ESRF	**Experiment title:** **Study of local premelting and precrystallization by simultaneous SAXS and wide angle X-ray scattering.**	**Experiment number: SC338**
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Report:

The purpose of the project was to verify the occurrence and characterize premelting and precrystallization effects in samples of isotactic polypropylene (iPP). Aside from lattice expansion these effects involve a lower resolution of diffraction data related to large increase of thermal motion and, in some cases, differences in the distribution of diffracted intensity among the main diffraction maxima [1]. For iPP WAXD evidence in previous literature [2] suggests the possible occurence of such phenomena as the crystalline component in diffraction patterns at the end of the fusion process and at the beginning of crystallization appear to differ from patterns of well crystallized polymer. Since the amorphous fraction is overwhelming high radiation fluxes are needed to avoid artifacts.
DSC annealed iPP of well characterized stereoregularity and molecular weight was used to avoid recrystallization and annealing processes concomitant with the fusion process. Most of the work was carried on polymer fractions of high stereoregularity: typically ca. 0.2mg of iPP with mmmm pentads content exceeding 99%, enclosed in a glass capillary.
The original objective was to observe phenomena simultaneously at wide and srnall angle but with the available experimental set-ups the angular ranges of interest could not be observed simultaneously and we chose to concentrate on WAXD. Initially a scintillation counter was used but we shifted to a CCD camera to improve counting statistics.

Preliminary refinement of crystallite dimensions from spectra at 170°C suggest, neglecting instrumental broadening, crystallite thickness well exceeding 50nm. The melting process was followed up to 180°C i.e. ca. 1°C lower than the melting onset (180.8°C) determined by DSC. The estimated crystalline component that remained in the final stages is less than 1%. Sample temperatures are probably accurate within 1 °C while stability is within 0.2°C: these values should be improved. Experiments show no substantial redistribution of intensity among the main diffraction maxima of the WAXD pattern (Figure 1). The peaks become sharper than at room temperature confirming that under the experimental conditions the largest and more perfect crystals of the a-modification of iPP melt last. Spectra closest to melting show noise levels that could prevent the observation of the weak peaks with d < 0.40 nm. Results with less stereoregular samples confirm the outlined picture.

Figure 2 shows patterns, after melting at 190°C, recorded at different times during crystallization at 134°C. The peak width is larger than in the melting study, due to the crystallization temperature. Two peaks are affected by more apparent broadening the initial crystallization stages and this could well be due to precrystallization effects. The intensity distribution also deviates at first from the expected ratios but preferred orientation may need to be considered. Additional weak diffraction maxima are initially apparent, some of them consistent with the initial development of iPP crystal modifications different than α-iPP.

The preliminary elaboration of the results of this project in the case of iPP suggest the possibility of precrystallization effects whereas significant premelting effects could not be clearly evidenced.

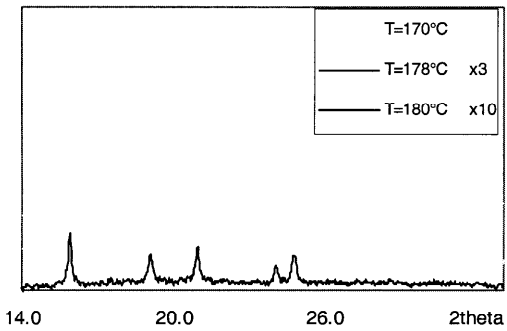

Figure 1: iPP melting,amorphous and glass subtracted out

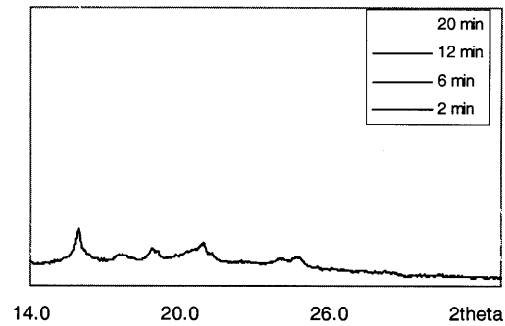

Figure 2: Crystallization at 134°C, amorphous and glass subtracted out

[l] Dorset, D., Alamo, R.G., Mandelkern, L., *Macromolecules*, 1992,25,6284.
[2] Forgacs, P., Sheromov, M.A., Tolochko, P., Mezentsev, N.A., Pindurin, V.F. *J.Polym.Sc., Polym. Phys. Ed.* 1980,18,2155.