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Evidence for a New Ferroelectric Switching Liquid Crystalline Phase Formed by a Carbosilane Based Dendrimer with Banana-Shaped Mesogenic Units

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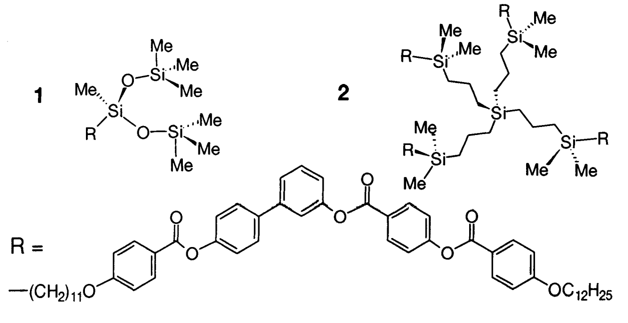
Materials with macroscopic polar order are of significant interest due to numerous potential applications in molecular electronic and photonics. Especially liquid crystalline (LC) materials with ferroelectric (FE) or antiferroelectric (AF) properties are of great interest, because they can be switched between different polar ordered states by electric fields. This was first reported for LC phases with tilted arrangement of chiral and nonracemic rodlike molecules (SmC*).[1] However, the discovery by Niori et al. that bent-core (banana-shaped) mesogenic compounds without molecular chirality can also organize in fluid smectic phases with polar order and the fact that such achiral molecules can additionally give rise to supramolecular chirality opened a new field in LC research.[2] Often, such molecules form layer structures in which the aromatic bent cores and the flexible terminal chains are segregated. Within these aromatic sublayers the bent rigid cores are mostly tilted (SmC) and additionally forced into a directed arrangement so that they point in the same direction, which leads to the polar order within the individual layers. Figures 1a and 1b give an overview over the possible phase structures. To escape from a macroscopic polar order in the bulk state, in most reported cases the bent direction in adjacent layers is antiparallel, so that the layer polarization alternates from layer to layer, leading to a macroscopic apolar AF structure (P_A).[3] The FE states (P_F) can be achieved after applying a sufficiently strong external electric field. Usually, these are not stable and rapidly relax back to the AF state after the electric field is switched off. However, recently it was found that a strong decoupling of the smectic layers, for example, by microsegregated oligosiloxane units (e.g., compound **1**) can produce a mesophase in which the ferroelectric states are stable also after switching off the field. Therefore a ferroelectric switching process was observed for such compounds.[4,5]



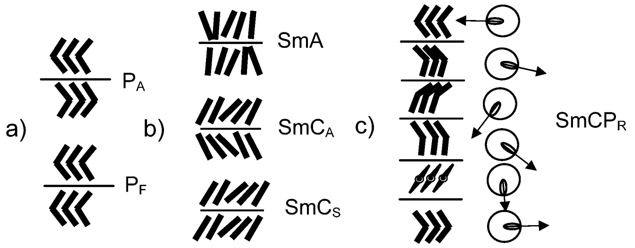


Figure 1. Organization of bent-core molecules in polar smectic phases: (a) antiferroelectric (P_A) and ferroelectric organization (P_F); (b) shows the projections of the molecules parallel to the bent direction (SmA = orthogonal aligned molecules; SmC_A = anticlinic tilted arrangement, the tilt-direction alternates from layer to layer; SmC_S = synclinic tilted arrangement, the tilt-direction in adjacent layers is identical); (c) proposed model of the molecular organization in the $SmCP_R$ mesophase (R = random) of compound **2** (side view and top view, the arrows indicate the direction of the polarization).

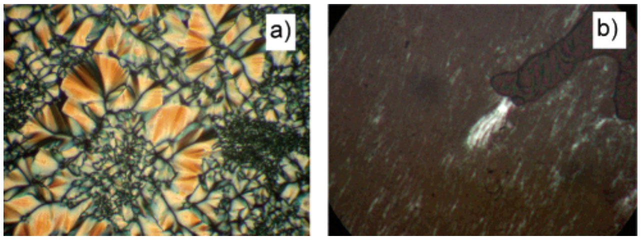


Figure 2. Textures (crossed polarizers) of the mesophase of compound **2** at 135 °C (a) as obtained by slow cooling from the isotropic liquid state and (b) after shearing.

Herein we report a novel organization of bent-core molecules. It was found for the molecule **2** which represents the first supermolecule in which bent mesogenic units are fixed to a dendritic carbosilane core.[6−8]

Polarized light optical microscopy (OM) and differential scanning calorimetry (DSC) indicate a liquid crystalline phase which is stable up to 139 °C (ΔH = 75.2 kJ mol^{-1}) and forms a glassy LC state on cooling below 47 °C, but no crystalline phase could be detected for this material. On cooling from the isotropic liquid state, the LC phase appears with a fanlike texture (Figure 2a). This texture disappears after shearing. In the new developing texture, optically isotropic areas are separated by birefringent oily streaks (see Figure 2b), which is very typical for homeotropically aligned SmA phases.

