Molecular length distribution and the formation of tilted smectic phases

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In the recent discovery of electroclinic effect amplification we reported (1) that the electroclinic effect in the chiral smectic A* (SmA*) phase of a phenylpyrimidine host is amplified by a factor of three after a small amount of another phenylpyrimidine which has substantially higher molecular length (~ 46 Å) than the host (~ 26 Å) was added. This raises the general question of how the mixing of homologues differing only in molecular length (and thus making the distribution of molecular length extremely bimodal) changes the structure and properties of the nematic and the SmA phases and its (possible) tilting transition to SmC.
In a naive model, the nematic phase is expected – due to the absence of translational order – to be the ideal LC phase for accommodating molecules of substantially different lengths. On the other hand the smectic phases – due to their layer structure – seem to be unsuited for these molecules. Comparing SmC and SmA, the SmC phase seems to be better suited to accommodate molecules of different lengths on account of the tilting of the molecules.
For several mixtures of liquid crystalline phenylpyrimidines and phenylpyridazines we have found:

- For all the mixtures where one of the pure compounds exhibits a nematic phase, it disappears quickly with increasing mole fraction of the other compound.
- Surprisingly, the temperature range of the smectic states is preserved. It even becomes broader in some cases.
- We observed that over a broad temperature range in the phase diagram the SmC phase is completely lost even though SmC is the dominating phase in the pure compounds. Instead of SmC, now the non-tilted SmA phase is stabilized.
- In the boundary area before the SmC phases disappear, they show exceptionally small tilt angles (maximum tilt < 10°).

These surprising results are of general interest for the understanding of the structure and dynamics of smectic phases and will be discussed in terms of present theoretical models.

(1) C.S. Hartley, N. Kapernaum, J.C. Roberts, F. Giesselmann, R.P. Lemieux, *J.Mater.Chem* **2006**, *16*, 2329.