

Experiment 26-02-510 at BM26, March 8-12. Main proposer: Giuseppe Portale.

During processing, surface layers of polymeric materials undergo very fast cooling which, in some cases, reaches hundreds of degrees per second. Under these extreme conditions the structuring of the material becomes critical and the resulting level of order reduces on increasing cooling rate. In some cases one observes the formation of a metastable state with intermediate degree of order which remarkably affects mechanical properties (e.g. scratch resistance). A particularly important case is that of isotactic polypropylene (iPP) and its random copolymers with ethylene (C3C2) or higher α -olefins (C3C4, C3C6, etc...). Upon fast cooling, a competition sets in between the development of the most stable monoclinic α -form, that of a low order structure, usually referred to as mesophase or smectic phase, and the freezing of the liquid-like disordered amorphous state. In view of the increasing commercial relevance of random copolymers of iPP, it seems important to establish what is the maximum cooling rate that can be imposed to these materials to avoid formation of the mesomorphic structure. So far, very little is known on the role of molecular features in smectic phase formation upon quenching.

We have developed a simple experimental approach to fill this gap. The method is based on the acquisition of the instantaneous temperature during the rapid cooling of a thin polymer film from the molten state. The resulting cooling curves have been interpreted as a Continuous-Cooling-Transformation (CCT) diagram, indicating when and at what temperature the phase transition takes place under a given cooling history. Even if CCT diagrams would be important for the understanding and modeling of polymer structuring under processing conditions, the experimental data currently available for this class of materials are largely behind, those available for metals, both in terms of quality and quantity. Detailed kinetic investigation, leading to iso-transformations curves (locus of time and temperature coordinates to reach the same extent of transformation in different cooling conditions) has been possible so far only for slowly crystallizing polymers like PEEK.

Basically, from the cooling curves T vs t , one can calculate the instantaneous cooling rate, dT/dt , which, when plotted as a function of actual temperature clearly shows a peak, which reflects the latent heat released by the phase transition. (see figure 1) This enables one to accurately determine the coordinates in the Temperature-time space corresponding to the onset, to the maximum rate of crystallization and to the end of the process. From these data the CCT curves shown in figure 2 are directly obtained.

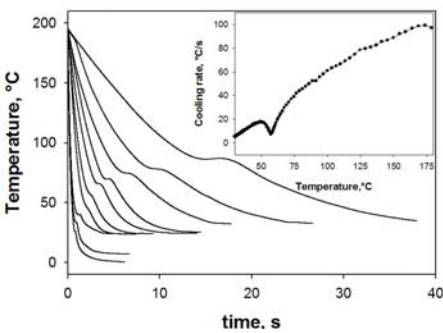


Figure 1 Examples of cooling curves. In the inset the curve obtained by plotting the cooling rate as a function of temperature is shown.

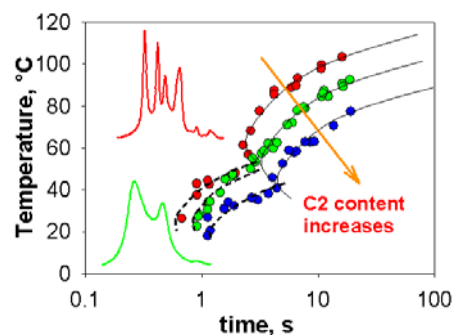


Figure 2. Example of CCT diagrams for propene/ethylene random copolymers. WAXD patterns of the characteristic obtained structures, alpha and meso phase, are included.

From figure 2, the presence of two distinct zones is clear. The one at higher temperature is associated to the crystallization in the stable α -modification, while the other is related to development of mesomorphic phase.

The aim of this project was to assess feasibility of using on-line WAXD to detect development of the two types of structures (α -modification and mesomorphic) in real time while the sample cools very fast.

This set of experiments needs coupling of our quenching device, which enables controlled heating and rapid cooling of thin polymer films by blowing compressed air or cold nitrogen vapors on the film surface, to a sensitive, accurate, low noise and extremely fast detector. Taking into account that from previous experience we know that the whole structuring process can last a fraction of a second, a sampling frequency of tens of Hz and a millisecond time resolution are required. In order to achieve a millisecond WAXS time resolution, we used the new Pilatus 300K detector available at DUBBLE. The detector has been used to both acquire the WAXS images and to trigger the Temperature acquisition in order to record the cooling curves as well. WAXS images-Temperature correlation has been achieved with a time precision better than 10ms.

