UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II



PhD IN CHEMICAL SCIENCES

XXXV CYCLE

POLYMER NANOSTRUCTURES OF TUNABLE PERIODICITY FROM HIERARCHICAL SELF-ASSEMBLY AND CRYSTALLIZATION OF CRYSTALLINE BLOCK-COPOLYMERS

SUPERVISOR PROF. CLAUDIO DE ROSA

Examiner Prof. Nadia Rega

COORDINATOR PROF. ANGELINA LOMBARDI

Ph.D. STUDENT Alessandra Cicolella

Abstract

Aim of this Ph.D. project was exploring the properties of a novel class of semicrystalline block copolymers (BCPs) composed of crystallizable blocks of stereoregular polyolefins. These innovative materials have been synthesized only recently thanks to the development of organometallic catalysts able to promote stereoselective and living olefin polymerization. The interest towards these systems is driven by the possibility of creating thermally resistant nanostructured materials with improved mechanical properties thanks to the presence of high temperature melting crystalline domains. Moreover, the orientation of such domains can be controlled through the control of the crystallization process. However, in semi-crystalline BCPs the solid-state morphology is more complex than in classic amorphous BCPs and is the result of the competition between the phase separation of incompatible blocks and the crystallization. To address the complexity of these systems, research activities have been focused on the systematic characterization of BCPs containing crystallizable isotactic or syndiotactic polypropylene linked to amorphous blocks of random propene-ethylene copolymers or to crystalline PE and LLDPE blocks. The influence of the different compositions and block lengths on the crystallization behavior and morphology on different length scales of these systems has been examined. The thermal characterization of the crystalline-crystalline samples generally showed an overlap of the crystallization processes of the two blocks, but the optical microscopy (POM) analysis allowed clarifying the sequence of crystallization from the melt. The phase-separated structure eventually present in the melt has been revealed by TEM analysis of samples crystallized by fast quenching from the melt. It was found that the fast quenching of thin films of BCPs and of their blends can freeze the eventual nanostructure existent in the melt, allowing to image it at room temperature with TEM. Phase-separated morphologies were observed in iPP-b-PE, iPP-b-LLDPE and PE-b-sPP copolymers due to the incompatibility of the constituting blocks. The segregation was partially retained even when the thin films were crystallized by slow cooling from the melt, however in this case thin crystalline lamellae randomly oriented and homogeneously distributed were also observed. The phase-separated morphologies displayed by blends of BCPs sharing a common block of PE or EPR rapidly cooled from the melt confirm the hypothetical formation of a tri-block copolymer with a central PE or EPR block linking iPP and sPP blocks. The presence of crystallizable components in the BCPs was exploited to induce crystal orientation in thin polymer films by epitaxial crystallization on suitable crystalline substrates. An extensive study of isothermal crystallization kinetics of the BCPs was performed with the aim to unveil how the different blocks mutually influence their crystallization rates. It was found that the presence of a linked amorphous EPR block or of a molten LLDPE block drastically reduces the overall crystallization rate of the iPP block, through dilution effect. Similarly, in iPP-*b*-PE copolymers the iPP block, which remains in the melt state or crystallizes partially, slows down the crystallization kinetics of PE, in contrast to what happens in a iPP/PE blend, where the crystallization kinetics of PE is not affected by the presence of iPP. Self-Nucleation experiments allowed to unveil the self-nucleation behavior of iPP, PE and LLDPE blocks in the BCPs, and revealed that when iPP block is linked to an amorphous block (EPR) or to a block that crystallizes at lower temperatures (LLDPE), higher temperatures with respect to the homopolymer are necessary to obtain an isotropic melt. On the other hand, when iPP is linked to a PE block, which crystallizes before iPP and acts as a nucleating agent, lower temperatures are needed to allow the self-nucleation of iPP block, which is drastically prevented. Finally, the copolymers have been thermally fractionated with experiments of Successive Self-Nucleation and Annealing.

