

Chain Length Dependence of Confined Liquid Crystals Configuration

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Abstract

The study of confined liquid crystals flourished in the decade of the nineties. Liquid crystals properties have been probed after confinement in well-defined or interconnected geometries as those available in porous media and in polymer networks. In this work we emphasized the power of the nuclear magnetic resonance technique to determine the confined liquid crystal structures. We also present unexpected results on the dependence of the confined liquid crystal configuration on the chain length.

Keywords: Liquid Crystals, Orientational Order, Director Configuration

1. Introduction

Liquid crystals (*LC*) materials can be oriented and ordered by an interface, and retain the induced order over macroscopic scales. This feature, rendering them technologically important, allows liquid crystals to exhibit different structural configurations when the interface consists of solid walls that completely surround the liquid crystal, when small particles are dispersed in it, or when the *LC* is confined to a polymer network [1].

In particular, studies of the orientational order of elongated liquid crystal molecules using deuterium nuclear magnetic resonance (DNMR) have significantly contributed in determining nematic director fields as well as important surface parameters under conditions when the liquid crystal is confined to submicrometer

cavities. Because of the large surface to volume ratio existing in a porous material, the surface-liquid crystal interaction is such that surface effects are maximized.

Cyanobiphenyl liquid crystals confined to the 200 nm parallel cylindrical pores of Anopore membranes have been extensively researched. Specifically, for nematic 5CB in Anopore, the director configuration that is exhibited is uniform axial, namely, the liquid crystal molecules are oriented by the surface parallel to the cylindrical pore axis [2-4]. Exactly the same director configuration was determined for the longer chain for 8CB at temperatures including the nematic and the smectic-A phases. The surface induced director configuration is unaffected by the strength of the magnetic field, it is perfectly stable and retained regardless of thermal cycling of the sample.

2. Experimental Technique

The deuteron nuclear magnetic resonance technique (*DNMR*) is a powerful tool to determine liquid crystal configurations in confined systems. *DNMR* is sensitive to the local degree of orientational order, $S(r)$, and the molecular ordering direction (or director field), $n(r)$, through the quadrupole frequency splitting

$$\delta\nu(r) = \delta\nu_0 S(r) [3\cos^2\theta(r) - 1]/2, \quad (1)$$

where $\delta\nu_0$ is the quadrupole splitting of a perfectly orientationally ordered phase (saturating typically at $\delta\nu_0 \sim 90\text{ kHz}$ for *nCB*'s) and $\theta(r)$ is the angle between the local director and the magnetic field \mathbf{B} [5].

A uniform axial alignment is indicated in the *DNMR* spectral patterns with quadrupole frequency splitting that is nearly equal to that of a perfectly aligned bulk sample. When the alignment is homeotropic, and consequently, $\theta = 90^\circ$ in Eq. (1), the quadrupole splitting is only one-half that of a fully aligned bulk sample. Sample rotation in the magnetic field allows orienting the cylindrical pore axis at any angle from parallel to perpendicular to the external \mathbf{B} . Since the magnetic coherence length for our 4.7 T magnet is larger than the Anopore pore diameter, there is no influence of the *NMR* field on the local director. The liquid crystal director field in Anopore is solely surface-induced.

3. Results

Given the known results for *5CB* and *8CB*, our expectations for smectic-A *10CB*, a longer chain member of the homologous series lacking the nematic phase, when confined to cylindrical Anopore, was to also find a uniform axial director configuration.

In contrast to the shorter chain liquid crystals, as seen in Fig. 1 cooling from the isotropic phase, the configuration that is formed in entering the Sm-A phase consists of two intense inner absorption peaks at half a bulk aligned splitting coexisting with two less intense outer peaks at a bulk-like size frequency splitting. Effectively, the director configuration for *10CB* is the coexistence of molecules radially aligned (inner peaks) with fewer of them axially aligned (outer peaks). The configuration is stable under thermal cycling as long as there is no crystallization.

