EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

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:** "Resolving Kinetics of Early Structure Formation During Shear Induced Crystallization of Polypropylene**"**	**Experiment number**: ME-1295
Beamline: BM26B	**Date of experiment**: from: 13-Feb-2006 to: 17-Feb-2006	**Date of report**: 05-March-2006
Shifts: 12	**Local contact(s)**: Dr. Florian Meneau	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

F.J. Balta-Calleja*, Araceli Flores, Fernando Ania*

Instituto de Estructura de la Materia, C.S.I.C. Serrano 119. 28006 Madrid, Spain

Julie A. Kornfield, Lucia Fernandez-Ballester*

California Institute of Technology, 1200 E. California Blvd, MC 210-41. Pasadena CA 91106, USA

Timothy Gough*, Bradford University, Ellen Heeley*, Open University

Report:

In our very recent beamtime (13-17 Feb06), we successfully modified our shear apparatus configuration to accomodate the 1-D MicroStrip Gas Chamber detector developed at the BM26b beamline (which has superior signal-to-noise and time resolution capabilities) for WAXD. We are currently analysing the data, which are likely to push back prior limitations on the earliest detectable structures. In addition, we implemented simultaneous measurements of molecular orientation (birefringence) and formation of micron-scale structures (turbidity). Using 'x-ray transparent mirrors' (thin mica sheets coated with aluminium) to bring light through the shear cell, we simultaneously measured 1D WAXD, 2D SAXS, birefringence and turbidity. Furthermore, during the Feb06 beamtime we obtained proof-of-concept results on bimodal blends consisting of a "base resin" (c. 180 kg/mol, [mmmm] > 96%) and a sparse amount of additional "long chains" of known stereochemistry, length and concentration (c. 3500kg/mol in quantities of 0.25% and 1% weight).

This work is part of a broader program to discover the molecular basis of the dramatic effects of flow on the early stages of flow-induced crystallization in semicrystalline polymers[1-3]. The presence of oriented precursors prior to crystallization has attracted scientific consideration in the last few years[4], and its impact on development of semicrystalline morphology during and after flow is of enormous commercial interest. Processing can accelerate crystallization kinetics by orders of magnitude. Indeed, for isotactic polypropylene (iPP), the time necessary for the appearance of wide angle X-ray diffraction (WAXD) crystallinity can be 100 times faster after cessation of short–term shearing than for quiescent conditions at temperatures near 145ºC[1].

Previous synchrotron work provided valuable information regarding the influence of shear stress, shearing duration and crystallization temperature on the nanostructure (lamellar thickness, crystallinity, orientation, etc.) of iPP subjected to shearing [1]. However, the initial stages of crystallization could not be resolved due to the limited time resolution detection capabilities (the fastest acquisition time was 5 s), and

the set up only allowed measurement of either WAXD or SAXS patterns. During the Feb05 run, we successful commissioned a new instrument specially designed to probe shear-induced crystallization at the DUBBLE beamline. Thanks to the detector capabilities at .BM26b, we were able to reduce by an order of magnitude the required WAXD acquisition times for resolution of early structure formation in sheared iPP from our previous 5 s to 500 ms. Also, the capability of simultaneous SAXS and WAXD allowed us to compare the time that structure emerges on the nanoscale and unit-cell scale.

During our recent Feb06 beamtime, our goals were modifying the apparatus configuration to be able to use the rapid time resolution 1D WAXD detector in BM26b along with 2D SAXS, implementing simultaneous optical measurements (turbidity and birefringence), and examining well characterized bimodal materials that allow to probe the influence of specific molecular variables on the formation of shear-induced precursors and the subsequent morphology development. Simultaneous SAXS and WAXD measurements were carried out using a 2-D multiwire gas-filled SAXS detector (placed 6.5 m away from the sample) and the DUBBLE 1D WAXD Microstrip Gas Detector positioned in such a way that the equatorial region of the crystalline reflections could be observed. The simultaneous birefringence and turbidity measurments were performed using "x-ray transparent mirrors" (consisting of Al coated mica sheets) that allow a He-Ne laser beam to go through the flow cell diamond windows coaxially along with the x-ray beam. A top view picture with an schematic diagram of the optical components and the x-ray and laser paths is shown in Figure 1.

