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Preliminary communication

Ferroelectric polysiloxane liquid crystals with 'de Vries'-type smectic A*–smectic C* transitions

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We report preliminary results of optical and small angle X-ray scattering (SAXS) experiments on the smectic A*−smectic C* transition in two ferroelectric liquid crystalline polysiloxanes. Although the optical tilt angle in the SmC* phases reaches values up to 30°, temperature-dependent SAXS measurements clearly reveal that the smectic layer spacing is basically conserved during the A*–C* transition as well as in the subsequent C* phase. Connected with the A*–C* transition we further observed a significant increase in birefringence, hence reflecting an increase of orientational order. The practical absence of layer shrinkage and the enhanced orientational ordering are consistent with the de Vries diffuse cone model of smectic A−smectic C transitions.

Many smectic A (SmA) phases undergo second-order transitions into the tilted smectic C (SmC) phases. When the temperature is lowered below the critical temperature T_c of the SmA–SmC transition, the optic axis, measuring the director **n**, starts to continuously tilt away from the smectic layer normal **k** [1]. The temperature-dependent angle now included between **k** and **n** defines the so-called 'optical tilt angle' $\theta_{opt}(T)$ of the SmC phase. In the majority of SmA–SmC transitions the appearance of the optical tilt is connected with a substantial shrinkage of the smectic layer thickness d, the origin of which is explained by a molecular tilt within the smectic layers of the same magnitude as the optical tilt at temperatures $T<T_c$. Assuming that the mesogenic molecules simply behave as rigid rods, the smectic layer spacing d_C of the SmC phase then decreases as:

$$d_C = d_A \cos\theta_{opt} \tag{1}$$

where d_A denotes the smectic layer thickness of the SmA phase. As a result, the smectic layers are thinner in SmC than in SmA and the layer spacing d_C essentially becomes temperature-dependent through the temperature dependence of $\theta_{opt}(T)$. The exact connection between director tilting and layer thickness is, however, still not fully understood and different materials show varying degrees of shrinkage during the tilting transition.

During the last few years the issue of smectic layer shrinkage has received considerable interest due to the recognition of its relevance in the performance of electro-optic devices based on chiral tilted smectics, i.e. ferroelectric SmC* and antiferroelectric SmC_a^* liquid crystals (FLCs, AFLCs). In these devices the competition between surface-anchoring and layer shrinkage induces the formation of so-called 'chevrons' which are folding instabilities of the smectic layer structure where domains of opposite fold direction are mediated by 'zigzag' walls [2]. These zigzag defects and the reduced effective switching angle in the chevron configuration considerably degrade the brightness and contrast of surface-stabilized FLC and AFLC devices. These technical problems proved to be a severe obstacle in the display application of chiral smectics and created a strong need for advanced materials with negligible layer shrinkage at the SmA*–SmC* transition. Indeed, since 1989 a few SmA*–SmC* materials have been reported

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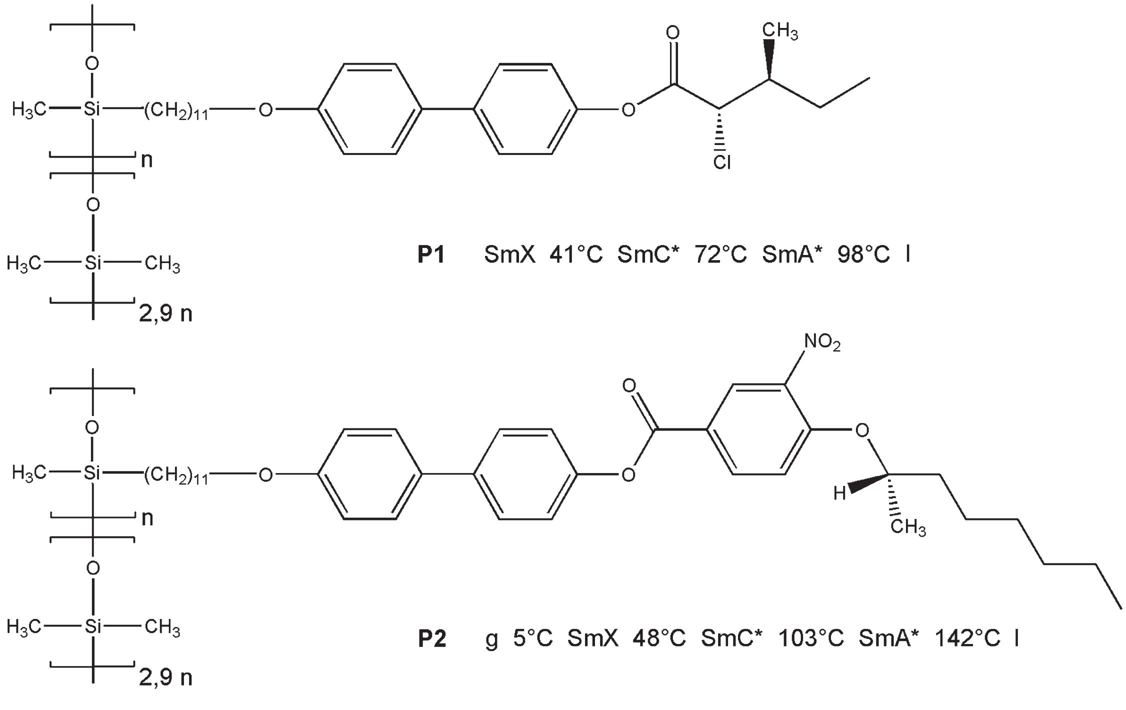
to exhibit little or no shrinkage of the layer spacing in the SmC* state [3–7].

