

Thermally Induced Aging in Bicyclohexane Compounds and its Influence on the N – SmB Phase Transition and Interface Morphology

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Although the alkyl-bicyclohexyl-carbonitrile compounds supposed to be chemically stable, an aging behaviour was observed which strongly influences the growth of smectic B germs in the undercooled nematic phase. The aging also results in a broadening of the phase coexistence temperature ranges and in a saturating shift of phase transition temperatures with a temperature dependent dynamics. The phenomenon has been characterized by polarizing microscopy and DSC, and an experimental evidence has been given that the air atmosphere is responsible for the thermally induced ageing.

Keywords: pattern formation; phase transitions; liquid crystals

INTRODUCTION

Interfacial pattern forming processes at phase transitions in liquid crystals have attracted a considerable attention in the last years^[1]. Liquid crystals possessing a first-order nematic (N) - smectic B (SmB) phase transition are especially suitable for such studies, since a large number of different morphologies of the phase boundary has been observed^[2, 3, 4, 5, 6, 7].

In general, the study of the interfacial pattern forming processes at phase transitions requires a high precision control of the undercooling and hence, the accurate value of the N - SmB phase transition temperature (T_{NS}). Thus

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such measurements should be carried out on substances with high chemical stability. Compounds of the 4'-alkyl-[1,1'-bicyclohexyl]-4-carbonitrile homologous series (CCH_n, n=3-5) are stated to meet this requirement^[8, 9]. Studying smectic growth in these substances, nevertheless, a thermal aging of the samples was detected. This phenomenon manifested itself in a series of effects such as a decrease of T_{NS} , a broadening of the temperature range of phase coexistence, some unusual (reentrant) phase sequences and a change of the growth properties (rate and morphology). Though the CCH_n homologous series has been studied extensively^[10, 11, 12, 13, 14, 15], such a phenomenon has not yet been reported. In order to reveal the background of this process, we studied the correlation between aging and the thermal prehistory of the sample by polarizing microscope and DSC.

OPTICAL INVESTIGATIONS

Aging and Pattern Formation

Anisotropy of the surface tension is one of the most important physical parameters governing the interfacial pattern forming processes at phase transitions^[1, 16, 17]. Experimentally one can obtain information on this parameter by determining the shape of the interface in thermal equilibrium (in our case the shape of the SmB germ surrounded by the N phase at T_{NS})^[16]. The size of the smectic germ is very sensitive to temperature variations since it grows below T_{NS} and melts if the temperature is above T_{NS} .

Such measurements were carried out on planarly oriented cells using three compounds from the CCH_n (n=3,4,5) homologous series^[8, 9]. All these substances possess a monotropic SmB phase. The thermal equilibrium shape of the N · SmB interface can be approached in a few hours. For the investigations a polarizing microscope was used equipped with a hot stage (Instec) having a thermal stability of $\pm 3mK$.

Measurements have shown that a smectic germ can be kept at a constant size only if the temperature of the cell is adjusted around a monotonically decreasing value as time elapses, which indicates a continuous decrease of T_{NS} . The rate of this aging depends on the thermal prehistory of the cell.

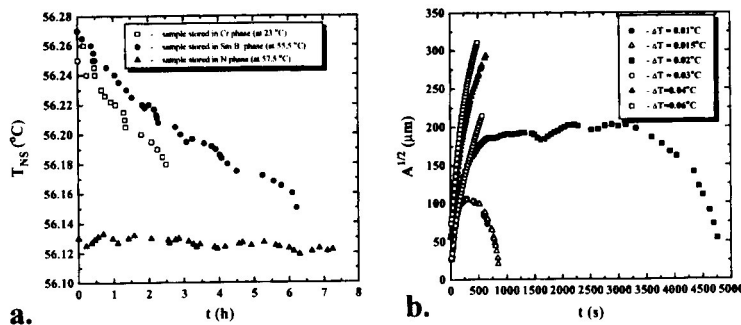


FIGURE 1: a. Temporal drift of T_{NS} depending on the thermal prehistory of CCH3 cells. b. Time evolution of the linear size (square root of the area A) of a smectic B germ in the nematic phase of CCH3 at various undercoolings. The initial size of the germ was $A^{1/2} \approx 20\mu m$ for all undercoolings.