This thesis work contributes to expand the knowledge in the field of semi-crystalline block copolymers, illustrating the influence of the nature and the length the blocks over the phase-separation, the morphology, and the crystallization behavior of polyolefin-based BCPs.

Table of contents

		1 "5
1. Iı	ntroduction	1
1.1	Block copolymers	1
1.2	Semi-crystalline BCPs	2
1.3	BCPs containing blocks of stereoregular polyolefins	3
1.4	Objectives of the work	7
Refe	rences	9
2. N	faterials and Methods	14
2.1	BCPs comprising an iPP block	14
2.2	BCPs comprising PE and sPP blocks	16
2.3	Wide Angle X-ray Scattering	18
2.4	Temperature and time resolved Wide-Angle X-ray Scattering	18
2.5	Differential Scanning Calorimetry	19
2.6	Polarized Optical Microscopy	22
2.7	Transmission Electron Microscopy	22
2.8	Preparation of polymer blends	23
Refe	rences	24
3. S ⁴	tructural and Thermal Characterization	26
3.1	iPP- <i>b</i> -PE copolymers	26
3.2	iPP- <i>b</i> -LLDPE copolymers	36
3.3	iPP- <i>b</i> -EPR copolymers	47
3.4	PE-b-EPR copolymers	50
3.5	PE- <i>b</i> -sPP block copolymers	53
3.6	sPP- <i>b</i> -EPR copolymer	63
Refe	prences	65

		Pag.
4. B	ulk Morphology	67
4.1	iPP and PE homopolymers	67
4.2	iPP- <i>b</i> -PE copolymers	68
4.3	iPP- <i>b</i> -LLDPE copolymers	69
4.4	PE- <i>b</i> -sPP copolymers	81
4.5	iPP- <i>b</i> -EPR copolymers	82
4.6	PE- <i>b</i> -EPR copolymers	82
4.7	sPP homopolymer and sPP-b-EPR copolymer	83
Refe	rences	84
5. T	hin Film Morphology	85
5.1	iPP- <i>b</i> -PE copolymers	85
	5.1.1 Films crystallized by quenching from the melt	85
	5.1.2 Films crystallized by slow cooling from the melt	87
5.2	iPP- <i>b</i> -LLDPE copolymers	88
	5.2.1 Films crystallized by quenching from the melt	88
	5.2.2 Films crystallized by slow cooling from the melt	91
5.3	iPP- <i>b</i> -EPR copolymers	96
5.4	PE- <i>b</i> -sPP copolymers	97
5.5	sPP-b-EPR copolymer	99
Refe	rences	100
6. M	forphology of Epitaxially Crystallized Thin Films	101
6.1	Epitaxial crystallization of PE, iPP and sPP homopolymers onto BA	101
6.2	Epitaxial crystallization of PE, iPP and sPP homopolymers onto 3Ph	104
6.3	Epitaxial crystallization of BCPs comprising an iPP block	107
	6.3.1 iPP- <i>b</i> -EPR copolymers	107
	6.3.2 iPP- <i>b</i> -PE copolymers	108
	(22) DD h LLDDE concluments	110

		Pag.
6.4	Epitaxial crystallization of BCPs comprising a sPP block	114
	6.4.1 PE- <i>b</i> -sPP copolymers	114
Refe	erences	119
7. B	lends of BCPs	121
7.1	Structural and thermal analysis	121
7.2	Thin film morphology	124
	7.2.1 iPP- <i>b</i> -PE/PE- <i>b</i> -sPP blend	124
	7.2.2 iPP- <i>b</i> -EPR/sPP- <i>b</i> -EPR blend	126
7.3	Morphology of epitaxially crystallized thin films	128
	7.3.1 iPP- <i>b</i> -PE/PE- <i>b</i> -sPP blend	128
	7.3.2 iPP- <i>b</i> -EPR/sPP- <i>b</i> -EPR blend	129
Refe	erences	132
8. C	Crystallization Kinetics	133
8.1	Crystallization theories	133
8.2	iPP and PE homopolymers	136
8.3	iPP- <i>b</i> -EPR copolymers	146
8.4	PE- <i>b</i> -EPR copolymer	153
8.5	iPP- <i>b</i> -LLDPE copolymers	159
8.6	iPP- <i>b</i> -PE copolymers	173
Refe	erences	187
Арр	endix	190
9. S	elf-Nucleation Behavior and Thermal Fractionation	202
9.1	Self-Nucleation	202
	9.1.1 iPP and PE homopolymers	203
	9.1.2 iPP- <i>b</i> -EPR copolymers	208
	9.1.3 PE- <i>b</i> -EPR copolymers	212
	9.1.4 iPP- <i>b</i> -LLDPE copolymers	216