Probably the most important contribution to the understanding of how it is possible that some materials do not show shrinkage at the SmA*–SmC* transition returns to the early ideas of de Vries who recognised that the non-perfect orientational order present in all SmA phases is associated with a substantial molecular tilt of about 20°–30° on average [8], depending on the details of the orientational distribution function. The absence of a macroscopic optical tilt necessarily requires randomly distributed directions of molecular tilt in the SmA state. The tilting transition to SmC can, in this model, occur simply through an ordering of the molecular tilt directions at temperatures below T_c. This kind of 'de Vries transition' is distinguished from regular SmA–SmC transitions by two characteristic properties:

1. The de Vries transition changes the distribution of the molecular tilt *directions*. Since the *magnitude* of molecular tilt remains basically unchanged, this process in itself produces no change of the layer thickness, i.e. $d_C \approx d_A \approx$constant.
2. The ordering of molecular tilt directions enhances the orientational order along the director **n** and, thereby, leads to considerable increase in birefringence Δn during the de Vries-type SmA–SmC transition, i.e. $\Delta n_C > \Delta n_A$.

In this communication we report experimental evidence for de Vries-type SmA*–SmC* transitions in two ferroelectric liquid crystalline polysiloxanes. This is, to our knowledge, the first time that de Vries behaviour is explicitly reported for ferroelectric liquid crystalline side group polymers.

In chiral smectics of the de Vries-type the electroclinic effect (i.e. the change in the optical tilt induced by an electric field) is expected to be rather high, since the optical tilt can be changed without affecting the smectic layer thickness [4, 9]. In working with ferroelectric polysiloxanes [10–13] there are especially two–better characterized–polymers (**P1** and **P2**) for which this criterion applies. Both are polysiloxane copolymers and show the phase sequence: higher ordered smectic (SmX), chiral smectic C* (SmC*), chiral smectic A* (SmA*) and isotropic (I). The Landau coefficients have been determined for polymer **P1** [10], as well as for the slightly modified crosslinkable polymer [11]. For **P2** high field-induced SmA* tilt angles up to $\theta_{opt} = 20°$ at $20\,V\,\mu m^{-1}$ are reported [12]. In addition it is possible to induce ferroelectric switching in the SmA* phase of **P2** by increasing the switching voltage (see figures 8 and 9 in ref. [13]). Therefore both polymers were studied more closely. They were synthesized according to [14] by hydrosililation of the appropriate mesogen with a terminal double bond and showed the phase transitions specified.



Formula P1/P2.

