase adopts an orientation when one of its mesogenic groups is parallel to the director while another group makes an angle $2\Theta_0$ with the director. In a similar way, one of the mesogenic groups of a linear molecule in the anticlinic phase is assumed to be parallel to the local director while the other group makes an angle of $3\Theta_0$ with the director in the adjacent layer. Here $2\Theta_0$ is the angle between two mesogenic groups in the V-shaped conformation.

Now the energies $U_{\alpha\beta}^{\perp}$ and $U_{\alpha\beta}^{\parallel}$ can be expressed as eqn. (3).

$$\begin{aligned} U_{LL}^{\perp} &= U_{VV}^{\perp} = 2V_0(\Theta) + V_{ss} \\ U_{LL}^{\parallel} &= U_{VV}^{\parallel} = V_0(\Theta) \\ U_{LV}^{\perp} &= V_0(\Theta) + V(\Theta,\Theta_0) + V_{ss} \\ U_{LV}^{\parallel} &= \frac{1}{2}(V_0(\Theta) + V(\Theta,\Theta_0) \end{aligned} \quad (3)$$

Here $V_0(\Theta)$ is an average energy of interaction between two parallel mesogenic groups within one layer. This energy depends on the tilt angle Θ. By contrast, $V(\Theta, \Theta_0)$ is an average energy of interaction between two *nonparallel* neighbouring mesogenic groups, one belonging to a linear molecule and another to a V-shaped one. That energy depends on the tilt angle Θ and on the angle Θ_0 between two mesogenic groups in the V-shaped dimer. Finally, V_{ss} is an interaction energy between two adjacent siloxane chains. It does not depend on Θ in a first approximation.

From eqns. (3) and (2) one obtains eqns. (4) and (5), the expressions for the interaction constants in eqn. (1).

$$U_{LL} = U_{VV} = \gamma(1+\sigma)V_0(\Theta) + \gamma\sigma V_{ss} \quad (4)$$

$$U_{VL} = \frac{1}{2}\gamma(1+\sigma)[V_0(\Theta) + V(\Theta,\Theta_0)] + \gamma\sigma V_{ss} \quad (5)$$

The energies $V_0(\Theta)$ and $V(\Theta, \Theta_0)$ can further be expressed as the corresponding averages of the pair interaction potential between the mesogenic groups [eqns. (6) and (7)]:

$$V_0(\Theta) = \int V(\boldsymbol{n}_0, \boldsymbol{r}_{12}, \boldsymbol{n}_0)\delta(\boldsymbol{u}_{12}.\boldsymbol{e}) r_{12}^2 dr_{12} d\boldsymbol{u}_{12} \quad (6)$$

$$V_0(\Theta,\Theta_0) = \int V(\boldsymbol{n}_0, \boldsymbol{r}_{12}, \boldsymbol{n}_1)\delta(\boldsymbol{u}_{12}.\boldsymbol{e}) r_{12}^2 dr_{12} d\boldsymbol{u}_{12} \quad (7)$$

where $\boldsymbol{r}_{12}$ is the vector pointing from the center of the mesogenic group '1' of one molecule to the center of the mesogenic group '2' of the neighbouring molecule, the unit vector $\boldsymbol{u}_{12} = \boldsymbol{r}_{12}/r_{12}$ is in the direction of $\boldsymbol{r}_{12}$ and the unit vector $\boldsymbol{e}$ is the smectic layer normal. Here $V(1,2) = V(\boldsymbol{n}_1, \boldsymbol{r}_{12}, \boldsymbol{n}_2)$ is the simplified interaction potential for mesogenic groups parallel to local directors $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$, respectively.

Now the free energy [eqn. (1)] can be written in the form of

eqn. (8):

$$\frac{F}{\rho kT} = x_V \log x_V + x_L \log x_L - x_V W_0 + \frac{1}{2} x_V x_L \gamma(1+\sigma)(V(\Theta,\Theta_0) - V_0(\Theta)) + \gamma(1+\sigma)V_0(\Theta) + \gamma\sigma V_{ss} \quad (8)$$

where we have taken into account that $x_V + x_L = 1$.

