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Transfer of the macroscopic alignment of mesophases into the solid state

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Abstract. For three substances with smectic low-temperature phases (G, H) we have observed by NMR a reversible transfer (storage) of the macroscopic alignment. From the mesophase to the solid phase, i.e. on melting an aligned solid sample and heating it up into the smectic A phase the alignment is chiefly conserved.

Usually it is assumed that a mesogen substance that has been aligned by a strong magnetic field (order of magnitude 0.2 ... 1.5 T, depending on the specific substance [1]) completely loses its macroscopic alignment on cooling into the crystalline solid phase, even if it is kept in the magnetic field during the freezing process. (Remark: We have used NMR sample tubes with an inner diameter of 5 mm.) Indeed this seems to be generally true for substances possessing only nematic phases (where a conservation of the orientation would be difficult to detect in any case because of the quick reorientation of the nematic director in the presence of a magnetic field), and very probably also for substances exhibiting only nematic, smectic A, and/or smectic C phases, resp. For example, nitrophenyl-octyloxybenzoate (NPOB) as well as bis-decyl-oxyazobenzene (DOAB) which have only nematic and smectic A phases (NPOB), and nematic and smectic C phases (DOAB), resp., did not reveal any angular dependence in the proton NMR spectra after melting the previously fully aligned samples into their smectic phases. The recorded lineshapes are characteristic of a mesomorphic polydomain sample (see, e.g. [2]). This indicates the solid state of these substances to be polycrystalline (disordered) after such pre-treatment.

If, however, a substance with a highly ordered low-temperature smectic phase (in our case G and H) is frozen one observes unambiguously a conservation of the macroscopic alignment of the sample, i.e. the sample « transfers » its orientation from the mesophase to a high degree into the solid phase. After melting such a substance one obtains a clear angular dependence in all smectic phases, with the angular dependence in the high-temperature smectic A phase being especially instructive since at the so-called « magic angle » orientation (angle between the preferred direction = normal to the smectic layers, and the magnetic field direction \( \varphi = 54.7^\circ \)) the broad, well-structured spectrum (for \( \varphi = 0 \)) with peak splittings of about 15-20 kHz collapses to a single, narrow line (\( \approx 500-1000 \) Hz) (cf. Figs. 1 to 3 and 4). The width of the line at magic angle orientation therefore may be used to judge the overall alignment.

The substances used in our investigations displayed a pronounced smectic polymorphism:

1) Terephthalylidene - bis - [4 - n - propylaniline] (TBPPrA)
Cr-382.2-H-388.8-G-415-C-421.7-A-
-453.6-N-528.2-I [3].

2) Terephthalylidene - bis - [4 - n - butylaniline] (TBBA)
Cr-325-(S\(_{4v}\))-341-(H)-357-G-415-C-
(metastable supercooled phases in parentheses, melting point 386 K).
Fig. 1. — Proton NMR spectra of TBPrA at \( v_0 = 32 \) MHz (\( H_0 = 0.752 \) T) : a) Smectic A phase at \( T = 435 \) K after cooling down from the nematic phase at angles \( \varphi = 0^\circ, 54.7^\circ, \) and \( 90^\circ \), resp. b) Aligned solid phase at room temperature (about 296 K) 26 days after freezing. c) Smectic A phase at \( T = 434.5 \) K after heating up the crystalline sample of b).

3) N - (p - pentoxybenzylidene) - p - hexylaniline (50-6)

Cr-308-G-310.4-F-313.1-B-323.5-C -324.5-A-333.4-N-345.8-I [4]

(transition temperatures are given in Kelvin). All three compounds can be considerably supercooled.

In all cases the substances have been oriented in a magnetic field of about 0.75 T by heating them up into their isotropic or nematic phases, resp. Then they have been cooled down in the magnetic field at least to the smectic A phase (mostly, however, down to room temperature), removed from the magnetic field, and kept at room temperature. Since 50-6 was still in the supercooled smectic G phase at room temperature it was crystallized by putting the sample tube into liquid nitrogen (77 K) for a few minutes.

Figure 1 presents the proton NMR spectra \( (v_0 = 32 \) MHz) for TBPrA. In figure 1a are shown the spectra of the smectic A phase after cooling the sample in the magnetic field from the nematic phase. The doublet peak splitting fairly well obeys the well-known \( P_2(\cos \varphi) \) dependence (\( \varphi \)-angle between magnetic field direction and director of the smectic A sample). Characteristic spectra are those for \( \varphi = 0^\circ \) (maximum splitting, \( P_2(\cos \varphi) = 1 \)), \( \varphi = 54.7^\circ \) (magic angle—single, narrow line, \( P_2(\cos \varphi) = 0 \)), and \( \varphi = 90^\circ \) (half maximum splitting, \( P_2(\cos \varphi) = -0.5 \)).

Figure 1b displays the angular dependence of the sample in the crystalline solid phase 26 days after removing it from the magnetic field. There is only a weak angular dependence of the structureless Gaussian lines, with the maximum linewidth at \( \varphi = 0^\circ \) and the minimum at \( \varphi = 90^\circ \).

Heating up this sample into the smectic A phase (same temperature as in figure 1a) one obtains the spectra represented in figure 1c. Again one observes a quite clear angular dependence, very similar to that of figure 1a. However, the quality of the alignment is not as good as after cooling directly from the nematic to the smectic A phase, which can be easily determined from the maximum splitting which is, especially distinct from the linewidth at the magic angle. The maximum splittings differ by about 14 % and the linewidth at magic angle orientation is now about 1.6 kHz compared to about 680 Hz after cooling from the nematic phase. Furthermore, the magic angle orientation spectrum of figure 1c is distinctly broader at the bottom (as measured, e.g., at one eighth of the maximum height) than that of figure 1a.