	Pag.		
9.1.5 iPP- <i>b</i> -PE copolymers	228		
Successive Self-Nucleation and Annealing	239		
9.2.1 iPP and PE homopolymers	241		
9.2.2 iPP- <i>b</i> -PE copolymers	242		
9.2.3 iPP- <i>b</i> -LLDPE copolymers	247		
References			
	 9.1.5 iPP-b-PE copolymers Successive Self-Nucleation and Annealing 9.2.1 iPP and PE homopolymers 9.2.2 iPP-b-PE copolymers 9.2.3 iPP-b-LLDPE copolymers 		

10. Conclusions

257

1. Introduction

1.1 Block copolymers

Block copolymers (BCPs) are remarkable materials in which the properties of distinct polymer chains are combined to yield materials with hybrid properties. BCPs can be obtained through living polymerization strategies and consist of chemically distinct macromolecules covalently linked. There are several different architectures within the class of block copolymers, such as linear di-block, triblock and multi-block, graft block and star-block copolymers.¹⁻⁴ The simplest molecular architecture is obtained by a linear connection of a block of A units with a block of B units (Figure 1.1). Chemical incompatibility between A and B blocks may lead to phase segregation of the different blocks in micro- or nano-domains with periodical order, a phenomenon known as "self-assembly".¹⁻⁶ The incompatibility between blocks in BCPs and the corresponding segregation strength is defined by the Flory-Huggins interaction parameter (χ), which depends on the temperature $\chi = A+B/T$. The segregation strength depends on the γ parameter and the molecular mass of the two blocks and can be estimated by the product γN , where N is the total number of connected segments, that is, the degree of polymerization of the block copolymer. For an A-B amorphous di-block copolymer, depending on the volume fraction of the blocks, the self-assembly process may lead to nanostructures characterized by cubic arrays of spheres, hexagonal arrays of cylinders, bicontinuous cubic phases or alternating lamellae (Figure 1.1).



Figure 1.1 The chains of the A-B di-block copolymer, depicted as two-colour chain for simplicity, self-organize such that contact between the immiscible blocks is minimized. The list of morphologies formed by di-block copolymers in the bulk is reported. The final morphology (spheres, cylinders, gyroids or lamellae) is determined primarily by the relative lengths of the two polymer blocks (f_B is the volume fraction of block B).

The structural features and dimensions of the microdomains can be easily tuned by changing the chemical nature of the polymeric blocks, the molecular architecture, and the molecular mass. The tunability of periodicity allows fabrication of nanostructures suitable for different applications, as lithographic masks in the field of microelectronics or devices in the photonic sensing. The possible applications of BCP-lithography are, however, only potential because precise control over the self-assembly process and the final structure is not routine.⁷⁻⁸ The potential properties of BCPs can be completely exploited only if we are able to induce perfect orientation of microdomains and create ordered structure in the nanometer scale, with order extending over sufficiently large area. This is possible only if an external bias field is applied during phase separation. To this aim, various processing techniques have been developed, for example by introducing mechanical, electric, and magnetic fields, or a temperature gradient during phase separation.⁷⁻⁸ A possibility is offered by the use of novel semi-crystalline BCPs where the self-assembly and the domains orientation can be controlled through the control of the crystallization process.

