ESRF	Experiment **title:** Kinetics of crystallisation in polyethylene terephthalate) subjected to rapid draw around the glass transition.	**Experiment number:** SC-120
Beamline: ID13	**Date of experiment:** **from. 22.10.95 to: 24.10.95**	**Date of report:** **30.08.96**
Shifts: 6	**Local contact(s):** Dr. C.Riekel & Dr. P.Engström	*Received at ESRF:*

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Report:

These experiments were aimed at extending our understanding of the molecular processes associated with strain induced crystallisation in the organic polymer polyethylene temphthalate) (PET). By exploiting the high brilliance of the ESRF and the availability of a purpose designed x-ray camera linked to a Photonics Science CCD detector which allowed a complete two-dimensional WAXS pattern to be recorded with exposure times as short as 40 msecs, we have been able to demonstrate that in contrast to widely held views crystallisation does not begin until drawing and the associated increase in polymer orientation was essentially complete (Blundell *et al*, 1996). The rates used in these experiments were very high and comparable to those used in industrial processing *i.e.* - 72,000% /minute. At these rates drawing was complete in less than a second and the success of these experiments was dependent on a Synoptic i860 frame grabber which allowed up to 31 frames (or 124 where some compromise was made in the fraction of the x-ray pattern which was recorded) to be collected without any "deadtime" between frames before the sequence of frames needed to be downloaded to a PC. Detailed analysis of these patterns showed that crystallisation followed the kinetics of a first order transformation process in which the degree of crystallinity levels off exponentially with time, possibly associated with the sporadic appearance of crystal nuclei. This is in contrast to the crystallisation of unoriented PET which is associated with spherulitic type growth which usually approximately follows Avrami kinetics with an exponent $n \sim 3$. Experiments were performed at a number of temperatures between 80°C and 110°C. Surprisingly it was also found that the crystallisation rate was insensitive to temperature. We also recorded the variation in the WAXS pattern for draw ratios varying from -1.5:1 to 4.0:1.

Data from the experiments performed at 90°C are shown in figure 1 where the variation in polymer orientation and crystallinity is plotted as a function of frame number for a range of draw ratios. The draw ratio is expressed in terms of the number of steps performed by the stepper motors to which the specimen was attached in the x-ray camera with 825 steps corresponding to a draw ratio of- 2.0:1.

From Figure 1 it can be seen that for draw ratios less than -2.0:1 (825 steps) the orientation which develops during the first ~ 8 frames is not sustained with the relaxation of orientation following a similar decay curve for all experiments were the number of steps was less than 825. Further in all these experiments there was no development of crystallinity. In contrast, for experiments in which the number of steps was greater than 825 the orientation developed was retained after drawing ceased with crystallinity starting to develop from the conclusion of drawing and continuing to develop exponentionally with a rate constant which was essentially independent of the draw ratio. The observations summarised in Figure 1 are important because for the first time the allow the dependence of the occurrence of stress induced crystallinity on draw ratio to be related to the changes in real-time of polymer orientation during the draw process. A detailed analysis of this data is in progress fof submission to polymer.

References

Blundell,D.J., MacKerron,D.H., Fuller,W., Mahendrasingam,A., Martin,C., Oldman,R.J., Rule,R.J. and Riekel,C., *Polymer* (1996), **37**, 3303-3311.

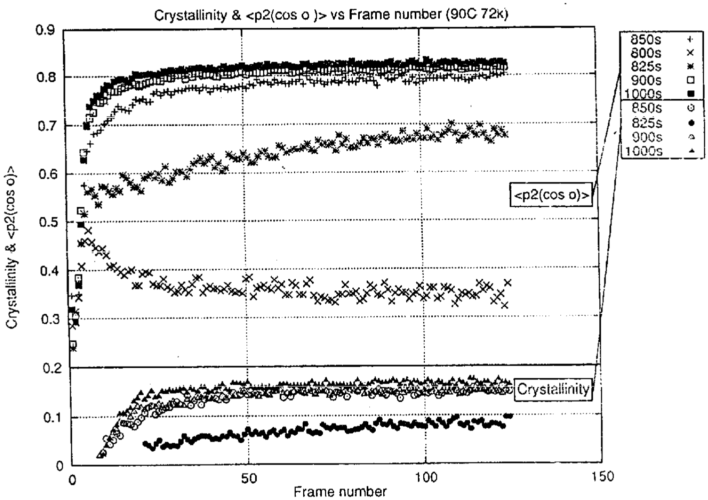

Figure 1: The variation in polymer orientation and crystallinity during drawing of PET at a draw rate of 72,000% per minute and a temperature of 90°C for various draw ratios (expressed as a number of steps with 825 corresponding to a draw ratio of ~ 2.0: 1).