X-ray investigations of aligned samples confirm the presence of a layer structure (d = 4.1 nm). The layer distance is less than half the length of the molecules in a double-forked stretched conformation (as shown in the graphical abstract; L = 12.0 nm), but it is in the same order as that of compound **1**.[4] This points to an interdigitated structure in which the layer period is determined by the length of the mesogenic groups and the size of the carbosilane unit, whereby the mesogenic units are additionally tilted. The outer

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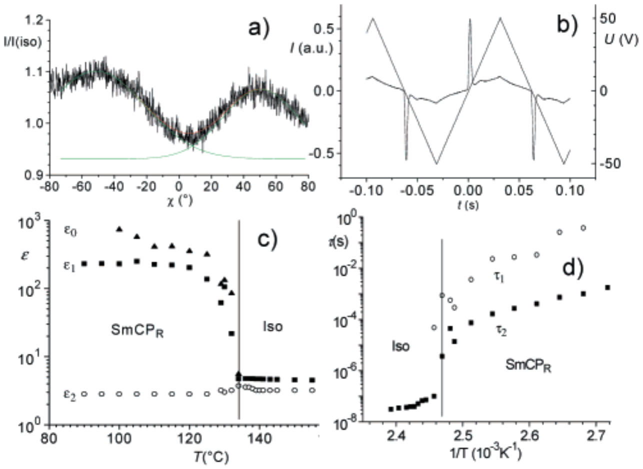

Figure 3. Characterization of the mesophase of **2**: (a) calibrated intensity distribution (χ-scan) of the crescent-like outer diffuse scattering at $T = 130$ °C; the point $\chi = 0$ was fixed by the position of the layer reflection; the complement of χ(max) to 90° reflects the tilt angle; (b) switching current response on applying a triangular wave voltage at 125 °C in a 5 μm noncoated ITO cell at a frequency of 8 Hz (c) dielectrictric constants and (d) relaxation times as obtained from the fit to two Cole−Cole equations as described in ref 9. The low-frequency relaxation process reduces the dielectric constant ϵ_0 to ϵ_1 with the time constant τ_1. This process is related to the dynamics of the superstructure. The second process (from ϵ_1 to ϵ_2, τ_2) is caused by the reorientation of the molecules about the long axis.[9]

scattering is diffuse with a maximum at $D = 0.47$ nm indicating a smectic phase without long-range in-plane order. There are four crescent-like diffuse scattering. Their maxima are located out of the equator (see Figure 3a), which confirms a *tilted* arrangement of the molecules with a tilt angle of ca. 40°.

Figures 3c and 3d show the results of the dielectric measurements on nonoriented samples. Despite of the relatively small polarity of the molecule, the dielectric constant ϵ_1 represents the highest value ever measured in a liquid crystalline phase formed by bent-core molecules. This can be explained by a strong positive dipole correlation of the lateral dipoles which also is responsible for the strong increase of the relaxation time τ_2 at the Iso/LC transition. The low-frequency relaxation (ϵ_0, τ_1) can be related to a polar superstructure on a larger length scale.

Electrooptical investigations were carried out in transparent sandwich type capacitor cells consisting of two indium−tin oxide (ITO) coated glass plates (EHC, Japan, thickness = 5 μm). The repolarization current in response to an applied triangular-wave field shows only one peak (Figure 3b), even at very low frequencies (0.05 Hz). This is a strong indication for a FE switching behavior. Although, well developed monodomains could not be grown, a bistable optical response on the applied electric field can be observed, which additionally confirms the ferroelectric switching process.

These investigations indicate a new mesophase type with unique properties. According to OM investigations, the ground state represents an optically uniaxial mesophase, but the polar order and the tilted organization of the molecules within the layers would require optical biaxiality. Uniaxiality could be expected if the polar axis slightly changes from layer to layer in a regular way, leading to a helical structure perpendicular to the substrate surfaces, as proposed for the chiral superstructures found in the mesophase of compound **1**.[4] However, no hint on the presence of such a chiral structure could be detected in the mesophase of the carbosilane **2**. Especially, no regions of different brightness can be found in the homeotropic aligned areas (Figure 2b) after slightly decrossing the polarizers as it was reported for **1**.[4] Therefore, it is most likely that compound **2** forms a smectic LC phase without long-range orientational correlation between the layers.[10] This means that the molecules are tilted and adapt a polar order within the layers, but the polar direction and the tilt direction change randomly ($SmCP_R$) from layer to layer as shown in Figure 1c. In this way the layer polarization is canceled out in the bulk sample and the phase should be optical uniaxial. On applying a sufficiently strong electric field, however, the polar directors of the layers align parallel to the field and a ferroelectric state results ($SmCP_F$). Once formed, it is additionally stabilized by interactions with the surfaces of the cell and therefore a ferroelectric switching process with a very high value of the spontaneous polarization ($P_S = 1400$ nC cm^{-2}) can be observed.

In summary, the reported material forms a new mesophase and has interesting properties for application. It is stable and has a low conductivity, and the liquid crystalline phase occurs over a broad temperature range. Furthermore, it can be frozen into the glassy state. It seems that the dendritic molecular structure is important for the special organization of the reported bent-core compounds. At first it fixes the bent-core units to each other which stabilizes the liquid crystalline phases, and leads to the formation of a glassy LC state. Second, it decouples the layers of the aromatic bent-cores to such an extent that the entropically favored AF (synclinic) interlayer correlation becomes disfavored.[4] On the other hand, intermolecular interactions which are responsible for the anticlinic (FE) correlation seem not to be strong enough to dominate the mesophase structure. Therefore, in the ground state the macroscopic polar order is canceled, but the switching into the ferroelectric organization can be achieved by applying external electric fields. Once formed, the ferroelectric states seems to be stable under the applied experimental conditions and can be switched between the different polarization states.

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Supporting Information Available: Analytical data of **2**. This material is available free of charge via Internet at http://pubs.acs.org.

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