



## 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**

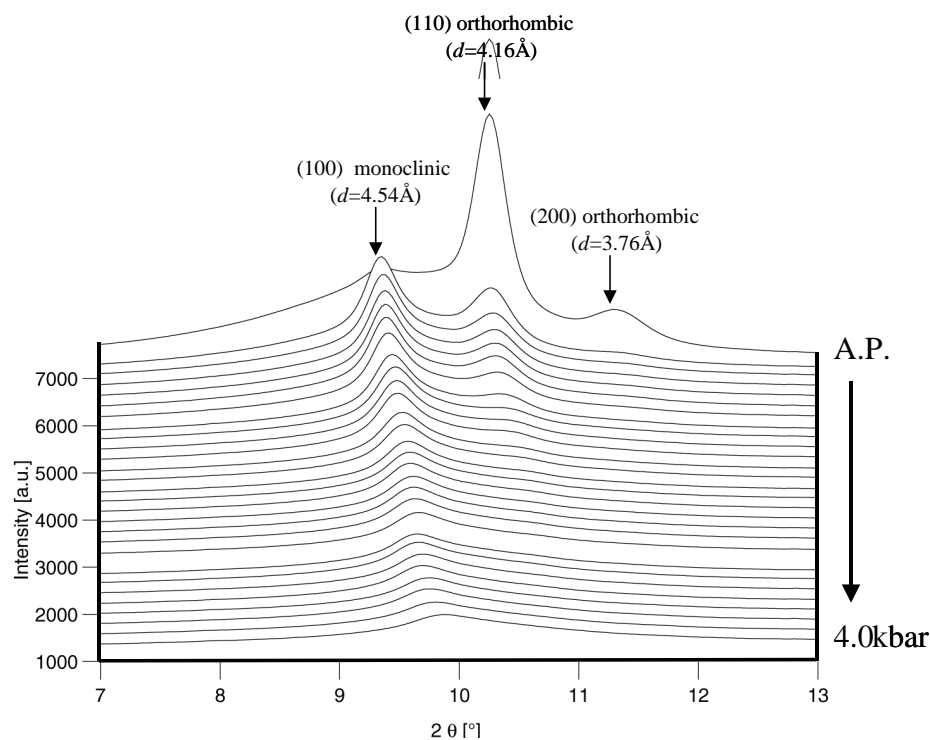
- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you 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.



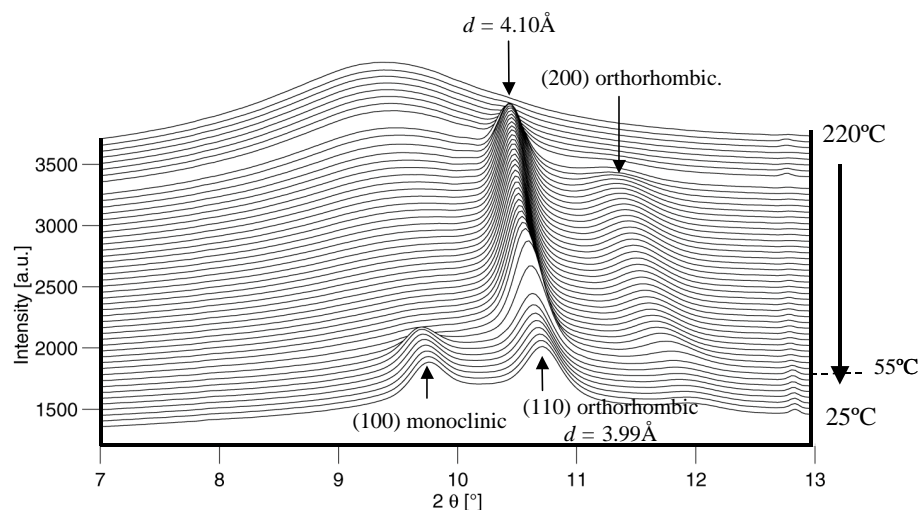
	<b>Experiment title:</b> Structure vs Performance; polymers for ultimate properties	<b>Experiment number:</b> ME161
<b>Beamline:</b> ID11	<b>Date of experiment:</b> from: 11 <sup>th</sup> April 2001 to: 14 <sup>th</sup> April 2001	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Dr. Ann Terry	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Ankur Rastogi (*) Ann Terry (*) Sanjay Rastogi (*)		

**Report:** In situ high-pressure wide-angle X-ray diffraction (WAXD) experiments were performed on a homogeneous ethylene-1-octene copolymer with a comonomer content of 5.2 mol%. The results reveal an apparent pressure induced disordering in the crystal structure at room temperature. Using Raman spectroscopy, it was found that at ca. 3.9 kbar, trans-trans peaks at 1060 and 1130  $\text{cm}^{-1}$  stay and a loss of the crystal field splitting in the methylene-bending region [1400 – 1500  $\text{cm}^{-1}$ ] is observed. This indicates the presence of small crystallites/entities even at these pressures overruling the possibility of amorphous nature akin to the melt. Crystallization of the copolymer at ca. 3.8kbar, results into a monoclinic phase at ca. 55°C simultaneous to the densification of the orthorhombic phase due to solid-solid transition. Further exposure of the pressure-crystallized sample to another pressure cycle yields three different crystalline phases emphasizing the role of pressure in phase segregation. Apart from the orthorhombic and monoclinic reflections, a new reflection at 4.19Å is observed at 3.0 kbar during pressure increase isothermally at 100°C and then again at ca. 80°C during crystallization at ca. 3.8 kbar. Owing to its position and intensity, the new