Fig. 1a. presents data on CCH3 samples having been stored after preparation in the crystalline (Cr), SmB (at $T_{NS}-1^{\circ}C$) and N phase (at $T_{NS}+1^{\circ}C$), respectively, one day long before the measurement. The temporal drift of T_{NS} is the largest (about $-0.03^{\circ}C/hour$) when starting from the Cr phase and only slightly smaller (about $-0.02^{\circ}C/hour$) if the cell was stored in the SmB phase. Storing the cell in the N phase for one day resulted in a change (decrease) of the initial value of T_{NS} by about $0.15^{\circ}C$ accompanied with a reduction of the drift (to about $-0.001^{\circ}C/hour$) – see Fig. 1a. These observations indicate that the change of T_{NS} occurs mainly in the N phase.

Another indication of aging emerged from studies of the smectic growth at low undercoolings. Fig. 1b. shows the temporal evolution of the linear size $A^{1/2}$ of a smectic germ (A – area of the germ) for a CCH3 sample at various undercoolings in the range of $\Delta T = T_{NS} - T = 0.01 - 0.06^{\circ}C$. It demonstrates the gradual decrease and a sign inversion of the growth rate for $\Delta T \leq 0.02^{\circ}C$ as time elapses. This leads finally to complete disappearance of the smectic object, that indicates that T_{NS} decreased by more than ΔT during the observation.

Reduction of the phase transition temperature is not the only consequence of aging. The morphology of patterns observed during smectic

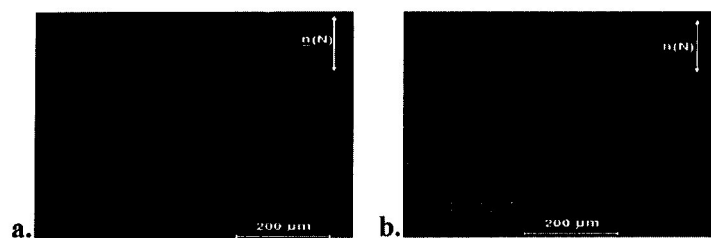


FIGURE 2: Planar SmB germ grown in the planar nematic phase of CCH3 at an undercooling of $\Delta T = 1.0^\circ\text{C}$. (a) Fresh sample, tip velocity is $v = 510\mu\text{m/s}$; (b) aged sample, tip velocity is $v = 17.5\mu\text{m/s}$.

growth in aged samples may differ from those seen in fresh ones. Comparing the patterns of spontaneous nucleation^[6] in CCH3 at high undercooling (Fig. 2., $\Delta T = 1.0^\circ\text{C}$) one can see the reduced side branching activity of the aged cells (longer wavelength, without second generation of side branches). This is accompanied by an enormous decrease of the tip velocity of the dendrites. However, the symmetry of the pattern is preserved.

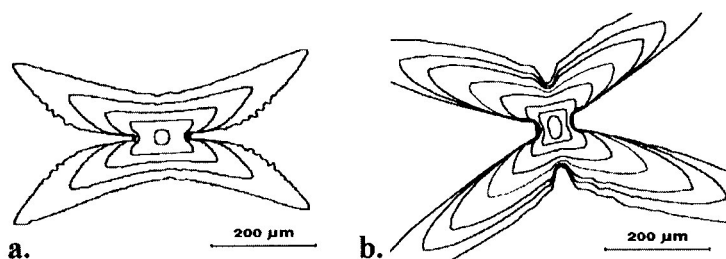


FIGURE 3: Growth of a planar SmB germ in the planar nematic phase of CCH3 at an undercooling of $\Delta T = 0.3^\circ\text{C}$. Contours of the same germ at various instants during its growth were copied on top of each other. (a) Fresh sample, $t = 0.6\text{s}, 3.3\text{s}, 5.7\text{s}, 7.5\text{s}, 10.1\text{s}$; (b) aged sample, $t = 0.6\text{s}, 43.4\text{s}, 71.5\text{s}, 116.0\text{s}, 182.6\text{s}, 304.4\text{s}, 420.6\text{s}, 692.0\text{s}$.

The decrease of the growth velocity in aged samples can be observed at lower undercooling ($\Delta T = 0.3^\circ\text{C}$) as well (Fig. 3.), but in this case it is accompanied by morphological changes too. In aged samples the faceted side

of the germ becomes unstable according to a different mechanism, instead of a uniform roughening (Fig. 3a.) a localized instability appears (protrusion, Fig. 3b). We note here that the morphology of this latter type has already been observed previously in an other substance which is supposed to be less stable chemically^[2]. Similar 'grooves' on facets have been observed in directional solidification experiments too^[17]. The formation of the grooves is caused there by the local increase of the impurity concentration on the liquid side of the phase boundary.

In other compounds of the homologous series (CCH4 and CCH5) a similar influence of aging on the pattern formation was detected.

