ESRF	**Experiment title:** *Study of the hierachical crystallization of crystalline-crystalline block copolymers containing an isotactic polypropylene block*	**Experiment number**: MA 3273
Beamline: BM26B	**Date of experiment**: from: 1/10/2016 to: 3/10/2016	**Date of report**: 03/06/2017
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Report:

The crystallization behavior of novel crystalline-crystalline block copolymers (BCPs) formed by an isotactic polypropylene (iPP) block linked to a polyethylene (PE) block, iPP-*b*-PE, or a random copolymer of propene/1-octadecene (P-*co*-C18) block, iPP-*b*-(P-*co*-C18), has been investigated combining SAXS and WAXS measurements. It is worth reminding that iPP shows a complex polymorphic behavior due to the existence of three different crystalline forms (α, β and γ) and of a mesomorphic form. They are obtained from the melt under different crystallization conditions[1] and show different physical and mechanical properties. By linking an iPP block with a chemically different block it is possible to combine the wide range of morphologies developing in crystalline BCPs with the polymorphism of iPP and, by choosing the proper crystallization conditions, it is possible to tailor the properties of this class of materials.

The phase segregation and crystallization behavior of these samples has been studied by time-temperature resolved simultaneous SAXS/WAXS measurements. The experiments have been focused on monitoring the structural development during crystallization and subsequent melting of iPP-*b*-PE and iPP-*b*-(P-*co*-C18) samples. The different structures have been easily identified by their WAXD pattern, thanks to the diagnostic reflections of the three different crystalline forms and mesomorphic form of iPP and of the orthorombic form of PE.

For the samples belonging to the iPP-*b*-PE series, the temperature profile employed was: first heating from 25 to 180 °C at 30 °C /min, isotherm at 180 °C for 1 min, first cooling from 180°C to 25 °C at 10 °C/min, second heatingfrom 25°C to 180 °C at 10 °C/min and last cooling from 180 to 25 °C at 30 °C/min.

The WAXS (A,B) and SAXS (C,D) profiles recorded during the first cooling and second heating for the sample RDG-1-91 having an iPP weight fraction *fw*=0.74 are shown in Figure 1. The WAXS profiles clearly indicate that upon cooling PE crystallizes first. This is shown by the appearance of the weak $(110)_{PE}$ reflection of PE at 114°C (Figure 1A). The iPP block crystallizes at lower temperatures, in particular at 109°C, as shown by the appearance of the reflections $(110)_\alpha$ and $(040)_\alpha$ of iPP. The WAXS profiles recorded during heating (Figure 1B) show that the PE crystals melt at a slightly lower temperature than iPP crystals. In fact on heating the sample, the intensities of the reflections of both PE and iPP blocks decrease but at 139°C, when the $(110)_\alpha$ reflection of iPP is still present, no reflections of the PE block are detectable.

The SAXS pattern of the melt (profile at 180 °C in Figure 1C) shows the absence of correlation peaks thus indicating that no microdomain structure is present in the melt. It is worth noting that the presence of phase-separated melt cannot be excluded since the contrast in electron density of PE and iPP in the melt is low. The SAXS profiles recorded at temperatures lower than 107°C present two broad peaks q^1*=0.20nm^{-1} and q^2*=0.54nm^{-1}, respectively correponding to Bragg distances of 31.4nm and 11.6nm. These peaks indicate the formation of a microphase-separated structure driven by crystallization. Although the two correlation peaks appear almost simultaneously during cooling, they are attributed to the periodicietes of the lammellar stacks of the PE block and iPP block respectively, as determined by comparison with the SAXS profiles of PE and iPP homopolymers (data not shown).

