Quadratic electroclinic effect in bent-core mesogens

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The electroclinic effect, an electrically induced tilt, is well known for chiral liquid crystal materials. We report a comparable phenomenon in achiral mesogens. In contrast to conventional rod-shaped molecules with $D_{\infty h}$ symmetry, bent-core mesogens have C_{2v} symmetry, which favours both polar and smectic order. This tendency is accounted by a steric moment exerted by the bow of the mesogen, which hinders the rotation of the molecules about their long axes. In contrast to conventional LC ferroelectrics, chirality is not required to sustain the polar order in the mesophases of bent-shaped molecules. A spontaneous breaking of the achiral symmetry, however, does take place in the polar smectic C phase (SmCP) [1]. But in the vicinity of the transition and into the SmA phase the chiral terms (for instance, the linear coupling term between the tilt and the polarization) are forbidden in the free energy expansion and typical chiral effects characteristic for, say, the SmA* phase cannot be expected. On the other hand, the second-order coupling term between the tilt and polarization is allowed and is able to give rise to novel electro-optic effects. It can be illustrated by a simple Landau-type model with order parameters tilt θ and polarization P. The free energy three types of terms: expansion in powers of θ, expansion in powers of P and the coupling term:

$$f = a_0(T - T_\theta)\theta^2 + b\theta^4 + \alpha_0(T - T_P)P^2 + \beta P^4 - \Omega(P\theta)^2 - PE$$

The temperatures T_θ and T_P are the transition temperatures for SmA-SmC and paraelectric-ferroelectric transitions, respectively. The negative coupling term $-\Omega(P\theta)^2$ originates from the excluded-volume interaction that favours polar order in the tilted state. This effect can be expected to be particularly strong when the constituting mesogens are bent. The equilibrium equations obtained by minimization of the free-energy show some interesting phenomena:

a) In the non-polar SmA phase, the electric field E induces tilt above a certain threshold value E_{th}. This effect is equivalent to a field-induced increase of the SmA-SmC transition by $\Delta T = \Omega P^2 / a_0$
b) The electric field leads to a continuous increase of the tilt angle θ in the SmC phase

In our research, we have shown that theses effects indeed take place in compounds with bent mesogens [2]. We used polarizing microscopy to estimate the apparent tilt angle in sandwich cells filled with the LC-compounds. The polar order has been detected using Second Harmonic Generation (SHG) measurements in the same cells. Electric field induced tilt in SmA and SmC phases can be easily seen in Fig. 1,2. Both effects of the quadratic coupling have been confirmed experimentally. In contrast to the linear electroclinic effect in the SmA* phase, our effect has a pronounced threshold behaviour. The threshold field diminishes as the temperature reaches the SmA-SmC transition.

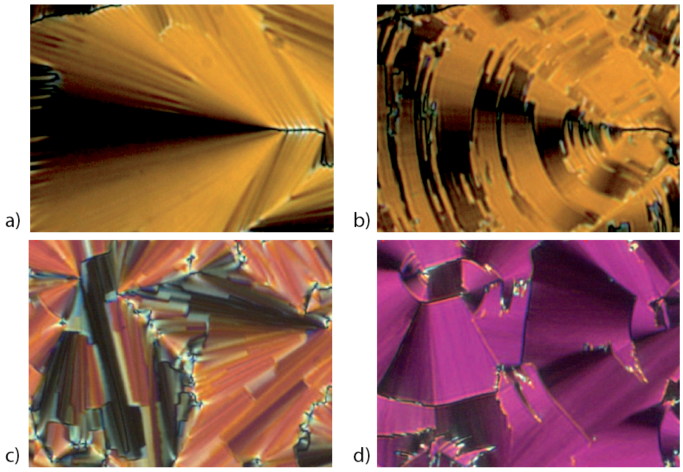

Figure 1: Polarizing-microscopy textures: a) SmA phase below threshold (E = 0V/μm) and b) a field induced SmC phase (E = 20V/μm), T = 115°C; c) initial texture of the SmC phase (E = 0V/μm) and d) a field induced texture (E = 24V/μm), T = 112°C. The polarizers are vertical and horizontal.

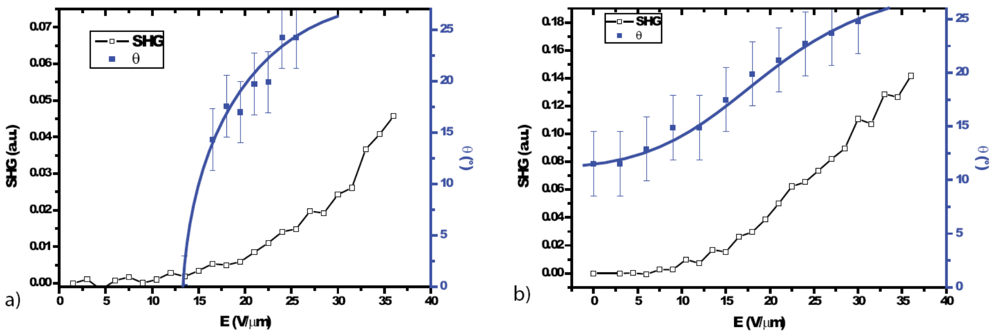

Figure 2: Dependence of the optical tilt $\theta(E)$ and the intensity of the SHG signal on the electric field in a) SmA T = 115°C and b) SmC T = 110°C phases. The connecting lines are for eye-guide only.

References

(1) D. R. Link et al, *Science*. **1997**, *278*, 1924

(2) A. Eremin, S. Stern, R. Stannarius, *Phys. Rev. Lett.* **2008**, *101*, 247802