The equilibrium concentration of dimer molecules in the V-shaped conformation can be determined by minimisation of the free energy [eqn. (8)] taking into account the constraint $x_L + x_V = 1$. One obtains eqn. (9) for the normalised molar fraction x_V.

$$\frac{x_V}{1-x_V} = \exp[-(1-2x_V)(V(\Theta,\Theta_0) - V_0(\Theta)) + W_0] \quad (9)$$

In eqn. (9) $V(\Theta, \Theta_0)$ is the average energy of interaction between two neighbouring mesogenic groups which make an angle of Θ_0. This energy is expected to be significantly higher than $V_0(\Theta)$ which is the averaged energy of interaction between two parallel mesogenic groups. Thus the difference $\Delta V = V(\Theta, \Theta_0) - V_0(\Theta)$ in the rhs of eqn. (9) is expected to be positive and sufficiently large. One notes that qualitatively the main contribution to ΔV comes from the Maier–Saupe orientational potential $V_2 P_2(\cos\Theta)$. The contribution from this potential to the difference ΔV is equal to $-(3/2)V_2 \sin^2\Theta_0$. This contribution is positive because $V_2 < 0$ and is expected to be larger than kT because in the context of the Maier–Saupe model $V_2 \approx 5\,kT$. We also assume that the conformational energy W_0 is smaller than ΔV. In this case eqn. (9) has two stable solutions. One solution corresponds to a very small concentration of V-shaped conformers [eqn. (10)].

$$x_V \approx \exp[-(V(\Theta,\Theta_0) - V_0(\Theta)) + W_0] \ll 1 \quad (10)$$

By contrast, the second solution [eqn. (11)] corresponds to a very low molar fraction of linear conformations $x_L = 1 - x_V \ll 1$.

$$x_L = 1 - x_V \approx \exp[-(V(\Theta,\Theta_0) - V_0(\Theta)) - W_0] \quad (11)$$

Nature of the SmC–SmC$_A$ transition in organosiloxane materials

The solutions $x_L \ll 1$ and $x_V \ll 1$, given by eqns. (10) and (11), actually correspond to the anticlinic SmC$_A$ and synclinic SmC phases, respectively, because V-shaped molecules are expected to form the anticlinic phase while the linear ones will form the synclinic phase. One notes that in the present system the SmC–SmC$_A$ transition is driven by an abrupt change of concentration of V-shaped conformations. Thus, from the formal point of view the concentration x_V can serve as an order paramater for this transition. At the same time the corresponding SmC–SmC$_A$ transition temperature is determined, as usual, by the condition that the free energies of the coexisting phases are equal.

The theory presented above is based on the same main assumptions as the semiphenomenological model of Carboni and Coles.[7] In that model the transition from the synclinic to the anticlinic phase is driven by a difference in energy between the V-shaped and linear conformations of a bimesogen molecule, specified by the parameter W_0. However, our numerical calculations of the energies of the two conformations (see earlier section: Structure and properties of the SmC and SmC$_A$ phases) suggest that the parameter W_0 is negligibly small. Then one can readily see from eqn. (8) that in this case the free energies of the synclinic and anticlinic smectic phases are exactly the same, at least in the framework of this simple model. This means that the model described above does not explain why the anticlinic phase is often more stable than the synclinic one in the system of organosiloxane bimesogen molecules.

One notes that, apparently, there exists an additional qualitative factor which favours the anticlinic phase, and which has not been taken taken into account so far. We suggest that this factor is related to the additional polar ordering of V-shaped molecules in the anticlinic SmC$_A$ phase. Indeed, although the smectic C phase is biaxial, one may assume in the first approximation that short molecular axes are distributed randomly in the planes perpendicular to the long molecular axes. This is related to a relatively low biaxiality of the linear molecular conformation. At the same time the V-shaped conformation possesses a strongly biaxial polar shape. As a result there exists a strong polar ordering of such molecules in the anticlinic phase, determined by polar packing effects. One notes that the existence of the spontaneous polarisation parallel to the tilt plane in the anticlinic SmC$_A$ phase follows from symmetry arguments.[6] As shown experimentally by Miyachi *et al.*[20] and Link *et al.*,[21] this polarisation oscillates from layer to layer together with the direction of the tilt. This polarisation is not related to molecular chirality. One notes that such polarisation also exists in conventional anticlinic smectic phases although it is not related to polar packing effects. This polarisation, however, is generally rather small and it does not influence the stability of the anticlinic phase.