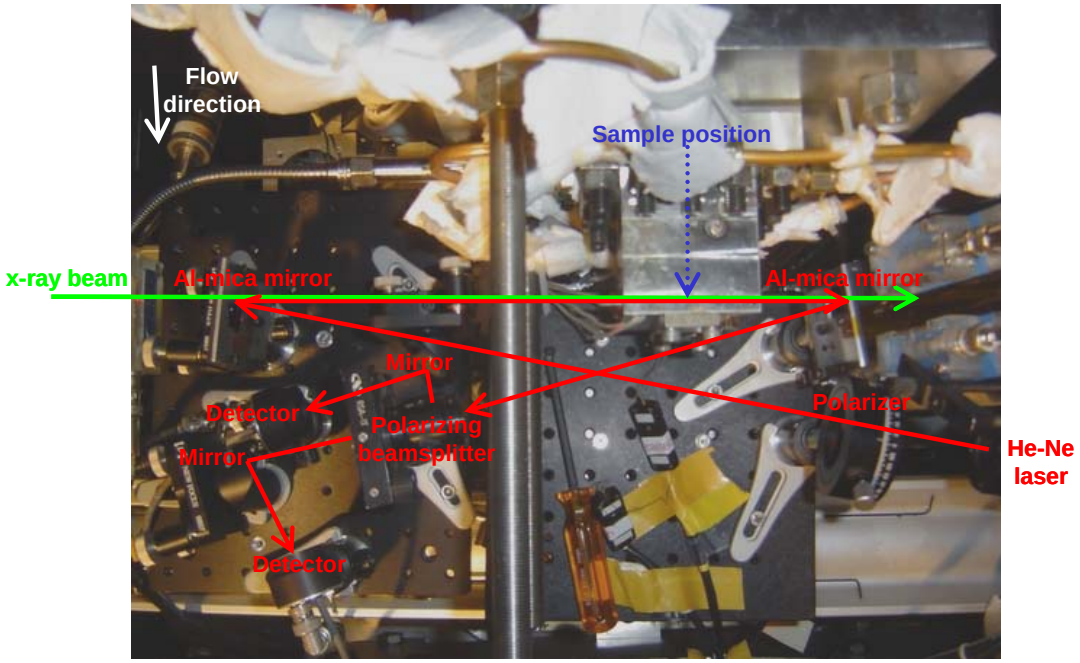

Figure 1. Top view of the simultaneous optical set up.

In the experiments performed, the flow cell was initially held at 215 ºC (above $T_{m,o}$ = 208°C) and filled with polymer melt from the reservoir. The cell was then cooled down to the crystallization temperature, and held isothermally thereafter. Then, a short-term high shear pulse was applied to the melt, and the diffraction patterns, as well as the birefringence and turbidity signals, were recorded during and after the shear pulse. Figure 2 shows an example of the four signals measured simultanously for a sample containing 1% of 3500kg/mol chains in a 186kg/mol matrix after being subjected to a wall shear stress of 0.065 MPa for 10s, which produces a highly oriented sking at high shear stresses (near the wall). It is interesting to note that a change in the growth rate is observed both in the integrated SAXS pattern as well as in the turbidty signal. This step in turbidity development has been observed in our home laboratory but has not previously been correlated with simultanous x-ray measurements. It has been hypothesized to correspond to the completion of the highly oriented skin near the flow cell walls (high overall growth rate) followed by slower growth of non-oriented crystallites in the areas of lower stress. Detailed analysis of the x-ray data will be able to determine whether this hypothesis is correct.

