"Role of microstructure on the melt crystallization of novel block ethylene/4-methyl-1-pentene copolymers from single site catalysts"

L. Boragno[1], P. Stagnaro[1], S. Losio[1], F. Azzurri[2] and G.C. Alfonso[2]

[1]Institute for Macromolecular Studies, ISMAC-CNR, Via De Marini 6 , 16149 Genoa, Italy
[2]Department of Chemistry and Industrial Chemistry – University of Genova, Via Dodecaneso 31,16146 Genoa, Italy

A series of WAXD experiments involving novel ethylene/4-methyl-1-pentene (E/Y) copolymers was performed. Though these copolymers are obtained from a non-living, single step polymerization, owing to combined effect of the catalytic system employed (single site stereospecific metallocenes) and of the bulky Y comonomer, they exhibit a "blocky" microstructure, *i.e.* they contain E and Y homosequences which might be long enough to be capable of crystallizing [1].
The samples were placed in a temperature controlled oven and structural changes during heating were recorded by acquiring temperature resolved patterns at 10 °C/min from -5 to 150 °C. Prior to the analysis at the beamline A2 of Hasylab, samples were submitted to a Successive Self-nucleation and Annealing (SSA) thermal fractionation [2], a procedure capable of enhancing the crystallinity of polymeric materials. Four samples, prepared with two different catalysts and with composition ranging from 45 to 69 mol% E, were analyzed. WAXD patterns collected for a sample containing 45.5 mol% Y obtained with EBTHI catalyst are reported as an example in Figure 1. Reflections ascribable to Form IV of poly(4-methyl-1-pentene) are visible at about 8, 9, 12, 16 and 21° 2θ.

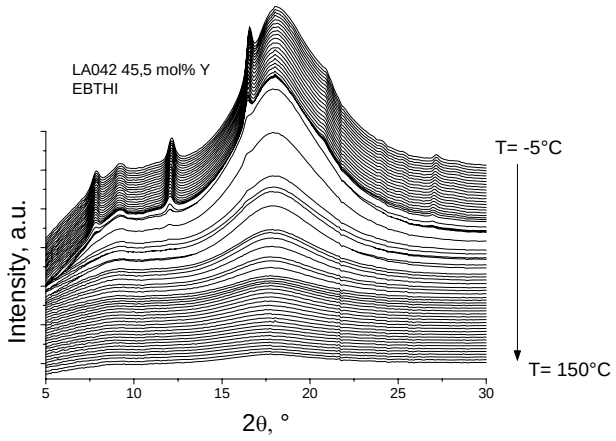

Figure 1: WAXD traces recorded during heating a E/Y copolymer containing 45.4 mol% of Y.

Despite the almost equimolar comonomer content, normally suggesting a completely amorphous behaviour, it is worth noting the presence of polyY crystals. On the other hand, due to the very low crystallinity of the sample, reflections from polyethylene crystals were not detected, Moreover, the adopted experimental approach is probably not fully adequate to provide undisputable evidence for the presence of polyE crystallites, since short E sequences might exhibit sub-ambient melting temperatures, which necessitates a more appropriate temperature controlled environment.

Three terpolymers made from propylene, 1-pentene and 1-hexene were also available for experimental investigations. Such samples were synthesized with a MAO activated metallocene catalyst and have molar composition around 75/25 – C3/(C5+C6) with C5/C6 molar ratios of about 1:1, 3:1 and 1:3. The C5/C6 ratio is used to name the samples.
Time resolved isothermal crystallization at 0 and 20 °C were conducted directly under the x-ray beam, by heating the sample to 220 °C and then cooling it down to sub-ambient temperatures. During these on-line WAXD measurements data were acquired, in general, every 2 min in the first part of the crystallization curve; when necessary, for longer crystallization times, the samples were kept in thermal baths maintained at 0 or 20 °C, acquiring a WAXD pattern every hour.
Crystallinity was evaluated for each pattern according to standard procedures. Figure 2 depicts the results obtained for the isothermal crystallization at 0 °C of the C3/C5/C6 terpolymers. Consistently with the results previously obtained for C3/C5 and C3/C6 copolymers [3], the larger is the amount of hexene in the terpolymer, the slower is the crystallization of the trigonal δ-form. The same trend was also observed in the experiments performed at 20 °C (not shown), but shorter crystallization times were necessary to attain the limiting value of crystallinity.

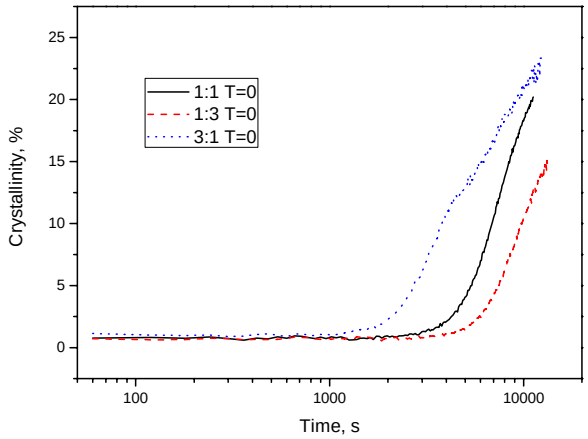

Figure 2: Crystallization kinetics for random C3/C5/C6 terpolymers at 0°C.

During our beamtime we also carried out a few experiments on copolyesters of poly(ethylene terephthalate), PET, with its homologues poly(trimethylene terephthalate), PTT, and poly(butylene terephthalate), PBT. Interestingly, the three 50/50 copolymers, PET/PTT, PET/PBT, PTT/PBT, obtained by entropically-driven ring-opening polymerization, despite the fact that were random with a sequence length of only 2, exhibited a certain crystallinity. Room temperature 2D WAXD patterns were collected on samples that were isothermally crystallized at a proper temperature in order to develop as much as possible the crystalline phase. These findings, which obviously deserve further investigations, may suggest a unit cell containing two different repeating units [4].

References

[1] *"Toward Block Copolymers from Nonliving Isospecific Single-Site Catalytic Systems"* M. Galimberti, F. Piemontesi, L. Alagia, S. Losio, L. Boragno, P. Stagnaro, M. C. Sacchi J. Polym. Sci. A: Polym. Chem. **48**, 2063 (2010).

[2] *"Thermal fractionation of polymers"* A.J. Muller, M.L. Arnal Prog. Polym. Sci., **30**, 559 (2005).

[3] *"Crystallization and morphology of the trigonal form in random propene/1-pentene copolymers"* P. Stagnaro, L. Boragno, M. Canetti, F. Forlini, F. Azzurri, G.C. Alfonso Polymer **50**, 5242 (2009) and references therein.

[4] *"Syntheses of Random PET-co-PTTs and Some Related Copolyesters by Entropically-Driven Ring-opening Polymerizations and by Melt blending: Thermal Properties and Crystallinity"* L. Conzatti, M. Alessi, P. Stagnaro, P. Hodge J. Polym. Sci. Part A: Polym. Chem. **49**, 995 (2011).