In the anticlinic SmC$_A$ phase the packing of V-shaped molecules results in a strong polar molecular ordering (see Fig. 1). This ordering can be interpreted as an ordering of transverse molecular steric dipoles. In the case of a symmetric V-shaped molecule the steric dipole, which characterises the polar asymmetry of the molecular shape, is parallel to the molecular C_2 axis. The ordering of steric dipoles is determined by excluded volume effects and is not related to any electrostatic interaction. At the same time, if molecules also possess transverse steric dipoles, they will be automatically ordered as well, and the macroscopic spontaneous polarisation (within one smectic layer) will appear. In any case, the additional polar ordering of V-shaped molecules leads to a decrease of the total free energy of the synclinic SmC$_A$ phase in comparison with that of the synclinic phase.

These ideas can be made more quantitave by considering a simple Landau–de Gennes expansion of the free energy of the anticlinic phase. Assuming that the nematic and smectic ordering is perfect, the free energy density of the SmC$_A$ phase can be written as eqn. (12):[6]

$$F_{CA} = F^0_{CA}(\boldsymbol{w}, T) + \kappa(\boldsymbol{p}.[\nabla \times \boldsymbol{w}]) + \frac{1}{2\chi} P^2 + \ldots \quad (12)$$

where $\boldsymbol{p}$ is the polar order parameter within one layer, χ is the generalised susceptibility and $\boldsymbol{w}$ is the vector order parameter of the smectic C phase. The order parameter $\boldsymbol{w}$ is expressed in terms of the director $\boldsymbol{n}$ and the smectic layer normal $\boldsymbol{k}^o$, $\boldsymbol{w} = (\boldsymbol{n}\boldsymbol{k}^o)[\boldsymbol{n} \times \boldsymbol{k}^o]\cos kz$, where k is the wave vector of the density wave in the smectic phase. The absolute value of $\boldsymbol{w}$ is determined by the tilt angle Θ, *i.e.* $w = \sin 2\Theta/2 \approx \Theta$ if $\Theta^2 \ll 1$.

The second term in eqn. (12) describes the coupling between the gradient of the tilt order parameter $\boldsymbol{w}$ and the polarisation in the tilt plane. In the anticlinic SmC$_A$ phase the polarisation parallel to the tilt plane is determined by an oscillation of the tilt direction from layer to layer. In the ideal anticlinic SmC structure the vector $\boldsymbol{w}$ possesses opposite signs in adjacent layers and the polarisation $\boldsymbol{p}$ is located at the boundary between them.

Minimisation of the free energy [eqn. (12)] with respect to the polar order parameter $\boldsymbol{p}$ yields eqn. (13):

$$\boldsymbol{p} = -\chi\kappa[\nabla \times \boldsymbol{w}] = \chi\kappa k[\boldsymbol{k}^o \times \boldsymbol{w}] \sin kz \quad (13)$$

Substituting eqn. (13) back into eqn. (12) and averaging over two adjacent smectic layers (*i.e.* from $z = 0$ to $z = 2d$) one

obtains the simplified expression given in eqn. (14) for the free energy of one smectic layer:

$$\tilde{F}_{CA} = 2dF^0_{CA}(\Theta,T) - \frac{\kappa^2\chi d^2}{4\pi} \quad (14)$$

where d is the half period of the smectic structure. One notes that the last term in eqn. (14) is negative. This term describes a contribution from the polar ordering of V-shaped molecules to the total free energy of the anticlinic phase. Thus the free energy is indeed decreased as a result of such ordering.