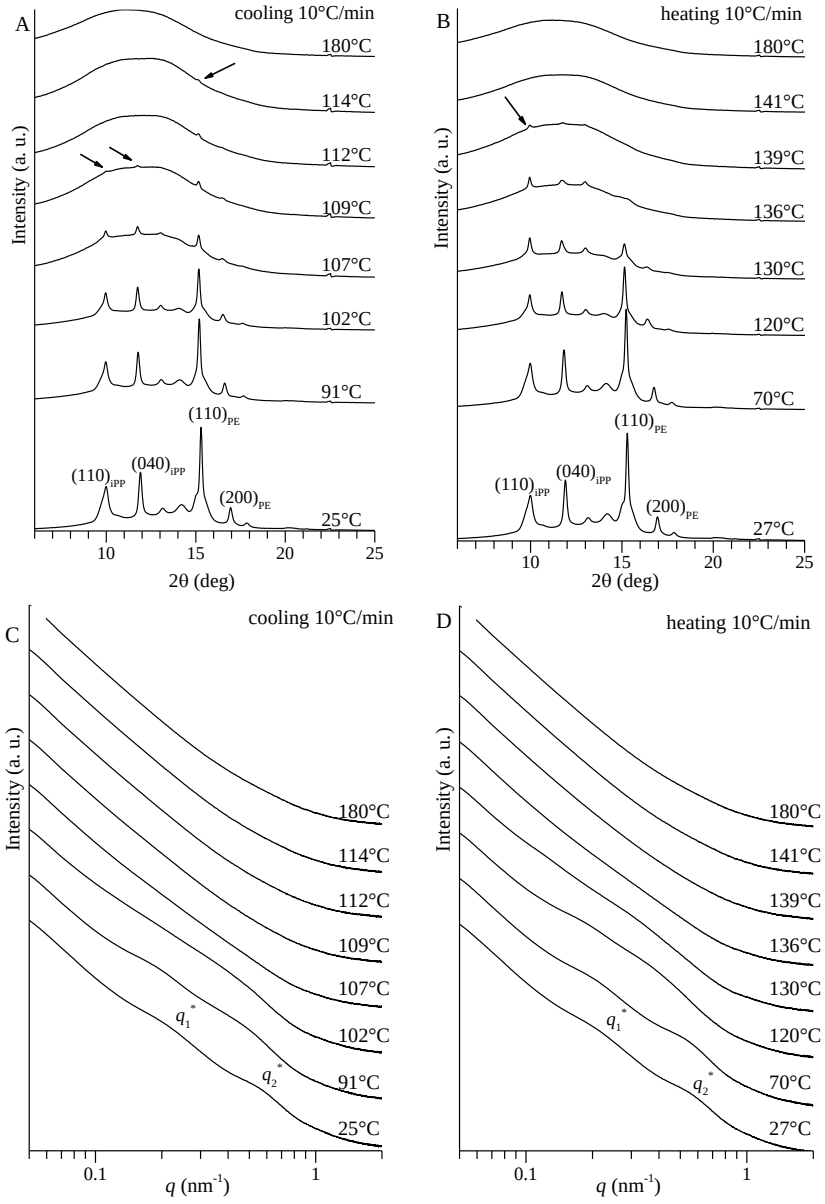

Figure 1 *WAXS (A,B) and SAXS (C,D) profiles of the sample RDG-1-91 ($f_{w\ iPP}$=0.74) belonging to the series of iPP-b-PE BCPs, recorded during cooling and heating scans at 10°C/min at the indicated temperatures.*

Similar results are obtained for samples belonging to the same series showing different mass fraction of the blocks.

For the samples belonging to the iPP-*b*-(P-*co*-C18) series, the temperature profile employed was: first heating from 25 to 180 °C at 30 °C /min, isotherm at 180 °C for 1 min, first cooling from 180°C to -40 °C at 10 °C/min, second heating from -40°C to 180 °C at 10 °C/min and a last cooling from 180 to 25 °C at 30 °C/min.

In Figure 2 the WAXS (A,B) and SAXS (C,D) profiles recorded during the first cooling and second heating are shown for the sample RDG-1-148P having an iPP weight fraction *fw*=0.49. The WAXS profiles cleary show that upon cooling (Ficure 2A) iPP block crystallizes in the α form of iPP and that on further cooling,

the crystallization of the side chains of C18 units occurs in an orthorhombic form similar to that of PE. In fact in the profile recorded at -40°C the intensity of the $(111)_{\alpha}$ reflection of iPP increases because of the superimposition of the $(110)_{PE}$ reflection of PE-like crystallites.

The SAXS pattern of the melt (profile at 180 °C in Figure 2C) shows the absence of correlation peaks thus indicating that no microdomain structure is present in the melt. As in the case of iPP-*b*-PE BCPs, the presence of a phase-separated melt cannot be excluded because of the too low contrast. The SAXS profile recorded at 101°C, when iPP block starts crystallizying, shows the appearance of a correlation peak at q^1*=0.38nm^{-1}, corresponding to a Bragg distance of 16.5 nm. At temperatures lower than 0 °C, also the P-*co*-C18 block (in particular the side chains of C18 units) start to crystallize and the correlation peak at q^1*=0.38nm^{-1} becomes less pronounced, due to the increase of the SAXS diffuse intensity at q>1nm^{-1} (correlation distances <6nm). The SAXS profile of the poly(1-octadecene) (PC18) homopolymer showing a correlation peak at q*=0.98nm-1 is reported for comparison (green profile in Figure 1C). Similar results are obtained for samples belonging to the same series showing different mass fraction of the blocks.