If the sample is further cooled so that it fully crystallizes and *DNMR* measurements then performed in heating, in the Sm-A phase, Fig. 2, the spectral pattern only consists of the half-splitting part, namely, a purely radial configuration that is retained until the isotropic phase. In heating, no axial alignment develops. Comparing with the results for *5CB* or *8CB*, longer chain cyanobiphenyls confined to Anopore exhibit an anchoring transition. The transition occurs for a chain length $8 < n < 10$ and consists of a structural change where molecules are no longer axially aligned.

We speculate that these effects are associated with a strongly temperature dependent anchoring energy and the very sharp dependence of the surface-liquid crystal interaction on the liquid crystal chain length.

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5. References

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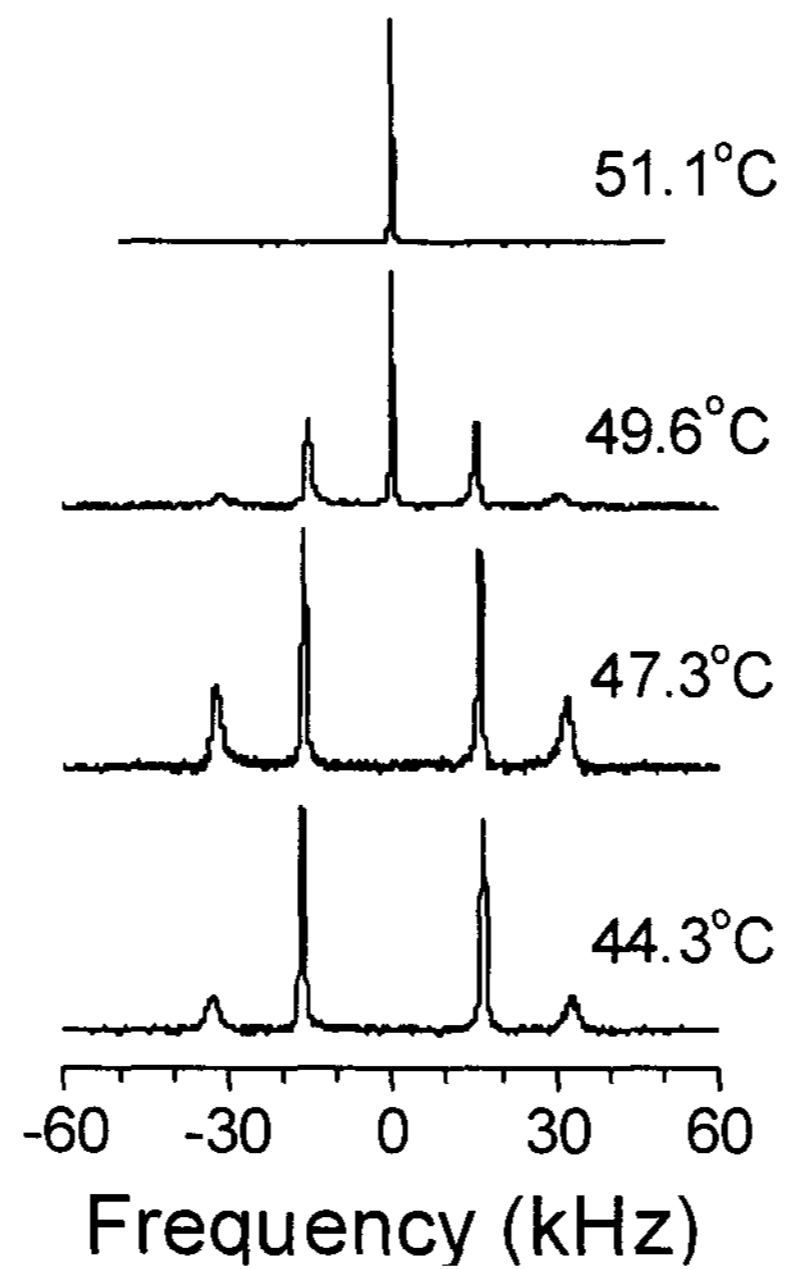