The first term in eqn. (14) describes the free energy associated with the tilt of the director in the synclinic or anticlinic smectic C phase which has been discussed in detail in the first part of this section. It should be noted that in the synclinic phase the tilt angle $\Theta(T)$ increases continuously with the decreasing temperature. By contrast, in the anticlinic phase composed of bimesogen molecules the tilt is nearly temperature independent because it is mainly determined by the geometry of the organosiloxane V-shaped molecule. Thus the free energy of the anticlinic phase is given by eqn. (14) where $F^0_{CA}(\Theta,T) = F^0_{CA}(\Theta_0,T)$ depends on the constant tilt angle $\Theta_0 \approx$ const. One notes that the angle Θ_0 is directly related to the angle between the two mesogenic groups in the V-shaped conformation $\alpha = \pi - 2\Theta_0$. However, the constant tilt angle Θ_0 generally does not correspond to the minimum of the free energy of the anticlinic phase at a given temperature T. Therefore, at the same temperature T the free energy $F^0_{CA}(\Theta_0,T)$, associated with the constant tilt in the anticlinic SmC_A phase, should be higher than the corresponding free energy $F^0_C(\Theta(T),T)$ of the synclinic SmC phase which depends on the tilt angle $\Theta(T)$ which does correspond to the minimum of the total free energy of the phase. This effect favours the synclinic SmC phase.

At sufficiently low temperatures (within the SmC range) the equilibrium tilt angle Θ differs significantly from Θ_0 and thus the difference $F^0_{CA}(\Theta_0,T) - F^0_{CA}(\Theta,T)$ is expected to be rather large. For some materials this difference may be larger than the absolute value of the second term in eqn. (14) which is determined by additional polar ordering in the anticlinic phase. In this case the synclinic phase is more stable than the anticlinic one at low temperatures. With the decreasing temperature, however, the equilibrium tilt angle $\Theta(T)$ approaches Θ_0 and the $F^0_{CA}(\Theta_0,T) - F^0_{CA}(\Theta,T)$ decreases. Finally the transition from the synclinic to the anticlinic SmC_A phase occurs when:

$$F^0_{CA}(\Theta_0,T) - F^0_C(\Theta,T) = \pi^2\kappa^2\chi/d^2$$

One notes, however, that the actual transition temperature may be lower because there exist several other factors which favour the synclinic phase. For example, the synclinic structure corresponds to a minimum of the isotropic intermolecular dispersion interaction modulated by anisotropic molecular shape.[6] Other relevant intermolecular interactions are discussed in detail in ref. 6. Thus the model presented in this section enables one to explain why the anticlinic SmC_A phase may be more stable than the synclinic one even if the energy of the V-shaped conformation is the same as that of the linear conformation. The model also explains why the synclinic SmC phase is always the higher temperature one (if it exists at all), and why in some organosiloxane materials the anticlinic phase does not appear.

Conclusion

In this paper, we considered the case of low molecular weight bimesogenic liquid crystals containing a siloxane moiety as the central part of their molecular architecture. These materials are now well known to develop ferroelectric phases with high values of the spontaneous polarisation and reasonably short response times, thus opening interesting possibilities for display application. When the siloxane moiety contains no more than five silicon atoms, an antiferroelectric phase may occur also. For some of them, both ferro- and antiferroelectric mesophases are present. The ferroelectric phase appears when the molecules have an elongated conformation, whereas the antiferroelectric phase does appear when the molecules have a V-shaped conformation. Thus these compounds may develop two distinct smectic structures as a function of temperature, the first one corresponding to a synclinic one at high temperature, and the second one to an anticlinic one at lower temperature. Temperature variations of the tilt angle and layer spacing in the vicinity of the synclinic–anticlinic phase transition presented in this paper indicate that the transition between synclinic ferroelectric phase and anticlinic antiferroelectric phase is of the first kind, as it should be according to the symmetries of the two phases.

Up to now it has been assumed[7] that the V-shaped conformation possesses a lower energy in comparison with the linear conformation. In such a case, the anticlinic SmC_A phase is preferable to the synclinic SmC phase, the driving force for the synclinic–anticlinic SmC–SmC_A transition being determined by a difference of energy between the V-shaped and linear conformations. However, numerical calculations of the energy of different conformations of these bimesogenic molecules presented in the present paper indicate that there is no difference in energy between V-shaped and linear conformations regardless of the number of silicon atoms in the siloxane moiety.

