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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: S. Krishna Prasad, S. Chandrasekhar & Geetha G. Nair (1996): Influence of Bond Orientational Order on the Switching Time of Ferroelectric Smectics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 63-72

To link to this article: http://dx.doi.org/10.1080/10587259608034584

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INFLUENCE OF BOND ORIENTATIONAL ORDER ON THE SWITCHING TIME OF FERROELECTRIC SMECTICS

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Abstract We report studies of the bulk switching time as a function of temperature in the chiral smectic C (C*) and chiral smectic I (I*) phases of 4-(2-methylbutyl) phenyl 4'-(octyloxy)-(1,1')-biphenyl-4-carboxylate (8OSI*) which shows a continuous evolution from the fluid C* to the hexatic I* phase. The thermal variation of the switching time is found (to our knowledge for the first time) to scale remarkably well with the hexatic order parameter for the two phases determined experimentally by Brock et al¹ for 8OSI, the racemic form of 8OSI*. Similar correlation is observed in the case of 8SI*, the alkyl analog of 8OSI*, which shows a first order C*-I* transition.

INTRODUCTION

It is now well established that smectic C (C) and smectic I (I) are isosymmetric. Consequently, the transformation from C to I is either via a first order transition or via a supercritical evolution of both bond orientational and tilt order parameters. Experimental proof of the supercritical evolution came from the synchrotron X-ray studies of Brock et al.¹ The hexatic order parameter measured using free standing films of 8OSI, the racemic form of 8OSI*, showed a continuous variation across the transition as seen in figure 1. Signatures of this effect have been seen in specific heat data of Garland and coworkers² and the thermal variation of layer spacing measured by us.³

The aim of the present study⁴ is to investigate the possible correlation that may exist between the hexatic order parameter Ψ_6 and the ferroelectric switching time of a chiral smectic system. With this in view, we have measured the switching time of 8OSI* as a function of temperature through the C* and I* phases and compared it with the experimental values of Ψ_6 available for 8OSI, where Ψ_6 is the the leading term in

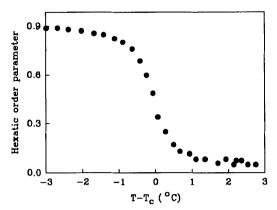


FIGURE 1 Thermal variation of the hexatic order parameter Ψ_6 in the C and I phases of 8OSI (from Ref. 1)

the fourier expansion of the hexatic order. As we shall see presently, the switching time scales remarkably well with Ψ_6 over the entire temperature range.

EXPERIMENTAL

The triangular wave method was employed to study the current response of the sample. A schematic diagram of the experimental set-up is shown in figure 2. The resistance bridge helps to balance the conductivity contribution to the current output from the sample. This enables one to set higher sensitivities on the data acquisition system. The output from the two arms of the bridge are fed to a wide band differential amplifier (AD 830). The output of the amplifier is in turn fed to an oscilloscope for visual monitoring. A parallel connection is made to an Analog-Digital converter board (Keithley-Metrabyte DAS50) with a very high sampling rate (10⁶ samples /sec) and high data resolution (12 bits). The board is plugged into a PC AT I/O slot. A large on-board memory bank (0.5MByte) helps fast acquisition of data.

The sample cell (thickness $10 \mu m$) was made up of two ITO-coated glass plates treated with polyimide solution to get planar alignment of the molecules. The cell was placed in a Mettler hot stage (FP82HT) and to get a better precision in reading, the

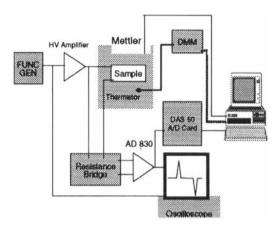


FIGURE 2 Schematic diagram of the experimental set up

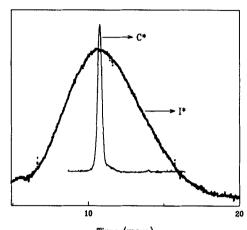
sample temperature was measured using a calibrated bead thermistor (YSI 44011) located very close to the sample position. The thermistor output was read on a digital multimeter (HP 34401A). The Mettler processor and the multimeter were interfaced to a PC which handled the data acquisition and control. A disadvantage with the triangular wave technique of measuring the current response is that it does not provide direct information as to whether the field applied is sufficient enough to unwind the helical structure. Of course, it can be estimated approximately by visual observations of the pitch lines. But a more accurate way is to look at the hysteresis loop obtained using the capacitance bridge technique. For this purpose we monitored the hysteresis loops frequently at close intervals of temperature.

MEASUREMENTS ON 80SI*

80SI* was chosen for the experiments as Ψ_6 data are available for its racemic form 80SI. Typical current-response curves obtained in the C* and I* phases are shown in figure 3. Notice that the half width of the peaks, which we have taken as the response time, shows a dramatic increase on going from the C* phase to the I* phase. The detailed temperature dependence of this switching time is shown in figure 4. There is a continuous variation in the magnitude of the response time confirming that the supercritical evolution can be observed even in the dynamics. (As we shall see later for

another material which shows a first order C* - I* transition, there is a discontinuous jump in the response time).

The pitch was measured by optical diffraction and found to be 1.8 μ m in the C* phase. Thus with a sample of thickness 10 μ m the switching can be considered as bulk switching, i.e. it involves reorientation of the azimuthal angle of the molecules in one layer relative to that of the neighboring layer. Figure 5 shows the comparative plot of the hexatic order parameter Ψ_6



Time (msec)
FIGURE 3 Typical switching current response curves in the C* and I* phases.