1.2 Semi-crystalline BCPs

For a semi-crystalline block copolymer, in which at least one of the two segments is able to crystallize, the phase behavior in the solid-state is further complicated by the competition between the phase segregation and the crystallization, the latter, in turn, taking place from a homogeneous or a heterogeneous melt.^{3,4} The result is the possible formation of numerous different structures that depend on the strength of the two phase-transitions, the phase-separation that favours the formation of nanometer sized microdomains, and crystallization that promotes the formation of crystalline layers alternating to amorphous layers. The final solid-state morphology depends on which transition occurs first when cooling the melt.⁹⁻¹¹ If crystallization takes place in a phase-separated melt, four situations may occur: break-out, confined, templated, and pass-through crystallization (Figure 1.2).¹² A break-out crystallization mode, typical of weakly segregated melt, is verified when crystallization completely destroys the ordered melt and leads to the formation of a lamellar crystalline morphology and to the possible organization of the lamellae in spherulitic superstructures.^{13,14} If the domainstructured morphology of the melt is preserved upon crystallization, confined crystallization is verified.¹⁵ This kind of crystallization mode is typical of systems in the strong segregation limit and involves nucleation events and crystal growth, both confined in each single domain. In the case of the templated crystallization, typical of melts with medium to low segregation strength, the ordered structure of the melt is preserved as in the confined crystallization, with the important difference residing in the sporadic occurrence of bridging events.¹⁶ The pass-through crystallization is found in the weak segregation limit and it is characterized by preservation of the general segregated morphology of the melt, confined crystallization with lamellar bridges connecting the different domains, and no crystal orientation.¹⁷ In the case of crystalline–crystalline di-block copolymers, the final morphology still depends on the competition between phase separation and crystallization, and if the two blocks crystallize at different temperatures, the final structure may be defined uniquely by the crystallization of the first block or may be modified by the subsequent crystallization of the other block.¹⁸⁻²⁰



Figure 1.2 Crystallization modes for a semi-crystalline block copolymer.

The studies performed so far on semicrystalline BCPs have mainly concerned with the crystallization behavior of block copolymers including poly(ethylene oxide),¹⁸ poly(ε -caprolactone),^{13,21,22} polyethylene^{18-20,23-25} and poly(L-lactide) blocks.^{19,21,23,24} The crystallization behavior of crystalline and double crystalline BCPs containing stereoregular polyolefin blocks, instead, has been less studied to date, due to the difficulty of the synthetic methods.

1.3 BCPs containing blocks of stereoregular polyolefins

The synthesis of BCPs composed of crystallizable polyolefins, as linear polyethylene (PE) or stereoregular poly(1-olefins), has encountered many difficulties for a long time due to intrinsic limitations of the living polymerization methods.

As a matter of fact, the main techniques employed for the synthesis of BCPs with defined architectures and monodisperse molecular weights are cationic, anionic and controlled radical polymerizations.³ These methods ensure a consecutive enchainment of monomer units without the occurrence of termination events (living polymerization) thus providing a precise control over the molecular weight of the resultant polymers and the possibility to synthesize polymers with a wide range of architectures. However, such synthetic routes are not able to ensure proper stereocontrol during olefin polymerization.

As a consequence, BCPs containing blocks based on crystallizable polyolefins have received less attention and the studies of the structure, crystallization behavior and morphology of these crystalline BCPs have been limited to BCPs constituted by blocks of irregular polyethylene (PE) synthesized by hydrogenation of BCPs containing 1,4-polybutadiene blocks prepared by classic anionic living polymerization.²⁶⁻²⁹ This resulted in highly defective PE blocks with low melting temperature (about 90°C) containing high amounts of constitutional defects of 1-butene units arising from hydrogenation of 1,2-butadiene units present as defects in the precursor 1,4-polybutadiene block.

BCPs containing blocks based on crystallizable stereoregular polyolefins have been synthesized only recently thanks to the development of metal-based insertion polymerization methods which are able to ensure a high stereochemical control in olefin polymerization.³⁰⁻³⁶ Depending on the ligand framework of the catalyst and on the nature of the coordination metal centre, linear or branched polyethylene, atactic, isotactic and syndiotactic poly(α -olefins), poly(cycloolefins), random copolymers of ethylene with branched α -olefins, can now be efficiently synthesized in a living manner.³⁷⁻⁴⁶ Examples of catalyst precursors for the living and stereocontrolled polymerization of 1-alkene monomers are shown in Figure 1.3.