This led us to develop a different microscopic model of the synclinic–anticlinic phase transition, which is driven indeed by a free energy difference between the two phases. Such a difference is determined by a strong polar ordering (or polar packing) of V-shaped molecules in the anticlinic phase. Thus the model explains why the anticlinic SmC_A phase is more stable than the synclinic SmC one, even if the energy of the V-shaped conformation is the same as that of the linear conformation. Moreover, it explains why the synclinic SmC phase is generally the higher temperature one, and why in some organosiloxane materials the anticlinic SmC_A phase is not present. It follows from the model that the tilt angle in the anticlinic phase should be weakly temperature dependent because it is mainly determined by the geometry of the V-shaped conformation. By contrast, the tilt angle in the synclinic phase is determined by relevant intermolecular interactions and thus it is expected to have a much stronger temperature dependence similar to that observed in conventional smectics C. The actual transition from the synclinic to the anticlinic phase occurs when the tilt angle of the synclinic phase is sufficiently close to its value in the anticlinic phase determined by molecular geometry. The tilt in the synclinic phase remains to be lower than that in the anticlinic one, and there is a discontinuity of the tilt angle at the transition point related to the first order nature of the synclinic–anticlinic phase transition. These qualitative features of the transition are confirmed by our measurements presented in this paper. Further experimental work is required to validate the model in full.

Experimental

X-Ray patterns were recorded on samples filled in Lindemann glass capillaries with a setup based on a focalised linear $CuK\alpha_1$ beam produced with sealed tube and bent quartz monochromator. Patterns were systematically recorded as a function of temperature by using a home made oven controlled by an INSTEC unit (residual temperature fluctuations of $\pm 0.02\,^{\circ}C$) and an INEL CPS120 counter.

The dilatometry technique used to measure the molar volume as a function of temperature was developed by Kovacs[22] for the study of polymers, and afterwards applied

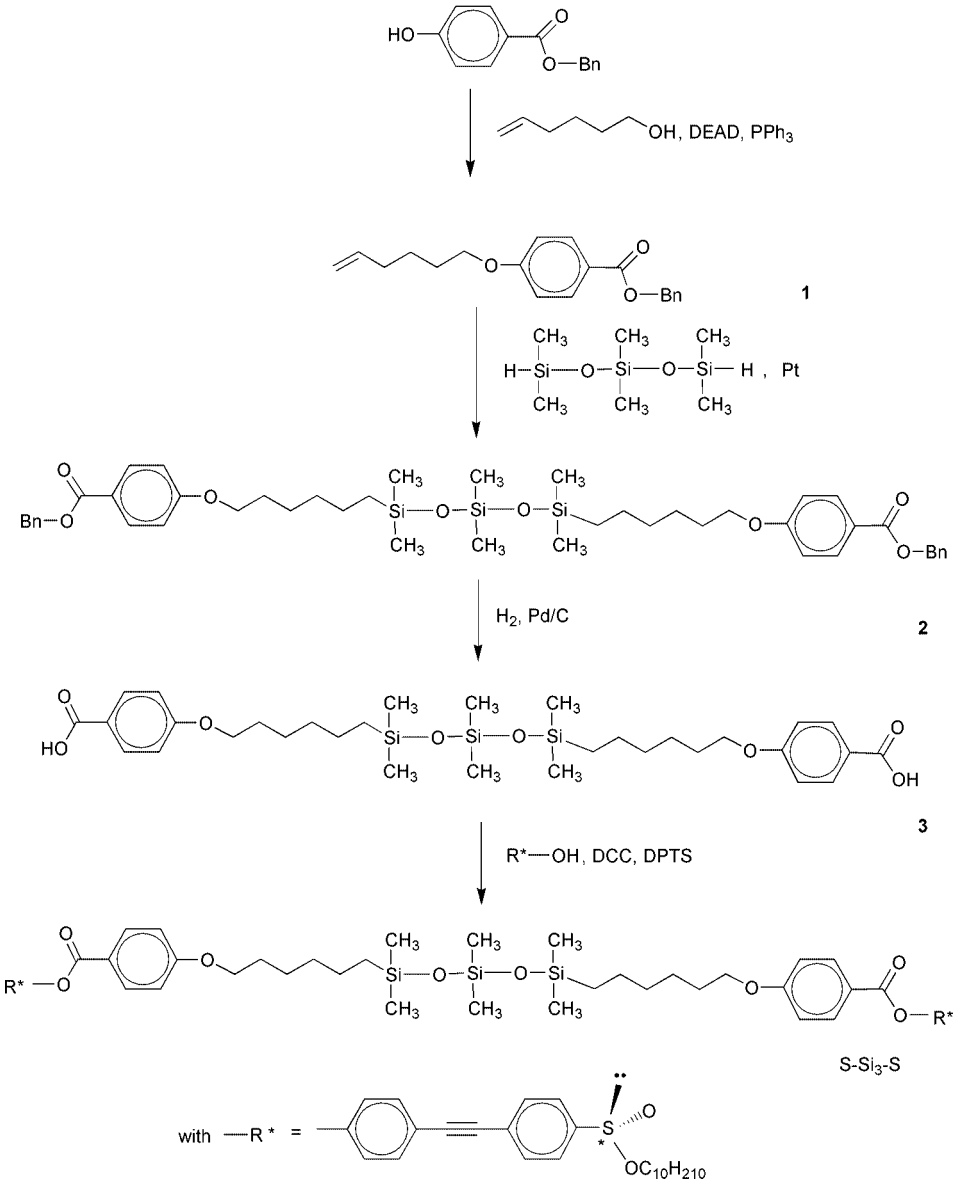
to liquid crystals.[23] The measurements were performed with a high precision home-built apparatus, automatically computer controlled, including data acquisition and temperature control $\pm 0.03\,^{\circ}C$.