Aging and Phase Sequences

In order to reveal the nature of the aging we prepared three partially sealed sandwich cells (i.e. the substance remained in contact with air). The cells were identical (same size and thickness, orientation by buffed polyimide, filled with CCH3). For all cells the phase transition temperatures were determined by polarizing microscopy in heating as well as in cooling immediately after preparation and no significant difference was detected among the cells.

The cells were subjected to different thermal treatments. In order to force aging one cell has been heated to the isotropic (I) phase and has been stored at $T = 80.4^{\circ}\text{C}$ for 6 days, the second cell has been stored in the nematic phase at $T = 57.5^{\circ}\text{C}$ for the same duration, while the third one remained at room temperature in the crystalline phase for reference. The phase transition temperatures were determined after this thermal treatment again. Fig. 4. compares the measured phase sequences and transition temperatures before and after the thermal treatment for both heating and cooling cycles. Cells stored in the I or N phases, show a large shift of the phase transition temperatures as well as a broadening of the phase coexistence ranges. The changes are more pronounced in cells stored at higher temperature (in the I phase). However, as it was expected, storing cells in the Cr phase did not cause any remarkable change.

The wide range of coexistence of the N-SmB phases seem to be strongly

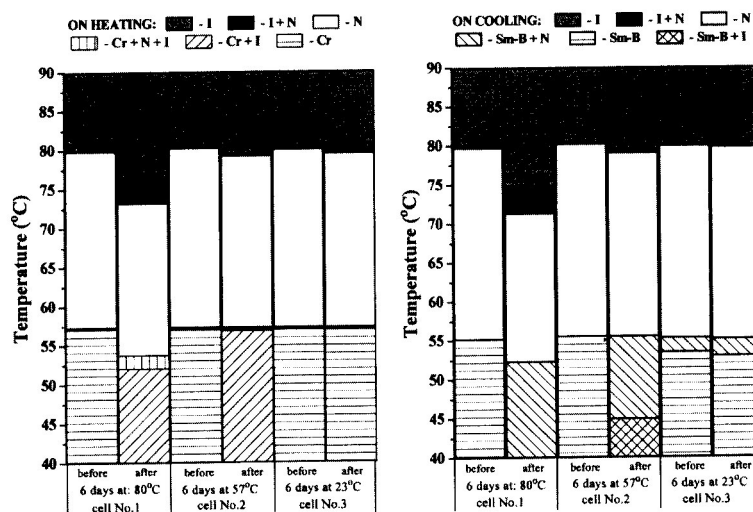


FIGURE 4: Phase sequences of CCH3 on heating and on cooling before and after thermal treatment at different temperatures.

related to the pattern forming mechanism at the transition. On cooling this transition is taking place via spontaneous nucleation and the subsequent dendritic growth of the SmB phase. Due to the reduced side branching activity of the aged cells (Fig. 2.) the final texture is usually inhomogeneous as the SmB phase surrounds several nematic islands (regions between branches). On further cooling the smectic matrix follows the regular monotropic SmB-SmX-Cr phase sequence (see DSC curves in Fig. 6) while (but not at the same time) the islands undergo a sequence of N-I-N phase transitions (Fig. 5). A coexistence of N and I phases within these islands can usually be observed in a rather broad temperature range. Contrary to the smectic matrix, the crystallization of the islands is very unprobable at room temperature. A similar reentrant phase sequence can be observed during melting too. On heating in aged cells one usually starts with nematic (or in some cases isotropic) islands in the crystalline (or SmX) matrix. Increasing the temperature the islands first become isotropic, then as the crystal melts they will be surrounded by nematic regions. The isotropic droplets



FIGURE 5: Microphotographs showing an example of phase coexistence in CCH3 on cooling. (a) Nematic islands in the smectic phase; (b) coexisting nematic and isotropic phases in the islands within the smectic matrix; (c) isotropic islands in the smectic phase.

disappear (become nematic) in a couple of minutes without further elevation of the temperature.

CALORIMETRIC INVESTIGATIONS

In addition to the optical observations the aging of the CCH3 compound has been followed by calorimetry too, using a Mettler FP85 DTA cell. Five aluminium DSC crucibles were filled with crystallites of the substance and were closed hermetically in air atmosphere. For all crucibles DSC curves were recorded at approximately the same time intervals. In between subsequent measurements the crucibles were stored at 25 °C (Cr phase of CCH3), at 48 °C (SmB phase), at 62 °C (N phase), at 85 °C and at 100 °C (I phase), respectively. Before each measurement the crucibles were kept at 15°C for 20 minutes to ensure crystallization. The measurements were composed of a heating, a cooling and again a heating cycle, each at a rate of 2 °C/min.