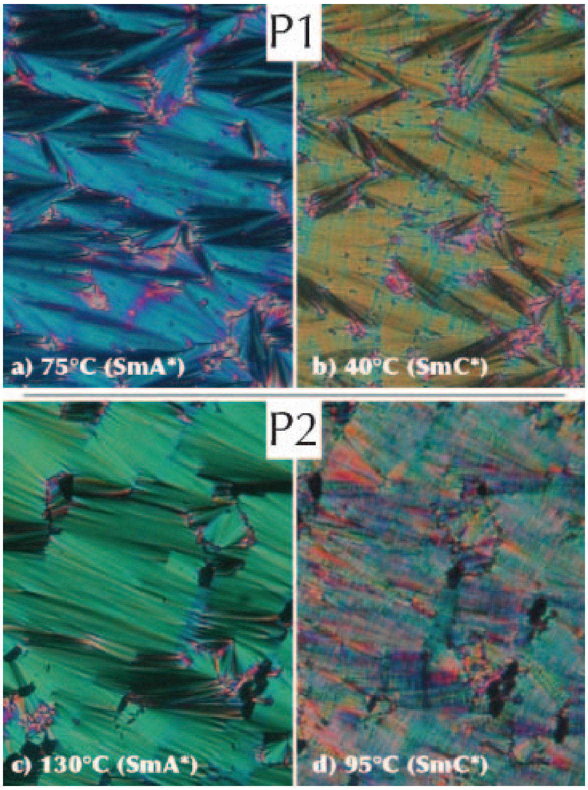


Figure 1. Textures of the SmA* (left column *a*, *c*) and SmC* (right column *b*, *d*) phases of 10-µm planar samples with **P1** (top row) and **P2** (bottom row). Note the distinct increase in birefringence on cooling **P1** into the non-helical SmC* phase (*b*). The **P2** sample is partially helical in the SmC* phase (*d*) and therefore exhibits helical regions, where the birefringence is close to that of the SmA* phase (blue areas), as well as non-helical regions where the birefringence is considerably higher (red areas).

It is typical for a de Vries-type SmA*–SmC* transition that the order parameter in the SmA phase is lower than in the SmC* phase. To test whether this applies qualitatively, texture observations between crossed polarizers are sufficient. For this purpose commercially available E.H.C. cells were filled with **P1** or **P2** in the isotropic phase by capillary forces. The alignment of the liquid crystals was improved by repeated cooling and heating cycles in the range of the phase transition (SmC*–SmA*) using a strong electric field (200 V, 2 Hz). The results presented in figure 1 show that the order parameter really decreases at the phase transition to the SmA phase. Filled into 10-µm planar-aligning cells, both polymers show SmA* textures, the interference colour of which is between blue and green (for **P1** with a two-ring mesogen it is more towards blue, corresponding to a lower birefringence and, hence, a lower order parameter value). On cooling both polymers into the SmC* phase the colour becomes more red, clearly showing that the birefringence increases as expected for an increasing order parameter value.

To obtain a direct proof of the de Vries-like behaviour, the change in the smectic layer thickness was determined by temperature-dependent small angle X-ray scattering (SAXS), using Cu K$_\alpha$ radiation, a Kratky-compact X-ray camera (Paar, Graz) and a position-sensitive electronic detector (Braun, Munich). The preparation of the polymer was carried out in a Mark capillary (diameter 0.7 mm). The tube was filled with isotropic melt, then the samples were exposed at different temperatures for 10 min. Selected scattering profiles from the **P2** sample are presented in figure 2,

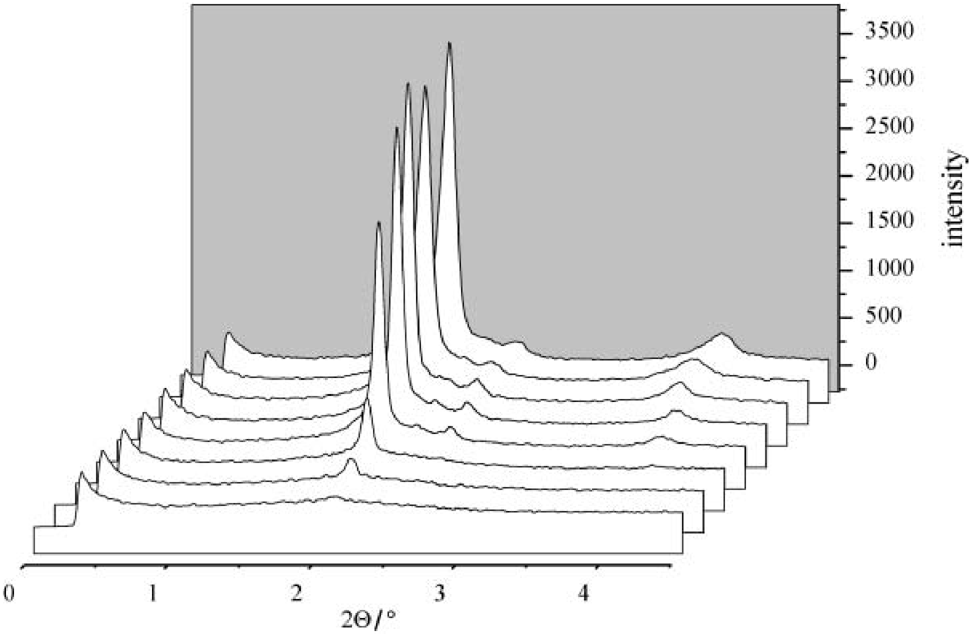


Figure 2. Temperature-dependent scattering profiles of **P2**. From back to front: 75, 94, 130, 142, 145, 152, 156 and 160°C.