Synthesis

The synthetic route of the preparation of the dimer S–Si_3–S is outlined in Scheme 2. The full detailed procedure for the preparation of the chiral precursor *n*-decyl (*R*)-(+)-4-[(4-hydroxyphenyl)ethynyl]benzenesulfinate can be found in previous publications.[24]

Benzyl 4-(hex-5-enyloxy)benzoate (1). To 10.95 g (48 mmol) of benzyl 4-hydroxybenzoate, 4.8 g (48 mmol) of hex-5-en-1-ol, and 13.4 g (51 mmol) of triphenylphosphine were introduced 150 ml of anhydrous tetrahydrofuran. To this mixture was added dropwise a solution of 8.0 ml (51 mmol) of diethyl azodicarboxylate in 20 ml of anhydrous tetrahydrofuran. The reaction mixture was kept under argon atmosphere and stirred overnight at room temperature. After evaporation of the solvent, the oily residue was purified by column chromatography on silica gel (dichloromethane–hexane). Further recrystallisation from isopropanol gave 10.4 g of white crystals (yield: 70%). Mp = 45 °C. ^{1}H NMR (200 MHz, $CDCl_3$, TMS), δ(ppm) 1.55 (m, 2H, CH_2=CH-CH_2-CH_2), 1.7 (m, 2H, CH_2-CH_2O), 2.1 (dd, 2H, CH_2=CH-CH_2), 4.02 (dd, 2H, CH_2-OAr), 5.0 (m, 2H, CH_2=CH), 5.34, (s, 2H, CH_2Ar), 5.8 (m, 1H, CH_2=CH), 6.9 (d, 2H, ArH), 7.45 (m, 5H, ArH), 8.03 (d, 2H, ArH).

