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# 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:**<br>**Time-resolved high-pressure SAXS studies of crystallization of PEO and its blends with PMMA** | **Experiment number**:<br>ME - 5 |
|---|---|---|
| **Beamline**:<br>ID02A | **Date of experiment**:<br>from:03-June-2000 to:06-June-2000 | **Date of report**:<br>25-August-2000 |
| **Shifts:9** | **Local contact(s)**:Dr.T.Narayan | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

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**Report:**

The aim of the measurements was to contribute to the better understanding of real-time structure development of PEO/PMMA blends with the help of crystallization under high pressure. Crystallization of low-molecular fractions of PEO (Mw ~ 3000, 4000) / PMMA (Mw 1300, 3900) of 8/2 and 6/4 compositions were studied by time-resolved SAXS method. The conditions of the experiment were as follows: wavelength 0.1 nm, sample detector distance 5 m, counting time per each frame 5s. Pressure up to 1600 bar was generated by syringe-type generator and transferred by water into the pressure cell with diamond windows.

After application of high-pressure to the molten blends followed by cooling, the PEO crystallizes in the most stable lamellar EC (extended chain) structures. The crystallization conditions at high pressures are apparently better than those at atmospheric pressure. Application of high-pressure to the blends, already having the EC structure, results in partial transformation of lamellae into the unstable NIF (non-integral folding) structure. In the blend PEO3000/PMMA1200 (8/2) (Fig. 1) pressurized to 1400 bar at 52$^{o}$C the thickness of NIF

lamellae starts at 13.6 nm and then grows up to 14.5 nm. After 100s NIF lamellae transform back to the EC crystals. Similarly, in the blend PEO3000/PMMA3900 (6/4) (Fig. 2) the pressure 1200 bar applied at 48°C initiates NIF lamellae crystallization with the thickness of 14.8 nm, which grows up to 15.9 nm and disappears after 90 s.

The PEO4000/PMMA1200 (8/2) blend displays different structure behaviour (Fig.3). After applying pressure of 1350 bar at 52°C to the lamellar system with periodicity of 18.9 nm a part of these lamellae changes thickness to 15 nm. After 295 s this new lamellar system, apparently favored under high-pressure conditions, dominates but both systems remain preserved even during subsequent heating to 65°C (600 s) and also after cooling and depressurizing (655 s). Then the structure slowly changes back to the one favored at atmospheric pressure. Due to the higher molecular weight of PEO the structures preferred at high or low pressure can co-exist for a long time. These both structures correspond to the unstable NIF lamellar systems. This has not been observed under atmospheric conditions.

The transition of NIF to IF crystals during isothermal crystallization had been attributed to the effort of the system to exclude all chain-ends from crystalline phase of lamellae. The development of NIF crystals after a pressure change is not simply explainable by this model. It is not probable, that pressure could return part of chain-ends back into the interior of crystals. Tilting of chains could cause the described thinning of lamellae after a pressure change. The formation of (only) NIF lamellar systems in blends with PEO4000 can be connected with higher molecular weight of PEO. The role of amorphous diluent PMMA to the structure development is also not clear. For better insight into the structure behaviour of these systems more systematic measurements at high-pressures are needed.

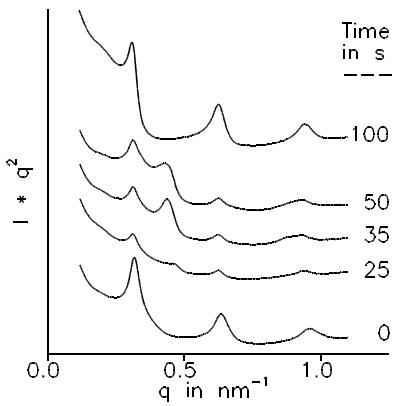


Fig.1

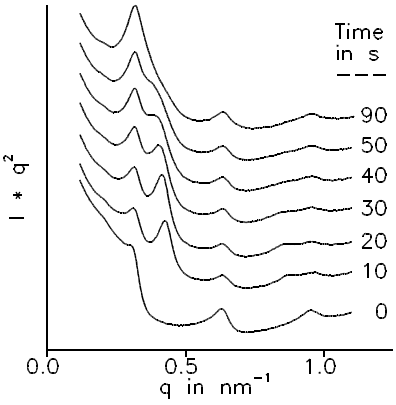


Fig.2

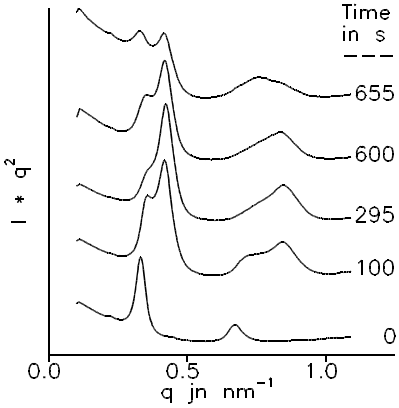


Fig.

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