Experimental report

18/05/2020

Proposal: **9-11-1737** **Council:** 4/2015

Title: Neutron spin-echo spectroscopy on chiral molecules forming self-assembling structures

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Chiral liquid crystal: lactic acid derivative
Chiral liquid crystal: lactic acid derivative deuterated H 10/8-d2
Chiral liquid crystal: lactic acid derivative deuterated H 10/8-d4

Instrument	Requested days	Allocated days	From	To
IN11	14	8	17/11/2015	25/11/2015

Abstract:

The study of materials that self-assemble into supramolecular structures with desirable functionality and physical properties at nano- and meso-scopic length scales is currently an area of intense research, because it provides a promising approach to the design of new functional materials. The general aim of these specific studies is to acquire new knowledge and to obtain systematic data on molecular architecture nano-organization relation for the chiral smectic materials that allows modifying the molecular structure and, hence, tuning the properties. Neutron scattering studied are quite rare in application to self-assembling materials and in particular to chiral liquid crystals forming the layered structures at the nanometre scale. We propose to make a detailed study of the H 10/8 chiral liquid crystalline material existing in three structural modifications (hydrogenated and two different deuterated ones) using the NSE spectrometer IN11. The measurements will be done at three different temperatures corresponding to different mesophases. Time domain analysis of the intermediate scattering function of H 10/8 molecules will be obtained.

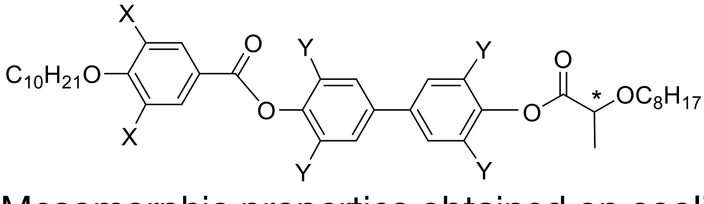
Title: **Neutron spin-echo spectroscopy on chiral molecules forming self-assembling structures**

Scientific background and aim of the experiment

The study of materials that self-assemble into supramolecular structures with desirable functionality and physical properties at nano- and meso-scopic length scales is currently an area of intense research, because it provides a promising approach to the design of new functional materials. Liquid crystals exhibit a large number of different phases, most of which spontaneously form complex nano-structures (smectic mesophases). The project focuses on polar liquid crystals (LC), materials that combine two features: polar order and fluidity. The combination of fluidity and sensitivity to el. field makes polar fluids ideal for photonics, telecommunications, non-linear optics, memories, optical transistors and as tuneable lasing or wave guiding materials [1]. The general aim of these specific studies is to acquire new knowledge and to obtain systematic data on molecular architecture – nano-organization relation for the chiral smectic materials that allows modifying the molecular structure and, hence, tuning the properties. Understanding of this relation is of fundamental interest but also is a starting point for future applications.

Our recent work

Neutron scattering studied are quite rare in application to self-assembling materials [2-3] and in particular to ***chiral*** ones forming the layered structures at the nanometre scale. As a result of a collaboration between A. Bubnov (Prague) & V. Domenici (Pisa) in the field of low molar mass and macromolecular self-assembling materials [4-7] a new chiral ferroelectric liquid crystalline material derived from lactic acid has been designed and characterised. The material exists in three structural modifications (see below) and possesses (on cooling from the isotropic phase) a narrow twist grain boundary smectic phase, quite broad tilted ferroelectric SmC* phase and highly ordered crystal phase. The specific interest in this material is due to a quite large tilt angle within the ferroelectric SmC* phase (more than 40°, see figure) and also the spontaneous unwinding of the SmC* (at about 89°C). Preliminary studies have been done and include DSC, POM, SAXS, electro-optics, dielectric spectroscopy and also advanced ^{2}H NMR and ^{13}C NMR studies.
Some of the results are summarised below. Chemical structure:

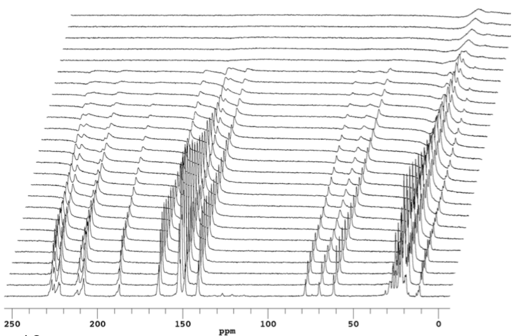


H 10/8-non X= H, Y = H
H 10/8-d2 X= D, Y = H
H 10/8-d4 X= H, Y = D

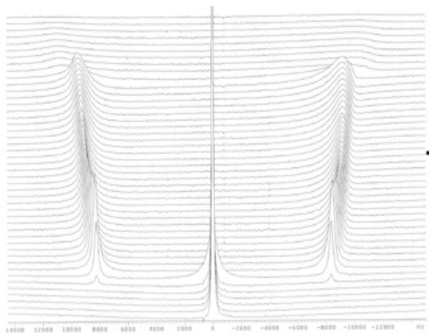
Mesomorphic properties obtained on cooling:

	c.p.	m.p.		°C		°C		°C		°C	Iso
H 10/8-non	133.5	72.4	**Cr**	43.8	**CrE**	69.7	**SmC***	132.1	**TGB_A**	132.6	**Iso**
H 10/8-d2	133.6	71.2	**Cr**	45.0	**CrE**	69.5	**SmC***	132.4	**TGB_A**	133.0	**Iso**
H 10/8-d4	133.3	71.6	**Cr**	44.0	**CrE**	69.3	**SmC***	131.9	**TGB_A**	132.4	**Iso**

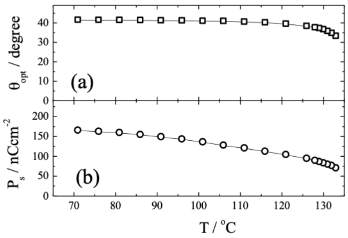
The relevant changes in the ^{13}C and ^{2}H line-shapes are ascribed to structural changes occurring at the corresponding phase transitions (see figure below).