Figure 1.3 Catalyst precursors for the synthesis, through living polymerization, of BCPs containing tactic poly(1-alkene) blocks.

In particular, the bis(phenoxyimine) titanium complex (1) activated with methylaluminoxane (MAO) produces BCPs containing highly stereoregular syndiotactic polypropylene (sPP) and/or polyethylene (PE) blocks;^{30,31} rational modifications to the structure of the titanium complex (1) resulted in an isoselective catalyst which retained the living behavior (2);³² the chiral, C_2 - symmetric, nickel diimine complex (3) activated with MAO produces BCPs containing iPP blocks (at low temperatures) and regioirregular polypropylene blocks at higher temperatures;³³ the ammine-phenolate zirconium complex (4) (Bn standing for the benzyl group) activated with B(C₆F₅)₃ produces BCPs containing highly isotactic poly(1-hexene) or poly(1-octene), iPP and PE blocks;^{34,35} C_s -symmetric pyridylamidohafnium dimethyl complex (5) activated with B(C₆F₅)₃ produces iPP, PE and isotactic poly(4-methyl-1- pentene) (iP4MP) blocks.³⁶

For what concerns the living polymerization of iPP, the pyridilamidohafnium complex (5) has received much attention recently, outclassing the other reported catalysts. Although systems 2, 3, 4 are active in isoselective living polymerization of propene, each of these catalysts is deficient in one or more of the following areas: degree of isoselectivity, activity, thermal stability, and molecular masses achieved. For instance, the nickel diimine complex (3) produces highly isotactic iPP (T_m =140°C) at temperatures of -60 °C or below. However, this catalyst suffers from extremely low activity at these temperatures (TOF = 1 h⁻¹ at -78 °C) and is not practical for large-scale polymer production.³³

Discovered by high-throughput screening (HTS) within Dow/Symyx collaboration,⁴⁷ pyridylamidohafnium catalysts are active for the high-temperature production of high-MW iPP and chain-shuttling polymerization.⁴⁸ The pyridylamidohafnium catalysts deviate from the "chiral growing chain orientation" mechanism of stereocontrol (i.e., the Corradini model) observed in the other isoselective catalysts. In fact, the selection of the propene enantioface is dictated directly by the active site through the substituents suitably located on the ligand framework.⁴⁹⁻⁵⁰ Knowing the origin of the stereocontrol operating in these systems, it was possible to rationally optimize the pyridylamidohafnium catalysts in order to achieve a living behavior, allowing the synthesis of BCPs containing stereoregular blocks of iPP with precise control of block lenghts.⁵⁰

There are several aspects that make semicrystalline polyolefin-based BCPs extremely attractive. From the practical point of view, it is worth mentioning that two-thirds of all thermoplastic polymers are polyolefins, because of their versatile thermal, mechanical and optical properties, excellent melt processability, good chemical and solvent resistance and last but not least, the low-cost of monomers and production process.

As an example, in the field of thermoplastic elastomers (TPEs), there are great research efforts aimed at developing cost-effective methods for the synthesis of polyolefin-based BCPs containing hard and soft blocks that ensure an overall elastic behavior in a wide range of temperatures.⁴⁶ Other important applications of polyolefin BCPs containing highly crystalline blocks may be envisaged in their use as compatibilizers in polymer blends. As a matter of fact, iPP-PE BCPs have recently received considerable attention because of their possible application for compatibilizing mixtures of immiscible iPP and PE, thus promoting the recycling of iPP/PE mixtures, where the separation of the two components is difficult and expensive.^{37,38} It has been demonstrated that the addition of iPP-PE diblock or multiblock copolymers improves mechanical properties of iPP/PE blends due to the combined effect of interfacial adhesion, reduced particle size and efficient stress transfer between phases.^{37,38} This affords opportunities for upcycling recovered PE and iPP into equal value products with lower sorting costs and opens the route for the mechanical recycling of post-consumer waste plastics that are in the form of mixtures of different polyolefins or blends and laminates.

