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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Structure vs Performance of polymers	**Experiment number**: ME161
Beamline: ID11 & ID2	**Date of experiment**: from:4th April 2001 to 7th April 2001 11th April to 14th April 2001	**Date of report**: Sept 1st, 2002
Shifts:	**Local contact(s)**: Dr. Ann Terry and Dr. Volker Urban	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Ankur Rastogi(*)

Jamie Hobbs(*)

Sanjay Rastogi(*)

Report: The crystallization behaviour and the morphological aspect of the butyl branched alkane $C_{96}H_{193}CH(C_4H_9)C_{94}H_{189}$ have been investigated using time-resolved wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) at atmospheric and elevated pressures. The solution crystallized sample shows pronounced crystalline reflections in WAXD with a lamellar thickness of 127 Å corresponding to a once folded structure in SAXS at atmospheric pressure. Cooling the sample from the melt at 4 ºC/min at atmospheric pressure results in a lamellar thickness of 104 Å with chains having a tilt angle of 35º. The crystallization of the branched alkane at pressures of ca. 4 kbar and the same cooling rate of 4 ºC/min reveal a new crystal reflection emerging between the (100) monoclinic and the (110) orthorhombic reflections. Simultaneous to the appearance of the new reflection, a sudden shift in the Bragg *d* value of the (110) orthorhombic reflection occurs indicating densification of the orthorhombic unit cell. The new reflection has been assigned as the pseudo-hexagonal phase attributed to the crystallization of the butyl branches at elevated pressures. The pseudo-hexagonal phase merged into the orthorhombic phase upon releasing pressure and

reappeared on increasing pressure. Compared to lamellar thickness at atmospheric pressure, an increased lamellar thickness of 118 Å was observed at ca. 4 kbar with SAXS.

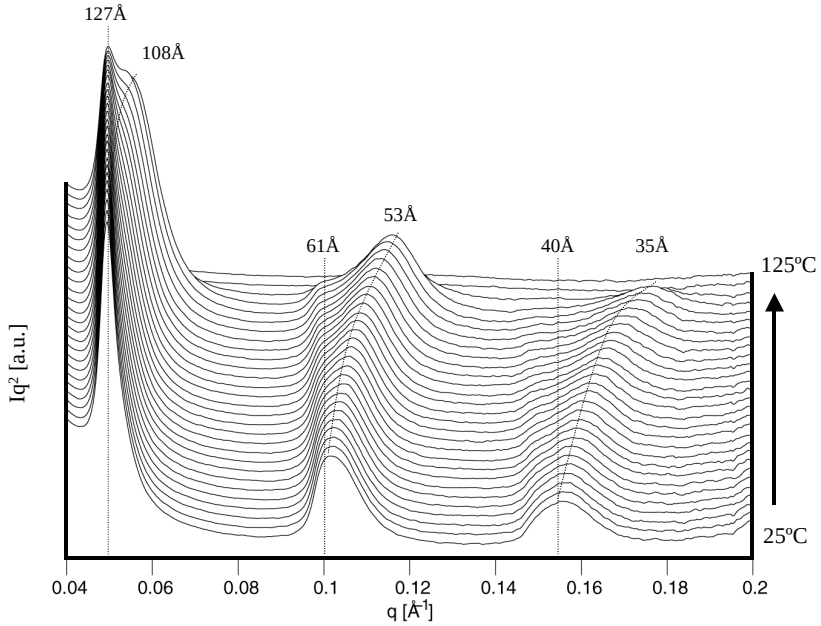

Figure 1. Integrated SAXS patterns showing Lorentz corrected intensity Iq^2 versus q plot during heating at 4 ºC/min at atmospheric pressure. The three orders at 127 Å, 61 Å and 40 Å show a gradual shift to higher 'q' values with increasing temperature.