^{13}C NMR static spectra of **H10/8-non** as a function of temperature.



Results of ^{2}H NMR of **H 10/8-d2** versus temperature.



Tilt angle (a) and spontaneous polarisation (b) versus temperature.

IN11 experiments

We proposed to make a detailed study of the H 10/8 chiral liquid crystalline material existing in three structural modifications (hydrogenated and two different deuterated ones) using the NSE spectrometer IN11 with the 30 degree detector bank (IN11C). The measurements were successful and a first study on the IN11 data has already been published [8]. The neutron spin-echo measurements (NSE) were performed at the NSE spectrometer IN11 at Institut Laue-Langevin (ILL), Grenoble, France [57]. The instrument was set-up with the 30 degrees' multi-detector option for maximum signal efficiency. The wavelength was λ = 5.5 Å with a spread of $\Delta\lambda/\lambda$ = 15%. We covered a time range of t = 5–500 ps. The momentum transfer range was Q = ki –kf = 0.1–1.2 Å−1. The samples were held in thin vacuum-tight aluminium sample holders. The sample temperature was controlled with a liquid helium cryo-furnace capable of varying the temperature in a range of −271.5–300°C. Data were corrected for resolution limitation and magnetic inhomogeneities through dividing the spectra by a low-temperature measurement of the sample itself. The data were verified in addition, by comparison with a standard elastic scattering sample made of a Ti-Zr alloy. A more detailed analysis of the IN11 is presently being prepared.

References

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[8] Alexej Bubnov, Mario Cifelli, Martin Cigl, Peter Fouquet, Vera Hamplova & Valentina Domenici, Liquid Crystals (2019) Mesomorphic, structural, electro-optic and dynamic properties of lactic acid derivative and its selectively deuterated isotopomers by means of electro-optics, SAXS, 2H-NMR and neutron spin-echo spectroscopy, Liquid Crystals, DOI: 10.1080/02678292.2019.1641232

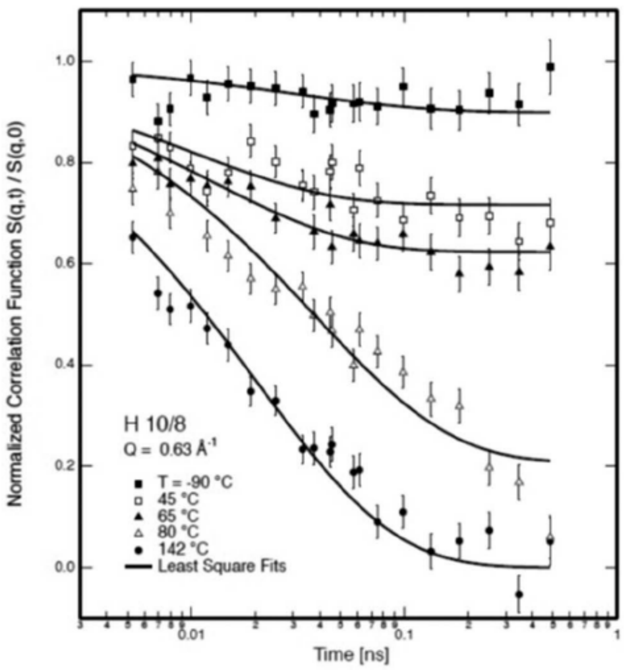

Figure 8. Exemplary NSE spectra of the non-deuterated **H 10/8** sample at a momentum transfer of 0.63 $Å^{-1}$. The spectra can be well fit by stretched exponential decay functions. Further details are given in the text.

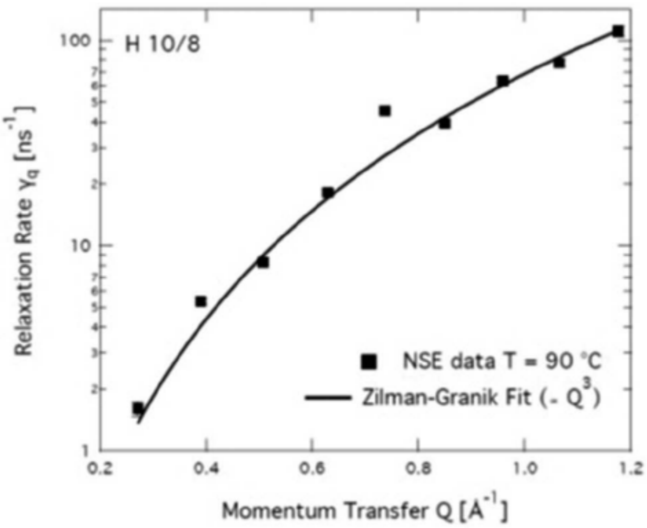

Figure 10. Relaxation rate γ_q obtained from fitting the NSE spectra of non-deuterated **H 10/8** compound with the Zilman-Granik model $\gamma_Q \sim Q^3$.