FIGURE 1: *DNMR* spectral patterns obtained in cooling from the isotropic phase for *10CB* in Anopore

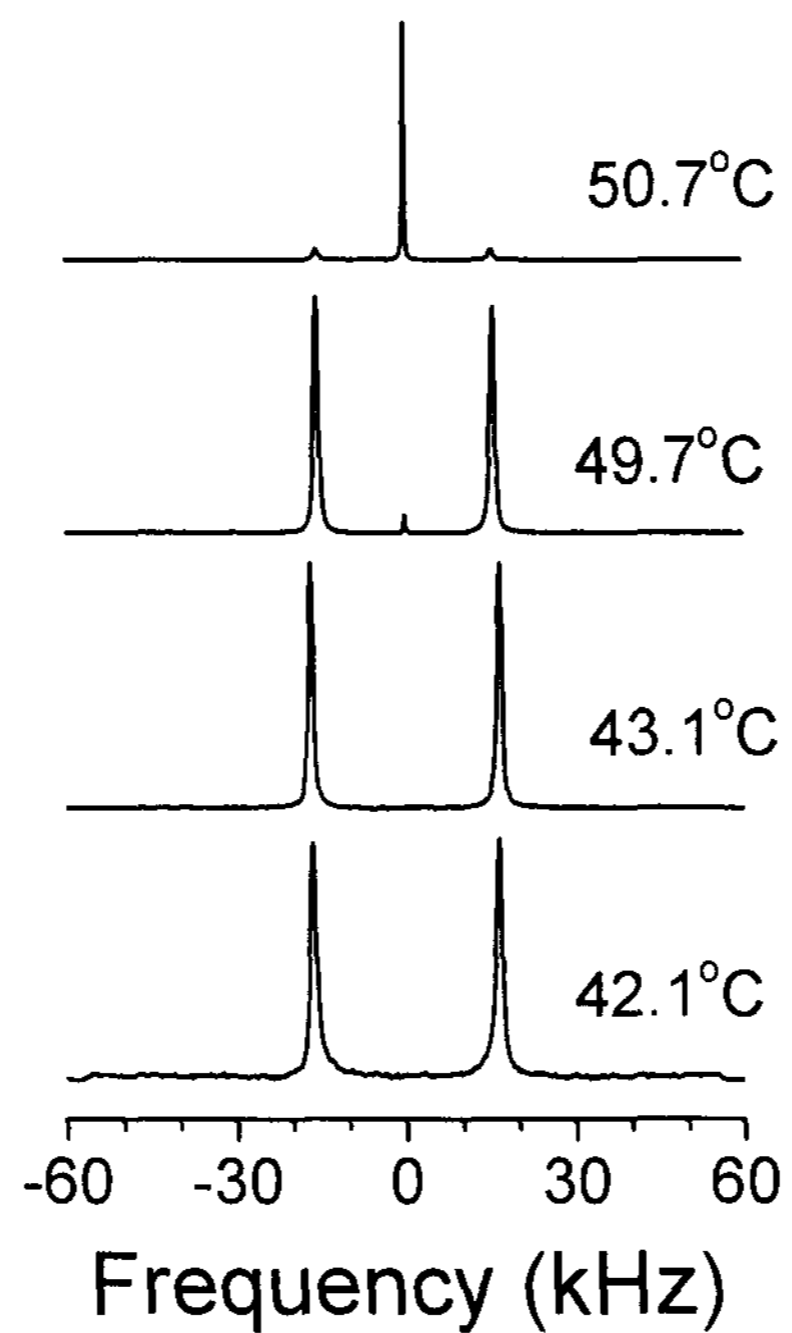


FIGURE 2: *DNMR* spectral patterns obtained in heating after crystallizing the *10CB* sample.