To estimate quantitatively the degree of loss of the homogeneous parallel orientation of smectic A domains, the proton NMR spectrum of TBPrA has been simulated using the spectra calculation programme described elsewhere [8].

For the determination of the decrease in the overall parallel orientation of the domains a simple procedure has been applied: the real distribution of domain orientations was approximated by superimposing a perfectly aligned portion (characterized by the spectrum for \( \varphi = 0^\circ \) of figure 2a), and a totally disordered one (corresponding to the polydomain spectrum of figure 2b). Comparison with the experimental

Fig. 2. — a) Computed spectra of TBPrA for perfect alignment of all molecules in the sample along the strong magnetic field without convolution (to the left) and after convoluting the lineshape by a Lorentzian of half width 740 Hz (to the right). b) Spectrum of TBPrA for a statistically disordered distribution of smectic A domain orientation (powder spectrum). c) Simulated proton NMR spectra of TBPrA supposing a totally disordered portion of 20 % and a perfectly aligned one of 80 % for rotation angles \( \varphi = 0^\circ \) and \( \varphi = 90^\circ \), resp. d) The same as in c) for a portion of disordered domains of 30 %.
spectra of figure 1c suggested the totally disordered portion to range between about 20 and 30%, as can be learnt from figures 2c and 2d. To exclude the (weak) possibility that the magnetic field is subsequently aligning the domains on melting, a crystalline TBPrA sample (treated as described above) has been rotated into the magic angle and heated up into the smectic A phase. As expected, the very narrow line characteristic of an aligned smectic A sample at magic angle orientation was observed. If, however, the magnetic field would have had any influence on the alignment of the sample on melting, the spectrum with maximum splitting should have been recorded.

Similarly, the two other substances have been investigated.

In figure 3 are presented the spectra of TBBA as obtained only about 30 min. after crystallization. There are only minor differences in the angular dependences of the sample after cooling directly from the nematic into the smectic A phase (Fig. 3a) and after heating up from the solid phase (Fig. 3c).

Figure 4 provides the same information for 50-6 where the sample has been investigated about four days after removal from the magnetic field. It has been crystallized by dipping the sample tube into liquid nitrogen (77 K). In this case the distinction between the two sets of spectra for cooling from the nematic state (Fig. 4a) and for heating from the solid are more evident, even from the spectral lineshapes alone.

Obviously there is a broader distribution of director orientation in the smectic domains for the case of melting an (oriented) solid phase into a smectic one, compared to the usual procedure of cooling a nematic phase into a smectic phase in the presence of a magnetic field.

Certainly there arises the question of whether we can be sure we have really produced solid phases. There exist some strong indications for this conclusion:

i) The aligned solid phases had the same appearance as totally disordered solid phases of the compounds described above and of other compounds.

ii) The NMR spectra of the solid phase differ from the spectra of all other phases exhibited by these compounds.

iii) The $T_1$ (longitudinal) nuclear spin relaxation time of the solid phases (some seconds) is distinctly greater than that of all other mesophases (some hundred milliseconds).

iv) After cooling with liquid nitrogen, each of these
substances with melting points clearly above 300 K is expected to become crystalline.

When the substances in the nematic phase are removed from the magnetic field and afterwards crystallized, there is only a very weak angular dependence after reheating into the smectic A phase. Of course, there is no conservation of the alignment at all on heating into the isotropic phase and then removing the substance from the field.

Summarizing all the facts we can state that for substances possessing low-temperature smectic phases (at least G, H) the macroscopic alignment of the smectic A can be transferred into the solid state without any expense, kept there with only minor losses for weeks (!) (and probably much longer) and detected again after heating into (for instance) the smectic A phase. Possibly this procedure works likewise for substances without A phases if there is only one orientable smectic phase (e.g. smectic C with a preceding nematic phase). For substances without smectic low-temperature phases (only nematic, A, and/or C phases) no transfer of the alignment into the solid state seems to be attainable.

A possible interpretation of this effect could be the following, preliminary one: Because of the similarity between the solid and the low-temperature smectic phases (which possess a high degree of orientational and positional order, even in three dimensions [5]), and (probably associated with this high order) the very high viscosity of these phases, the latent heat of crystallization is not able to destroy the homogeneous alignment, so that a polycrystalline solid with statistically disordered crystallites could arise. Rather, one might think of a sample of non-perfectly aligned crystallites whose sizes we have not yet been able to estimate.

The above-described investigations demonstrate that it is apparently possible to get not only highly aligned smectic low-temperature phases by melting single crystals of mesogen compounds [6] but, inversely, one can even transfer the macroscopic alignment of mesophases into the solid (without growing single crystals in the usual sense).

Future investigations should firstly consist in a thorough X-ray analysis of these solid phases, but calorimetric studies as well as measurements of the diamagnetic anisotropy promise to be instructive, too. Furthermore the dependence of the alignment-transfer on the strength of the polarizing magnetic field should be investigated in more detail. Further quantitative calculations of the loss of alignment by means of computer simulations of the proton NMR lineshape are under way. In addition we must clarify the extent to which this phenomenon is associated with the well-known solid polymorphism of the TBBA homologous series [3].

The original alignment of the sample should, of course, be obtained also by an electric field.

Something similar as the above-described effect seems to have been observed independently by Diele [7].

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References