The following conditions have been successfully adopted: exposure time of 47 ms, collection of 20 frames each second.

The quality of the WAXD patterns obtained with this short exposure time can be appreciated in Figure 3, in which the patterns corresponding to the α -modification and the mesomorphic structure are compared to those acquired using 15 s of exposure.

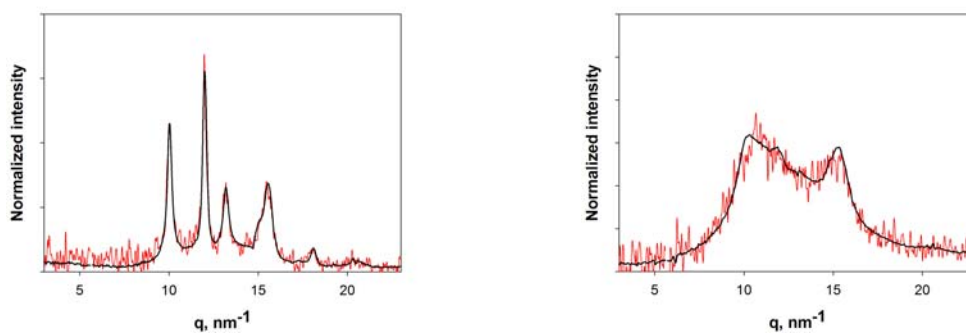


Figure 3. Comparison of WAXD patterns of the α -form (left) and of the mesomorphic form (right) collected from an *i*-PP homopolymer with exposure of 15 s (black lines) and of 47 ms (red curves).

Selected galleries of images corresponding to different fast cooling experiments have been examined during the beamtime and compared with the information gathered from the thermocouple signal. It has been verified that there is a perfect correspondence between the start, the progress and the end of the crystallization process determined from the two independent techniques, i.e. X-rays and cooling curve analysis.

The evolution of the WAXS profiles as a function of time during fast cooling (about 100 $^{\circ}\text{C}/\text{s}$) for *i*PP homopolymer and of a random copolymer C3C4M5 (random propane/butane copolymer with 5% w/w% butane content) is reported in Figure 4.

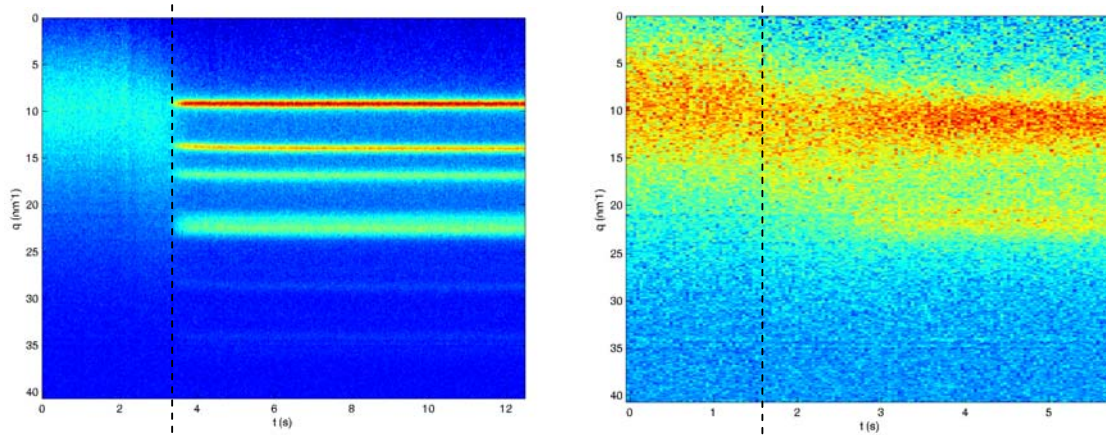


Figure 4. Comparison of fast cooling experiments on iPP homopolymer (left) and of a random copolymer C3C4M5 (right). Each profile has been acquired using a 47ms exposure time with a 20 Hz sampling rate. The same cooling rate has been used for both the experiments. The cooling rate was about 100 °C/s. The broken lines helps to visualize the onset of crystallization in the two experiments.

From Figure 4, it can be easily noted that, at the selected cooling rate, only monoclinic structure formation is found for the iPP homopolymer, while pure mesophase is formed for the C3C4M5 copolymer under cooling.

The data obtained will help us to construct the phase diagrams for the iPP homopolymer and its copolymers under very fast cooling conditions.