The temporal evolution of the DSC curves has clearly demonstrated the aging phenomenon by the shift of all phase transition temperatures towards lower values and by the broadening of the DSC peaks. Fig. 6. compares the DSC curves of samples after a thermal treatment of several days in various phases. It can be seen that the higher the storage temperature, the larger the shift of the DSC peaks.

Figs. 7a. and 7b. illustrate the temporal evolution of the onset of the N-I and N-SmB phase transition temperatures T_{NI} and T_{NS} , respectively

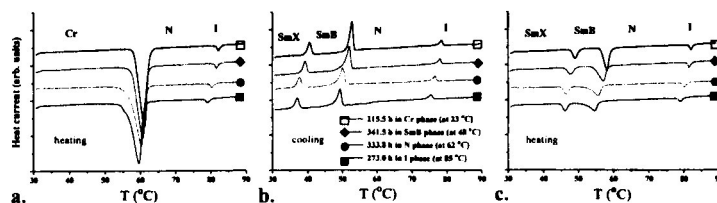


FIGURE 6: DSC curves of samples stored in various phases for several days. The curves are shifted in the vertical direction to allow easier comparison. (a) Heating from the Cr phase; (b) cooling from the I phase; (c) heating from the SmX phase.

(extracted from the DSC curves). The curves indicate an exponential decay and saturation, i.e. the onset phase transition temperatures (T_c) can be well fitted with $T_c(t) = T_c(\infty) + [T_c(0) - T_c(\infty)] \cdot \exp(-t/\tau)$, where $T_c(0)$ is the onset transition temperature of the fresh sample, $T_c(\infty)$ is the saturation temperature, and τ the time constant for the decay. Both the total shift $T_c(0) - T_c(\infty)$ and the rate of the shift ($1/\tau$) increase with the storage temperature. The rate varies over two orders of magnitude and it becomes undetectably slow for the samples stored in the SmB or Cr phases.

We point out that phase transition temperatures in fresh samples determined by DSC (Fig. 7.) somewhat differ from those measured by polarizing microscopy (Fig. 4.). DSC measurements have been performed with a relatively large heating/cooling rate, and $T_c(0)$ is the temperature at which the phase transition begins in the bulk. On the other hand, measurements done with the polarizing microscope give the local T_c at the spot of observation, determined under a heating/cooling rate of about two orders of magnitude smaller than in the DSC measurements.

A set of measurements similar to that presented on Fig. 6. has been performed with DSC crucible filled in an inert gas (argon) atmosphere. After storing the sample at 100°C for several days, no indication of the aging process was found, i.e. neither shift nor broadening of the DSC peaks could be detected. Thus, we conclude that the air atmosphere is responsible for the thermal aging of the investigated substances.

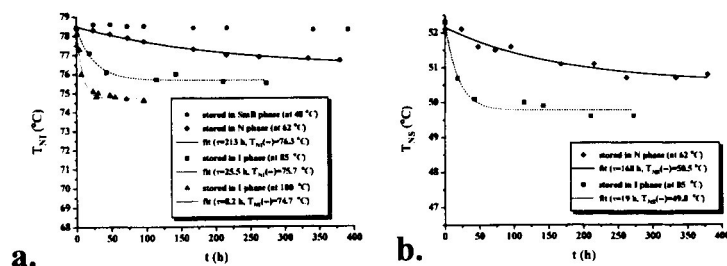


FIGURE 7: Temporal evolution of the onset temperatures of phase transitions in samples stored in various phases. The curves correspond to a fit to the equation $T_c(t) = T_c(\infty) + [T_c(0) - T_c(\infty)] \cdot \exp(-t/\tau)$. **a.** N-I phase transition, $T_c(0) = 78.5^\circ\text{C}$; **b.** N-SmB phase transition, $T_c(0) = 52.2^\circ\text{C}$.

DISCUSSION

Aging as a result of contamination and/or chemical degradation of the substance is quite common in liquid crystals. The increasing impurity content during aging is known to be responsible for the shift of T_c and the broadening of the phase transitions.

Fresh samples of CCH3 possess relatively sharp phase transitions as it is expected for a substance of high purity ($> 99.5\%$ according to the manufacturer [18, 19]). Our measurements have shown that even this stable substance may suffer from aging if in contact with air. The temporal evolution of T_c in Fig. 7 indicates an increase and saturation of the concentration of the impurities generated during aging. The higher the storage temperature, the larger the final concentration and the faster the aging process. It should be mentioned, however, that the generation of impurities seem to be governed not simply by the temperature (and time) but also by the phase which the sample was stored in. Thus, a relatively small temperature difference in the storage temperature (2°C) might yield different behaviour as shown in Fig. 1a. The determination of the actual chemical process of aging would, however, require a more sophisticated chemical analysis.