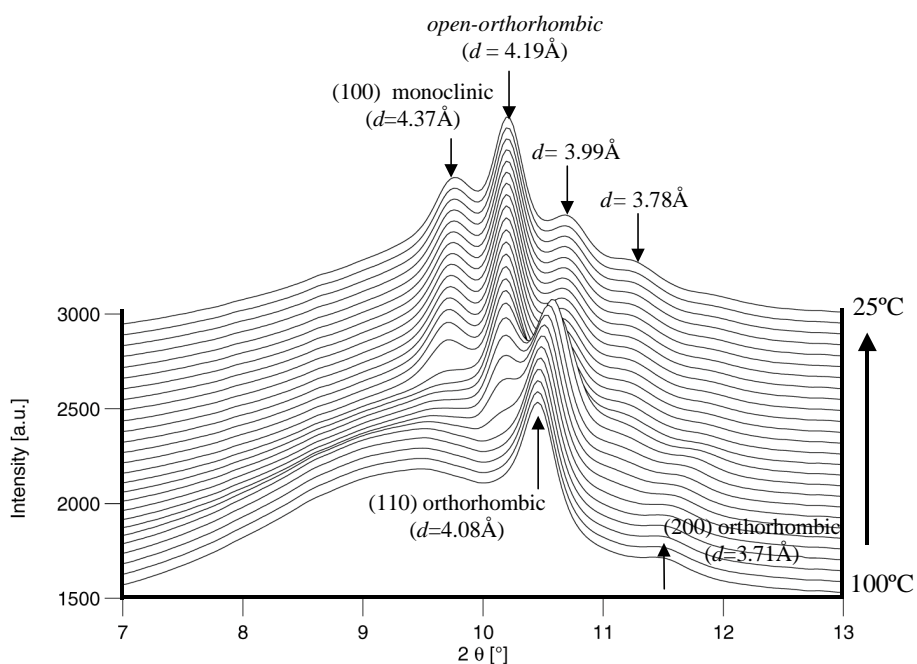
reflection termed *open-orthorhombic* phase is attributed to the crystallization of the hexyl branches including fold surface and other ethylene sequence length distributions (ESLDs), which might crystallize at low temperature, high-pressure conditions. A comprehensive discussion on its origin with respect to comonomer content, a contrast behavior with regard to linear polyethylene and parallelism with monodisperse butyl branched alkane is provided.



**Figure1:** 3-D plot of WAXD patterns integrated along the azimuthal angle during pressure increase at room temperature. Loss of crystalline reflections occurs and a broad asymmetric pattern is obtained at 4.0 kbar

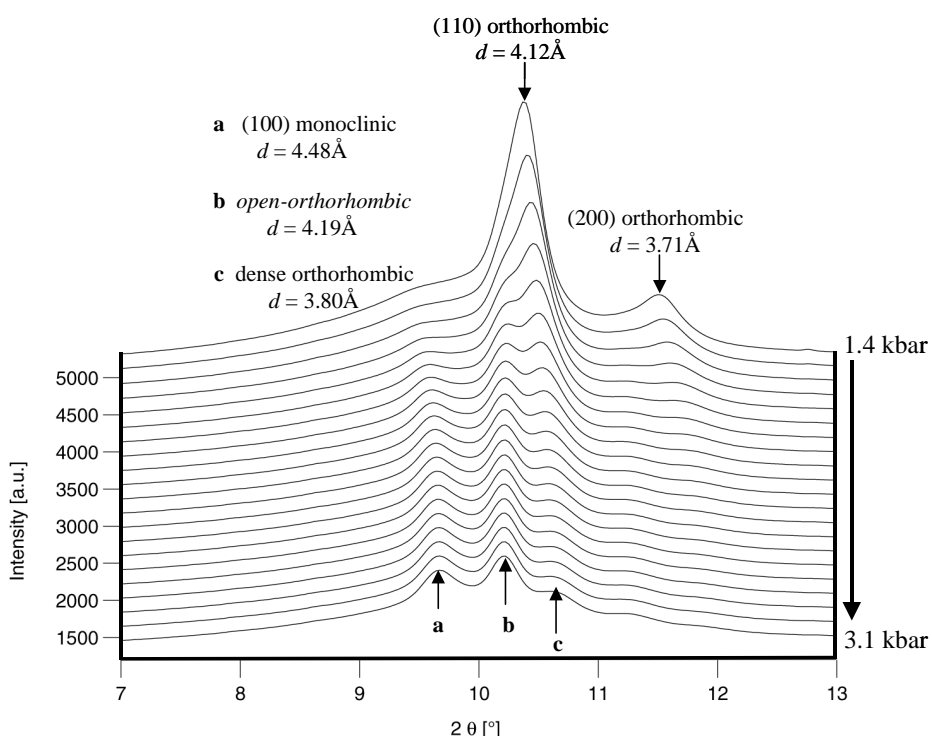


**Figure 2.** WAXD patterns showing a sudden drop in the intensity and a concomitant shift to higher angles of the (110) orthorhombic reflection at ca. 55°C with the incoming of the (100) monoclinic reflection during



cooling at 4°C/min at 3.9 kbar.

**Figure 3.** Diffraction patterns of 5mole% octenes recorded during cooling at 10°C/min from 100°C onwards at ca. 3.8 kbar. The open orthorhombic phase appears at ca. 80°C. This is followed by the incoming of the (100) monoclinic reflection simultaneous with the shift and drop in the intensity of the (110) orthorhombic reflection.



**Figure 4.** Diffraction patterns of 5mole% octene showing the reappearance of the three crystalline phases namely monoclinic, *open orthorhombic* and dense orthorhombic during pressure increase after the sample was subjected to a certain pressure cycle. *A comparison to Figure 1 clearly demonstrates distinction between the sample before and after pressure cycle when subjected to same compression conditions.*

**Manuscript submitted to Macromolecules 2002, under reviewing process (MA020761H)**