the corresponding layer spacings obtained for **P2** and **P1** are seen in figure 3. Several results are evident. Firstly, the smectic layer reflection does not disappear directly at the phase transition into the isotropic phase (figure 2). Even 10° above the clearing temperature some hints of a short-range layered ordering can still be seen. This may be a result of the microphase separation between polysiloxane chains and mesogenic groups, which is typical for copolysiloxanes [13, 15]. This remaining order in the isotropic phase may explain the observation that free standing films from these polymers are best drawn in the isotropic phase [16]. The next observation concerns the layer spacing, the variation of which is very small in the SmC* phases. The minimum layer spacing in the SmC* phase of **P1** is only 2% (0.8 Å) smaller than the maximum layer spacing observed in the SmA* phase at the onset of the transition to SmC*. The minimum SmC* layer spacing of **P2** differs by no more than 3.5% (1.7 Å) from the maximum SmA* layer spacing. However, on heating through the SmA* phases the layer spacing decreases strongly, with a drop of nearly 3 Å for **P1** and **P2** before the transition into the isotropic phase is reached.

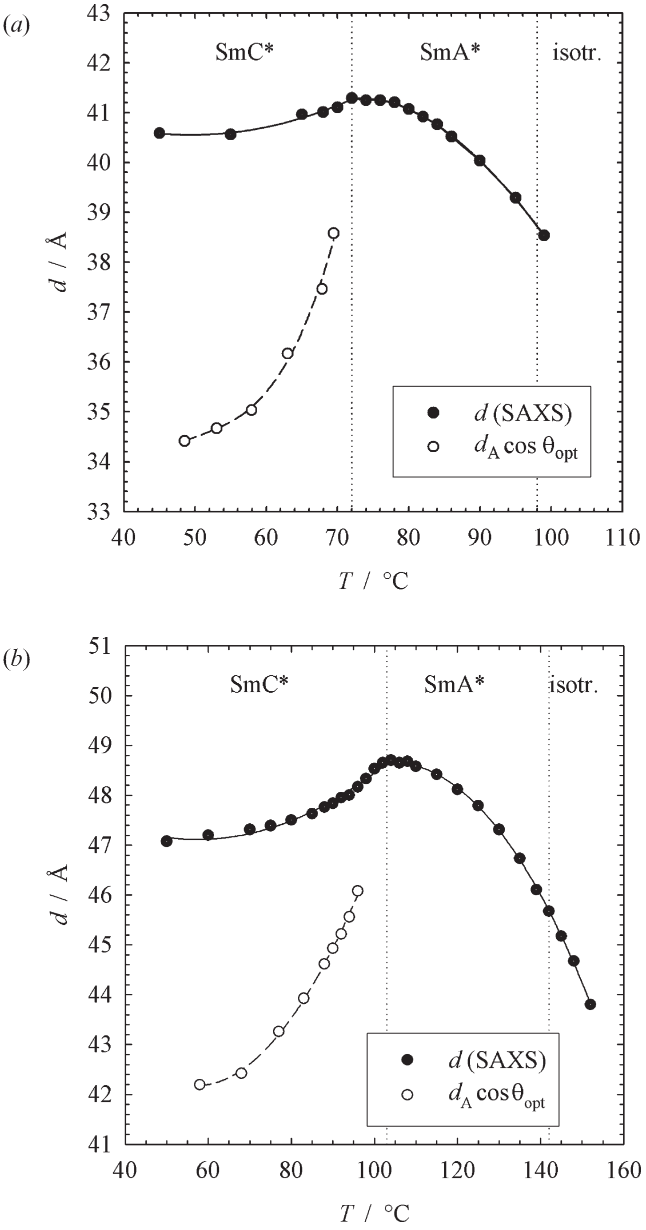


Figure 3. Temperature-dependent layer spacing d in the polysiloxanes (*a*) **P1** and (*b*) **P2**. The actual d-values experimentally observed by small angle X-ray scattering (closed symbols) are compared with the hypothetical values (open symbols) which are expected from the optical tilt angle θ_{opt} in the SmC* state according to equation (1).

The very small change of the layer spacing at the SmA*–SmC* transition is contrasted by a large optical tilt angle, which saturates at about 33° for **P1** (at 50°C) and 30° (at 60°C) for **P2** [13, 17]. The expected SmC* layer spacing estimated from equation (1) on the basis of these optical tilt angle data is included in figure 3. From the optical data a drop of 6.7 Å for **P1** and about 6.5 Å for **P2** would be expected on cooling the SmA* phase into the tilted SmC* phase. Compared with these estimates, the layer shrinkage actually observed in the X-ray measurements is truly negligible.