Siloxane dimer with benzyl benzoate moieties (2). To a degassed solution of 7.13 g (23 mmol) of compound **1** in 50 ml of anhydrous toluene, were added 2.6 ml (10 mmol) of 1,1,3,3,5,5-hexamethyltrisiloxane. The solution was stirred under argon atmosphere and 1.6 mL of a solution of dicyclopentadienylplatinum(II) chloride in anhydrous dichloromethane (2 mg ml^{-1}, *e.g.* 400 ppm per silane function) were introduced. The reaction mixture was heated up to 70 °C for 24 hours. Then, toluene was evaporated and the residue was subjected to column chromatography on silica gel (dichloromethane–hexane) to give 7.6 g of colorless oil (yield: 92%). Anal. Calcd (found) for $Si_3C_{46}H_{64}O_8$: C 66.63 (66.69); H 7.78 (7.85). ^{1}H NMR (200 MHz, $CDCl_3$), δ(ppm) 0.05 (18H, Si-CH_3), 0.52 (t, 4H, Si-CH_2), 1.27–1.43 (m, 12H, Si-CH_2-$(CH_2)_3$-), 1.7 (m, 4H, CH_2-CH_2-O), 4.02 (t, 4H, CH_2-OAr), 5.34 (s, 4H, CH_2Ar), 7.45 (m, 10H, ArH), 6.9 (d, 4H, ArH), 8.02 (d, 4H, ArH).



Scheme 2

Siloxane dimer with benzoic acid moieties (3). A suspension of 450 mg of 5% palladium on activated carbon in 20 ml of anhydrous tetrahydrofuran was charged with a solution of 3.05 g (3.68 mmol) of benzyl benzoate-based siloxane dimer **2** in 15 ml of anhydrous tetrahydrofuran. Hydrogen gas was allowed to slightly bubble into the reaction mixture at room temperature. The reaction was run to completion as followed by thin layer chromatography. The mixture was filtered through Celite, then through a 0.45 mm pore size filter. The filtrate was finally concentrated and dried out without further purification to give 2.29 g of white crystals (yield: 96%). Mp = 133 °C. Anal. Calcd (found) for $Si_3C_{32}H_{52}O_8$: C 59.22 (59.52); H 8.08 (8.18). ^{1}H NMR (200 MHz, $CDCl_3$), δ(ppm) 0.05 (18H, Si-CH_3), 0.52 (t, 4H, Si-CH_2), 1.25–1.45 (m, 12H, Si-CH_2-$(CH_2)_3$-), 1.7 (m, 4H, CH_2-CH_2-O), 4.0 (t, 4H, CH_2-OAr), 6.9 (d, 4H, Ar-H), 8.0 (d, 4H, Ar-H).

Siloxane dimer with mesogenic moieties (S–Si_3–S). To a flask equipped with a $CaCl_2$ drying tube were introduced 1.24 g (1.91 mmol) of the acid-based siloxane dimer **3**, 1.68 g (4.21 mmol) of the phenolic chiral moiety, 170 mg (0.6 mmol) of catalyst 4-(dimethylamino)pyridinium toluene-*p*-sulfonate (DPTS) and 20 mL of anhydrous dichloromethane. The suspension was stirred for a few minutes then 870 mg (4.21 mmol) of dicyclohexylcarbodiimide (DCC) were added. The mixture was stirred for 2 days at room temperature. The precipitate of dicyclohexylurea was filtered off and the filtrate was washed with brine and water. After drying the solution over Na_2SO_4, the solvent was removed, and the residue chromatographed on silica gel (dichloromethane–hexane) to give 2.47 g of white wax-like product (yield: 92%). Enantiomeric excess, ee = 90% (*R* configuration), was determined by ^{1}H-NMR (200 MHz in $CDCl_3$) by using tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$, Aldrich, 98%] as chiral shift reagent. Anal. Calcd (found) for $Si_3C_{80}H_{108}O_{12}S_2$: Si 5.98 (5.89); C 68.14 (68.36); H 7.72 (7.75); S 4.55 (4.42). ^{1}H NMR (200 MHz, $CDCl_3$), δ(ppm) 0.07 (18H, Si-CH_3), 0.53 (t, 4H, Si-CH_2), 0.9 (t, 6H, CH_3), 1.30–1.60 (m, 40H, CH_2), 1.65 (m, 4H, SOO-CH_2-CH_2), 1.83 (m, 4H, CH_2-CH_2-OAr), 3.62 (m, 2H, SOO-CH_2), 4.05 [m, (4H, CH_2O) and (2H, SOO-CH_2)], 6.98 (d, 4H, ArH), 7.24 (d, 4H, ArH), 7.61 (d, 4H, ArH), 7.70 (d, 4H, ArH), 8.15 (d, 4H, ArH).

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