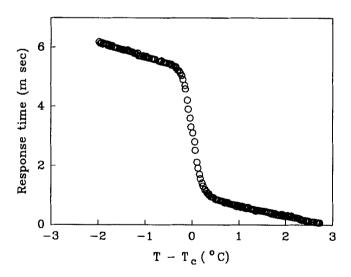


FIGURE 4 Thermal variation of response time for 8OSI*.

as determined by Brock et al for 8OSI (Figure 1) and our data for the response time (Figure 4). It can be seen that the two sets of data overlap remarkably well over the

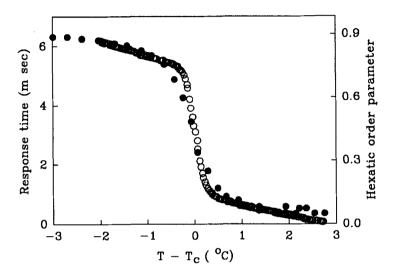


FIGURE 5 Comparative plot of hexatic order parameter for 8OSI (open circles) and the switching time for 8OSI* (filled circles).

entire range of temperature, indicative of a simple scaling relationship between Ψ_6 and the ferroelectric switching time.

MEASUREMENTS ON 8SI*

We now present the data for 8SI*, the alkyl analog of 8OSI*. The current-response profiles obtained for 8SI* at different temperatures are given in figure 6. Unlike 8OSI*, we see in this case that, in the transition region the peaks due to both the phases coexist. This is clear signature of a first order transition. The temperature dependence of the response time is plotted in figure 7. The data in the two-phase region are shown as filled circles. To our knowledge, this is the first time that the contributions of coexisting liquid crystal phases have been separated out in the measurement of a

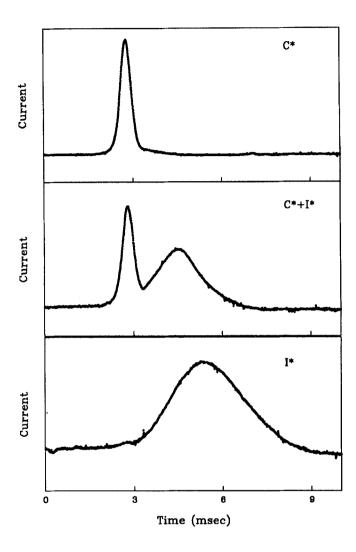


FIGURE 6 Current response profiles in the C* phase, two-phase region and I* phases for the compound 8SI*.

dynamic quantity. For this material the Ψ_6 data have not been reported. Therefore we followed a method used by Spector and Litster ⁵ to extract Ψ_6 from the in-plane elastic

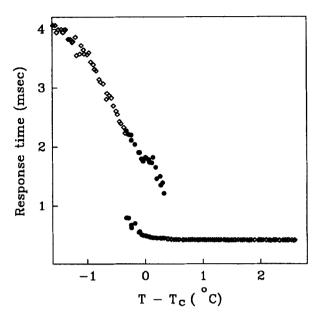


FIGURE 7 Temperature dependence of the response time for 8SI*. The filled circles represent data in the two-phase region.

constant data. The assumption is that the positional correlation length is small near the C-I transition and hence there is a direct enhancement of the elastic constant by the hexatic order parameter. In a mean field approximation, the elastic constant K_{hex} is expected to be proportional to the square of the hexatic order parameter. A comparison between the response time and the square root of K_{hex} is shown in figure 8. The agreement is extraordinarily good, and again there appears to be a simple scaling relationship between the two. This can perhaps be interpreted in the following manner. The relaxation time τ of any overdamped mode is controlled by the ratio of the viscous to the elastic torque.

This can be written as,

$$\tau \sim \frac{\eta}{K_{xx}q^2}$$

where η the viscosity and q the wavevector. As the process we are interested in involves the unwinding of the helix one may take $q=2\pi/p$, p being the pitch of the helix. For the unwinding of the helix in bulk samples (as in the present case) the

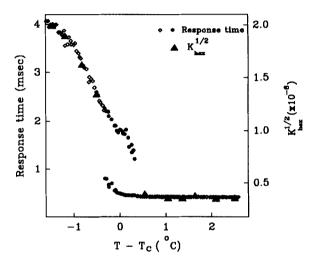


FIGURE 8 Comparative plot of the response time and the square root of the hexatic elastic constant.

elastic constant and viscosity are expected to be proportional to the square of the order parameter.⁶ In such a case we see from expression (1) that the temperature dependence of τ should mimic the variation of the square of the helical pitch. The pitch for 8SI* has been measured by Kuczynski and Stegemeyer⁷ and using their data, we find that the p^2 values do indeed vary like K_{hex} over the entire temperature range (Figure 9).

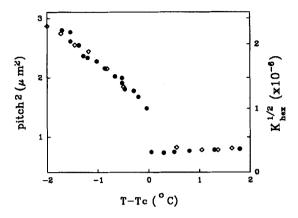


FIGURE 9 Plot showing similar temperature dependences of the square of the helical pitch (filled circles) and the hexatic elastic constant (open circles).

ACKNOWLEDGEMENTS

Thanks are due to BDH, Poole, for the free samples of compounds used in this study. Research grants from the Department of Science and Technology, New Delhi and from the US Office of Naval Research (Grant No. N00014-93-1-0760) are gratefully acknowledged.

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