EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** X-ray diffraction investigation of oligothiophene mesomorphism	**Experiment number**: SC-4523
Beamline: BM26B	**Date of experiment**: from: 13 July 2017 to: 17 July 2017	**Date of report**: 01 March 2020
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. F. Vita*, Prof. O. Francescangeli*, Dr. M. Pisani*, Dr. S. Marino*, Dip. SIMAU, Università Politecnica delle Marche, via Brecce Bianche, I-60131, Ancona, Italy

Report:

The experiment aimed at studying the mesomorphic behaviour of unsubstituted α-oligothiophenes (α-*n*T) taking advantage from the unique experimental set-up available at the beamline BM26B, allowing simultaneous SAXS-WAXS measurements at high temperature (exceeding 400 °C) under strong magnetic field. Most of the goals have been successfully achieved for α-sexithiophene (α-6T), while for longer compounds α-septithiophene (α-7T) and α-octothiophene (α-8T) we could not study the full nematic range because of the sample sublimation at high temperature.

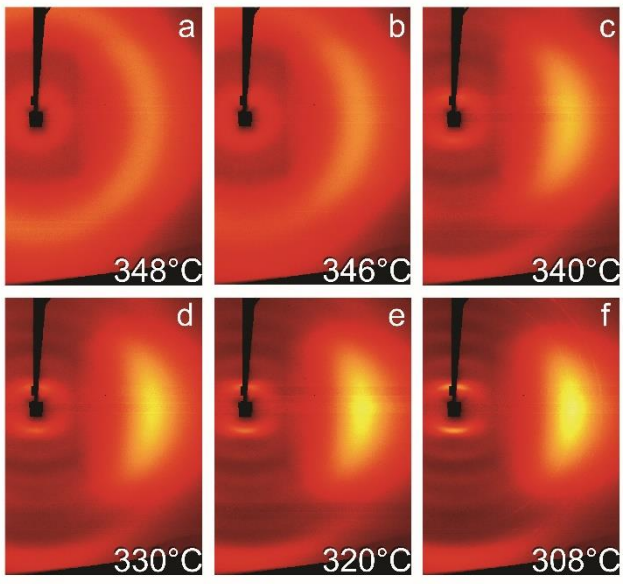

Figure 1. α-6T X-ray diffraction patterns taken on cooling from the isotropic phase under a vertical magnetic field (meridional direction). Only the right half of the patterns is shown because of the pattern symmetry.

Measurements on α-6T were performed, both heating and cooling, under an aligning magnetic field (Fig. 1). Obtaining these results over the full nematic range as well as in the higher temperature isotropic phase required several attempts given the strong tendency to sublimation of the material. The change of the wide-angle diffraction pattern from an isotropic ring to a pair of broad equatorial crescents observed at T_{NI} = 346 °C (Figure 1) indicates the transition from the isotropic to the nematic phase. Cooling down the sample, it exhibits the typical anisotropic X-ray diffraction pattern of rod-like nematics, with a pair of small-angle peaks along the meridional direction (due to short-range positional order in the longitudianla direction) and a pair of diffuse equatorial crescents in the wide-angle region along the equatorial direction (caused by short-range positional order in the transverse direction). A peculair feature already observed in other all aromatic compounds is the presence of additional wide-angle reflections in the meridional direction, reflecting the intramolecular repetition of the thiophene rings.

Further cooling from the nematic phase at T < 308 °C resulted in the sample crystallization, with no evidence of underlying smectic phases. The experimental assesment of the α-6T phase diagram, at present only known from very few old and unconclusive reports, is a first important result of the experiment. An interesting result is the lack of smectic phases below the nematic phase, as this is in sharp contrast with predicitons of recently published

molecular dynamics simulations. It would be interesting to confirm these results by performing supplementary measurements under different experimental conditions (e.g., by paying attention to the thermal history of the sample or by varying parameters such as the cooling/heating rate and the magnetic field).