Based on these data we are convinced that polymers **P1** and **P2** present the first examples of polymers with a 'de Vries type' SmA*–SmC* transition. Based on their molecular structure, which promotes a microphase separation between mesogens and polysiloxane chains [13, 15], this seems reasonable, because the polysiloxane sublayers should reduce inter-layer orientational coupling between the mesogenic sublayers. Thus a disorder transition with regard to the tilt direction should become more likely. In this context the copolysiloxanes presented here correspond well to various low molar mass systems with siloxane or perfluorinated tails [5–7, 18].

Finally this result should be discussed in relation to the observation of a giant electrostrictive effect in LC-elastomers prepared from **P1** [19]. This effect was concluded based on interferometric experiments on free-standing films, which basically measure the optical path length, i.e. the product of ordinary refractive index n_0 and film thickness Δz. As the birefringence and thus n_o of smectics with de Vries-type tilting changes during application of an electric field, these data have to be reanalysed.

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References

[1] Taylor, T. R., Arora, S. L., and Fergason, J. L., 1970, *Phys. Rev. Lett.*, **25,** 722.

[2] Rieker, T. P., Clark, N. A., Smith, G. S., Parmar, D. S., Sirota, E. B., and Safinya, C. R., 1987, *Phys. Rev. Lett.*, **59,** 2658.

[3] Takanishi, Y., Ouchi, Y., Takezoe, H., Fukuda, A., Mochizuki, A., and Nakatsuka, M., 1990, *Jpn. J. appl. Phys. 2*, **29,** L984.

[4] Giesselmann, F., Zugenmaier, P., Dierking, I., Lagerwall, S. T., Stebler, B., Kaspar, M., Hamplova, V., and Glogarova, M., 1999, *Phys. Rev. E*, **60,** 598.

[5] Radcliffe, M. D., Brostrom, M. L., Epstein, K. A., Rappaport, A. G., Thomas, B. N., Shao, R. F., and Clark, N. A., 1999, *Liq. Cryst.*, **26,** 789.

[6] Spector, M. S., Heiney, P. A., Naciri, J., Weslowski, B. T., Holt, D. B., and Shashidhar, R., 2000, *Phys. Rev. E*, **61,** 1579.

[7] Lagerwall, J. P. F., Giesselmann, F., and Radcliffe, M. D., 2002, *Phys. Rev. E*, **66,** 031 703; Giesselmann, F., Lagerwall, J. P. F., Andersson, G., and Radcliffe, M. D., 2002, *Phys. Rev. E*, **66,** 051 704.

[8] De Vries, A., Ekachai, A., and Spielberg, N., 1979, *Mol. Cryst. liq. Cryst. Lett.,* **49,** 143; de Vries, A., 1979, *J. chem. Phys.*, **71**, 25.

[9] Selinger, J. V., Collings, P. J., and Shashidhar, R., 2001, *Phys. Rev. E*, **64,** 061 705.

[10] Kocot, A., Wrzalik, R., Vij, J. K., Brehmer, M., and Zentel, R., 1994, *Phys. Rev. B*, **50,** 16 346.

[11] Brehmer, M., Zentel, R., Giesselmann, F., Germer, R., and Zugenmaier, P., 1996, *Liq. Cryst.*, **21,** 589.

[12] Poths, H., Andersson, G., Skarp, K., and Zentel, R., 1992, *Adv. Mater.*, **4,** 792.

[13] Poths, H., and Zentel, R., 1994, *Liq. Cryst.*, **16,** 749.

[14] Wischerhoff, E., and Zentel, R., 1994, *Macromol. Chem. Phys.*, **195,** 1593.

[15] Diele, S., Oelsner, S., Kuschel, F., Hisgen, B., Ringsdorf, H., and Zentel, R., 1987, *Makromol. Chem.*, **188,** 1993.

[16] Reibel, J., Brehmer, M., Zentel, R., and Decher, G., 1995, *Adv. Mater.,* **7,** 849; Schüring, H., Stannarius, R., Tolksdorf, C., and Zentel, R., 2001, *Macromolecules*, **34,** 3962.

[17] Gebhard, E., and Zentel, R., 2000, *Macromol. Chem. Phys.*, **201,** 911.

[18] Carboni, C., Mehdi, R., George, A. K., al-Harthi, S. H., and Naciri, J., 2002, in Proceedings of the International Liquid Crystal Conference, Edinburgh, UK (in the press).

[19] Lehmann, W., Skupin, H., Tolksdorf, C., Gebhard, E., Zentel, R., Krüger, P., Lösche, M., and Kremer, F., 2001, *Nature*, **410,** 447.