The unusual ('reentrant') phase sequences found in the phase coexistence range (Fig. 5.) occur due to the presence of impurities too. It is well

known for crystal-melt systems (with partition coefficient < 1) that during crystal growth the impurities favour the melt phase^[17]. It is plausible to assume that the impurities in the CCHn substances do not fit into the more ordered SmB structure and hence stay mainly in the nematic phase. As the SmB phase grows on cooling the volume of the surrounded N decreases. The SmB-N interface pushes the impurities forward increasing their concentration and consequently decreasing the local T_{NI} within the N. At a critical volume this reduced T_{NI} can reach the actual temperature inducing a 'reentrant' transition to the isotropic phase. Further cooling exerts the regular sequence of phase transitions corresponding to this new composition. On heating, just before melting, isotropic islands (locations with high impurity concentration) are surrounded by the crystalline matrix. During melting a nematic phase (with small impurity concentration) appears around these islands. The concentration gradient exerts a diffusion of the impurities leading to homogenization and thus an I-N phase transition in the islands.

The differences observed in the pattern formation of fresh and aged CCHn samples can also be explained by the presence of impurities. The concentration gradient at the SmB-N interface causes the growth to be controlled not only by the undercooling. The actual driving force of the process is a combination of the undercooling and the concentration gradient. This can give an account of the appearance of the groove on the faceted side of the phase front in the aged samples (Fig. 3b.). As the mass diffusion coefficient is several orders of magnitude smaller than that of the heat diffusion, the velocity of the phase boundary is drastically decreased in the aged samples. As both the morphology and the dynamics of the interface growth is extremely sensitive to the presence of impurities, the pattern formation studies provide a tool for checking the purity of the substance.

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References

- [1] J. Bechhoefer, in *Pattern formation in liquid crystals* edited by L. Kramer and Á. Buka (Springer-Verlag, New York, 1996), Chap. 7, p. 257.
- [2] Á. Buka and N. Éber. *Europhys. Lett.*, **21**, 477 (1993).
- [3] Á. Buka, T. Tóth-Katona, and L. Kramer. *Phys. Rev. E*, **49**, 5271 (1994).
- [4] Á. Buka, T. Tóth-Katona, and L. Kramer. *Phys. Rev. E*, **51**, 571 (1995).
- [5] T. Tóth-Katona and Á. Buka. *Mol. Cryst. Liq. Cryst.*, **261**, 349 (1995).
- [6] T. Tóth-Katona, T. Börzsönyi, Z. Váradi, J. Szabon, Á. Buka, R. González-Cinca, L. Ramírez-Piscina, J. Casademunt, and A. Hernández-Machado. *Phys. Rev. E*, **54**, 1574 (1996).
- [7] R. González-Cinca, L. Ramírez-Piscina, J. Casademunt, A. Hernández-Machado, L. Kramer, T. Tóth-Katona, T. Börzsönyi, and A. Buka. *Physica D*, **99**, 359 (1996).
- [8] R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl. *Angew. Chem.*, **90**, 133 (1978).
- [9] L. Pohl, R. Eidenschink, J. Krause, and G. Weber. *Phys. Lett.*, **65**, (1978).
- [10] W. Haase and H. Paulus. *Mol. Cryst. Liq. Cryst.*, **100**, 111 (1983).
- [11] E. Rahimzadeh, T. Tsang, and L. Yin. *Mol. Cryst. Liq. Cryst.*, **139**, 291 (1986).
- [12] D. Grasso, S. Fasone, G. Pasquale, and F. Castelli. *Thermochim. Acta*, **140**, 31 (1989).
- [13] D.S. Mitchell and W.J. Leigh. *Liquid Crystals*, **4**, 39 (1989).
- [14] S. Asahina, M. Sorai, and R. Eidenschink. *Liquid Crystals*, **10**, 675 (1991).
- [15] R. Brownsey and A. Leadbetter. *J. Phys. Lett.*, **42**, 135 (1981).
- [16] R. Kern, in *Morphology of crystals*, edited by I. Sunagawa (Terra Scientific Publishing Company, Tokyo, 1987), Chap. 2, p. 79.
- [17] B. Caroli, C. Caroli, and B. Roulet, in *Solids Far from Equilibrium*, edited by C. Godrèche (Cambridge University Press, 1991), Chap. 2, p. 155.
- [18] Merck (Darmstadt), data sheet.
- [19] B.O. Myrvold and P. Klæboe. *Spectrochim. Acta*, **42**, (1986).