Following this first data analysis that clarifies the crystallization sequence in these BCPs, state of art analytical tools for the analysis of SAXS and WAXS profiles are going to be applied. This will let us gain a deeper understanding of the crystallization behaviour of these BCPs in order to tailor the properties of this new class of materials.

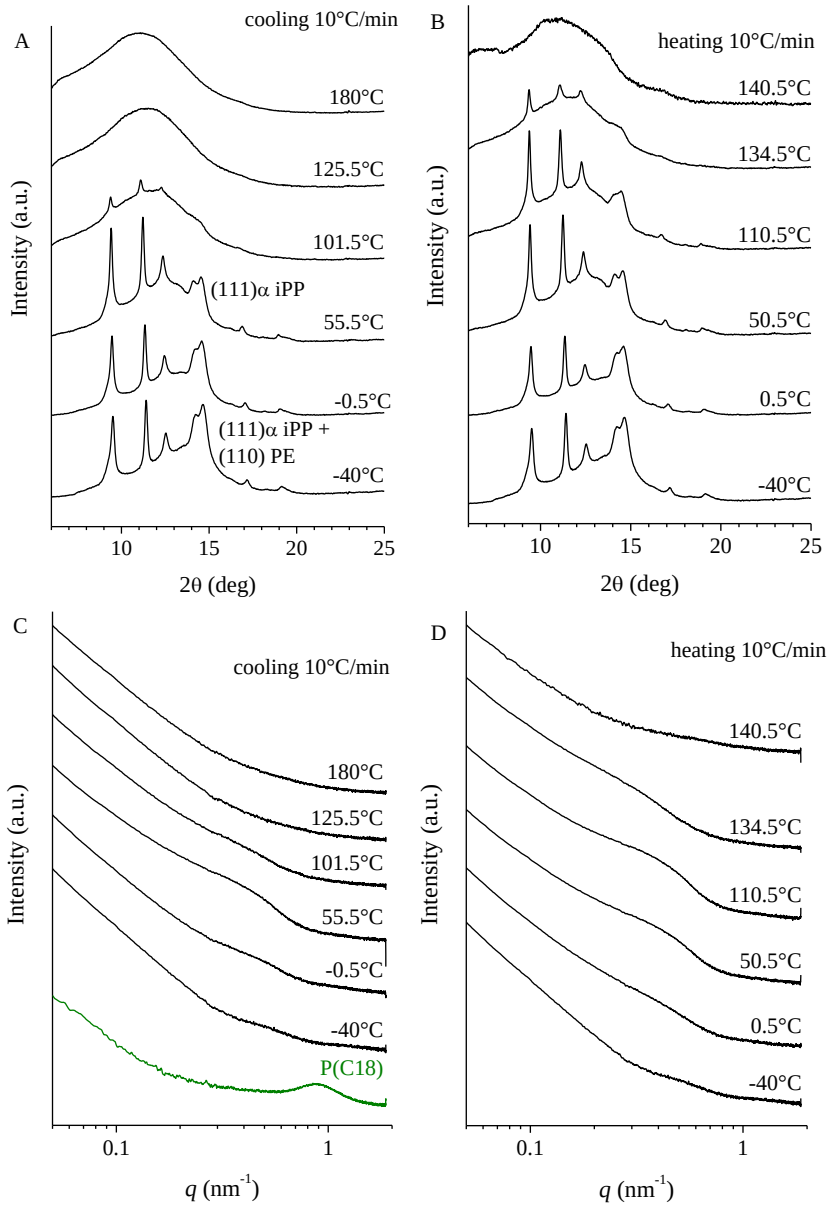

Figure 2 *WAXS (A,B) and SAXS (C,D) profiles of the sample RDG-1-148 ($f_{w\ iPP}$=0.49) belonging to the series of iPP-b-(P-co-C18), recorded during cooling and heating scans at 10°C/min at the indicated temperatures.*

References:

1. Bruckner, S.; Meille, S.V.; Petraccone, V.; Pirozzi, B. *Prog. Polym. Sci.* **1991**, *16*, 361.