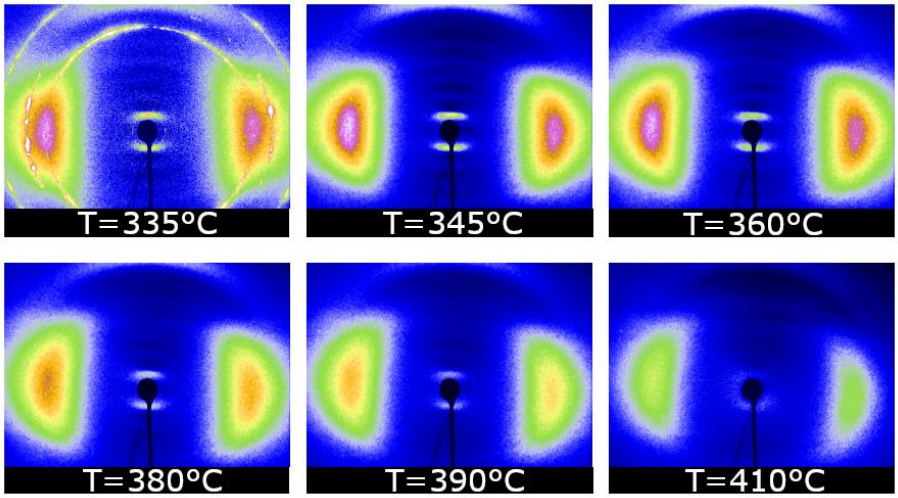

Figure 2. α-7T diffraction patterns taken on heating from the crystal phase under a vertical magnetic field (meridional direction).

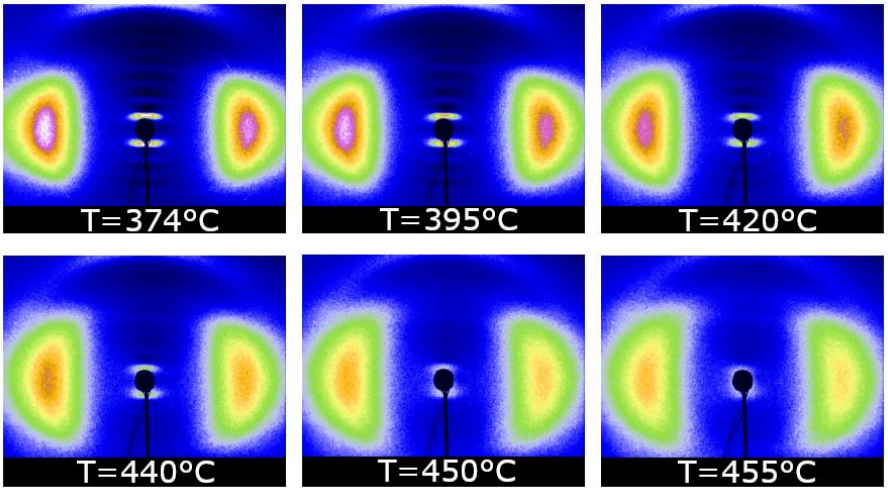

Figure 3. α-8T diffraction patterns taken on heating from the crystal phase under a vertical magnetic field (meridional direction).

Longer compounds α-7T and α-8T proved even more difficult to study, as their nematic temperature range extended at higher temperatures. In particular, measurements on these compounds could be performed only on heating (Figures 2 and 3). Increasing the temperature from the crystal phase, both samples exhibited a nematic phase with diffraction patterns similar to those observed for α-6T and no evidence of any smectic phase. In these cases we were not able to reach the isotropic phase (and hence to perform measurements on cooling), because of material sublimation. We expect that a different preparation of the samples, a more accurate sealing of the capillaries, and some modification of the sample holder (specifically developed by the beamline staff) could alleviate the problem, allowing a more accurate study of the phase diagram of these longer compounds.

At present, a more detailed analysis of α-6T diffraction patterns is ongoing, aiming at obtaining quantitative information on both the long-range orientational and the short-range positional order. We plan to extend this analysis to longer (α-7T and α-8T) and shorter compounds (α-5T) in future experiments.