The connection between nanosegregation and de Vries behaviour in ferroelectric liquid crystals

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Most 'de Vries-type' materials feature nanosegregating structural elements such as siloxane end-groups which strongly promote smectic layering. However, the correlation between these two effects is not understood yet.¹ Lemieux et al. recently showed that nanosegregating SmC*-mesogens with a trisiloxane end-group exhibit de Vries-type behaviour due to their end-groups.² We now further investigated the ferroelectric liquid crystalline phase transitions in these compounds and in two similar substances by means of calorimetry, X-ray and high temperature resolution electro-optical measurements. In all cases the layer spacing in the SmA*-phase is 1.2 times larger than the molecular length, which is consistent with a partially double layered structure. All substances also exhibited first order SmC*-SmA* phase transitions and hence very high values of the tilt angle. In two cases the tilt angle saturates while the spontaneous polarization continues to grow with convex curvature at decreasing temperature. This behaviour has not been described in literature so far, and was interpreted in terms of molecular theory. All substances show a substantial de Vries character in the range of 40%, which is a reasonably high value as other non-siloxane analogues exhibit only 20% de Vries character. Also, for the latter materials, second order phase transitions are common, while the siloxane materials exhibit first order SmA*-SmC* phase transitions. These results clearly suggest that nanosegregation is a powerful tool to induce de Vries behaviour and to promote first order SmA*-SmC* phase transitions.

References

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- (2) J. C. Roberts, N. Kapernaum, F. Giesselmann, M. D. Wand, R. Lemieux, *J. Mater. Chem.*, **2008**, *18*, 5301.