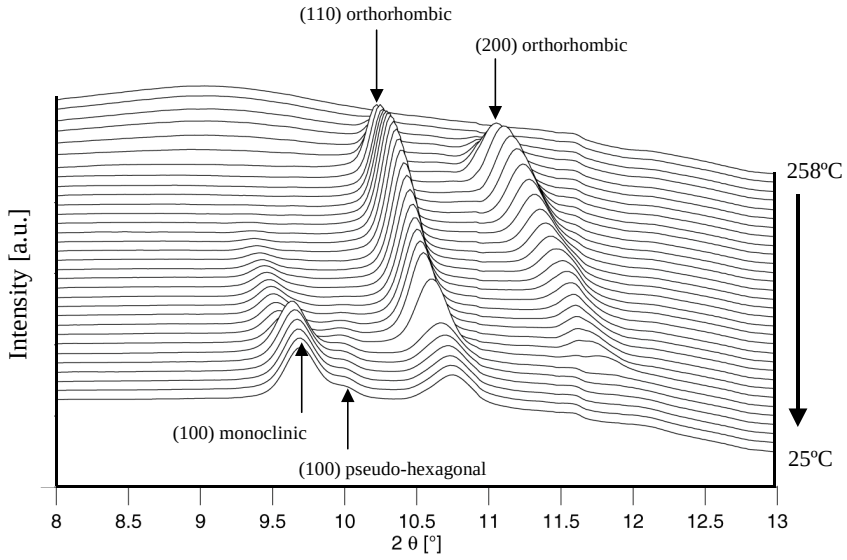

Figure 2. Crystallization of butyl branched alkane at elevated pressures of 4.0 kbar is depicted with a series of integrated WAXD patterns recorded while cooling at a rate of 4ºC/min. The orthorhombic (110) and (200) reflections appear first which gain intensity with increasing supercooling. A weak (100) monoclinic reflection appears at ca. 148 ºC. Upon further cooling at ca. 70 ºC, sudden drop in the intensity of the (110) orthorhombic reflection is observed with the appearance of a new reflection and a simultaneous increase in the intensity of (100) monoclinic reflection. Consider ing the position of the new reflection (d = 4.16 Å) between the (100) monoclinic and (110) orthorhombic reflection, it has been termed as 'pseudo-hexagonal' phase.

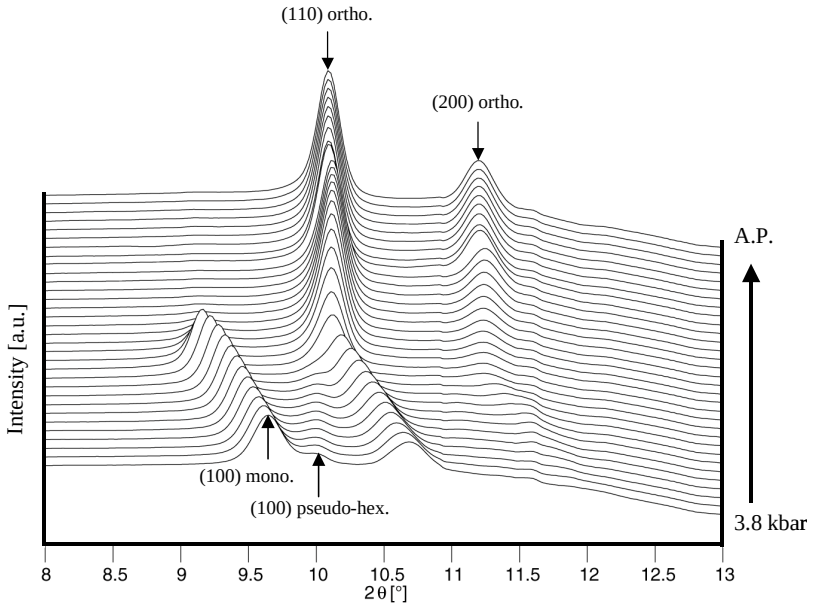

Figure 3. 3-D WAXD plot shows that upon releasing pressure at room temperature, (100) monoclinic and (110) orthorhombic reflections move to lower angles while the (100) pseudo-hexagonal reflection stays at the same position. The latter finally merges in the (110) orthorhombic reflection resulting in an overall increase in the intensity of the orthorhombic reflections.

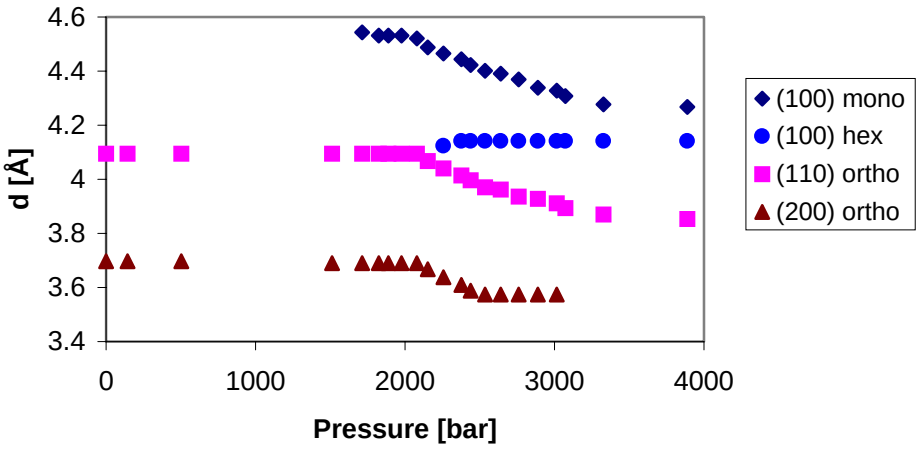

Figure 4. The *d*-values for the various crystalline reflections are plotted against pressure. Upon releasing pressure at room temperature along path 4, the *d* value of the (110) orthorhombic reflection increases from 3.85 Å to 4.08 Å while the $d_{100\ hex.}$ = 4.16 Å merges with that of the (110) orthorhombic reflection at ca. 2 kbar. At atmospheric pressure the *d* values for the various crystalline reflections attain values similar to those in linear paraffins.

For details see publication**: Macromolecules 2002, 35, 5861-5868.**