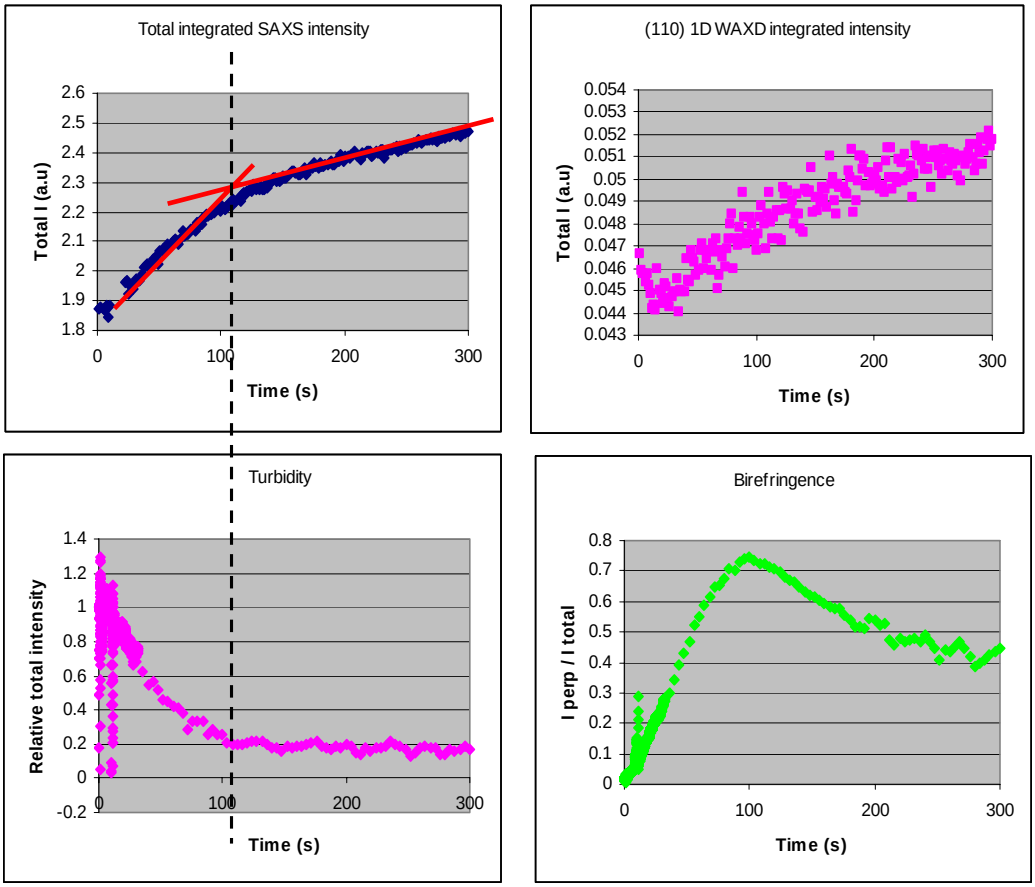

Figure 2. Simultaneous 2D SAXS, 1D WAXD, turbidity and birefringence for 1% 3500kg/mol in 186kg/mol matrix (137C 0.065MPa 10s).

During this Feb06 run, we tested bimodal blends with a sparse amount of "long chains" of known stereochemistry, length and concentration (c. 3500kg/mol in quantities of 0.25% and 1% weight) in a "base resin" (c. 180 kg/mol, [mmmm] > 96%). These materials are intended to extend our prior work[5] with well-characterized model iPP systems consisting of the same "base resin" with "long chains" of 920 kg/mol. Based on rheo-optical results obtained in our home laboratory and on the preliminary results of this Feb06 run, we know that these much longer chains (3500 kg/mol) have particularly dramatic effects on flow induced crystallization (see Figure 3 where birefringence and total integrated SAXS intensity are shown for the same shearing conditions for the base polymer alone and for a blend with 0.25% weight of long chains).

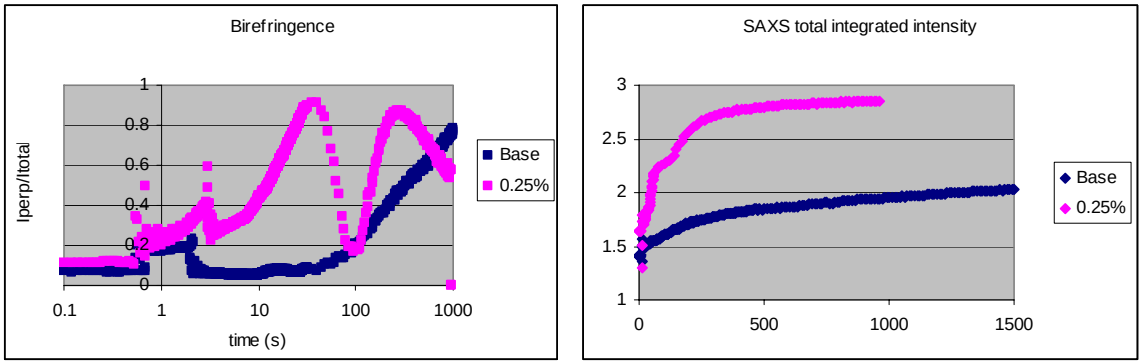

Figure 3. Birefringence and total integrated SAXS intensity for 0% and 0.25% of "long chains" (137C 0.11MPa maximum strain)

References

1. G Kumaraswamy, RK Verma, JA Kornfield, F Yeh, BS Hsiao. Macromolecules 2004, 37, 9005-9017.
2. G Kumaraswamy, JA Kornfield, F Yeh, BS Hsiao. Macromolecules 2002, 35, 1762-1769.
3. G Kumaraswamy, RK Verma, AM Issaian, P Wang, JA Kornfield, F Yeh, BS Hsiao, RH Olley. Polymer 2000, 41, 8931-8940.
4. RH Somani, L Yang, BS Hsiao. Physica A 2002, 304, 145-157.
5. M. Seki, D.W. Thurman, J.P. Oberhauser, J.A. Kornfield, *Macromolecules*, 35, 2583 (2002)