As mentioned above, semi-crystalline polyolefin-based BCPs provide new means to create nanoscale patterns on thin films, through the control of the crystallization. Epitaxial crystallization of the crystallizable blocks of BCPs on the surface of low molecular mass crystalline substances has indeed shown great potential for inducing precise orientation of the high temperature melting domains.^{29,41-44} Moreover, the possibility of dispersing an inorganic filler in an already nanostructured polymeric

matrix, allows the production of heterogeneous polymeric nanocomposites with potential technological application in the field of microelectronics.⁴⁰

Eventually, BCPs produced by living polymerization could represent paradigmatic models of more complex systems as the olefin-based multiblock copolymers (OBCs) obtained via chain-shuttling technology.⁴⁸ As a matter of fact, the chain-shuttling represents the industrial strategy to synthesize block copolymers with alternating crystalline and amorphous segments from mixtures of ethylene with 1-alkenes such as 1-hexene or 1-octene. However, due to the stochastic exchange of the polymer chain between two organometallic catalysts, such copolymers are characterized by an intrinsic complexity as the distribution in the length and number of blocks per chain are statistical and vary from chain to chain resulting in a non-uniform molecular architecture. Therefore, the study of monodispersed BCPs comprising blocks of ethylene and 1-alkenes can help comprehend the behavior of more complicated systems.

Moreover, from the point of view of basic research, semicrystalline BCPs are interesting systems *per se*. As a matter of fact, the comprehension of the key phenomena that govern the phase behavior of these systems in order to develop strategies for improving the control over the formation of ordered nanostructures still represents an ambitious goal in polymer science.

1.4 Objectives of the work

The present work aims at exploring the properties of a novel class of semicrystalline BCPs, that are block copolymers having crystallizable blocks made of stereoregular polyolefins. Such BCPs, obtained with living organometallic catalysts, contain crystallizable isotactic or syndiotactic polypropylene linked to amorphous blocks of random propene-ethylene copolymers or to crystalline PE and LLDPE blocks. Research activities have been focused on the systematic characterization of these systems with the aim to unveil the influence of the different compositions and block lengths on the crystallization behavior and on the morphology on different length scales. In particular, object of the work are crystalline-crystalline systems such as polypropylene-*block*-polyethylene (iPP-*b*-PE), isotactic polypropylene/*block*-linear low-density polyethylene (iPP-*b*-LLDPE), polyethylene-*block*-syndiotactic polypropylene (PE-*b*-sPP) copolymers, as well as crystalline-amorphous systems as isotactic polypropylene-*block*-ethylene-propylene rubber (iPP-*b*-EPR), polyethylene-*block*-ethylene-propylene rubber (sPP-*b*-EPR) copolymers. The description of all the studied samples and of the experimental techniques employed in this work is reported in Chapter 2. Chapter 3 features the structural analysis

performed by WAXS as well as the results of the thermal analysis of the BCPs. Chapter 4 is dedicated to a study of the bulk morphology of the BCPs conducted with polarized light optical microscopy (POM), whereas in Chapter 5 the eventual phase-separation occurring in these systems is investigated with transmission electron microscopy (TEM) on thin films of BCPs crystallized in different cooling conditions. Chapter 6 describes the use of epitaxial crystallization on suitable substrates to produce different oriented nanostructures and morphologies of BCPs depending on the BCP composition and on the substrates. In Chapter 7 the structural, thermal, and morphological analysis of blends of blockcopolymers is reported. Blends of selected copolymer samples were prepared in order study phaseseparation in blends of BCPs sharing a common block of PE or EPR. In Chapter 8, an extensive study of isothermal crystallization kinetics of BCPs performed by differential scanning calorimetry (DSC) is reported, with the aim to clarify the influence of amorphous and crystalline blocks on the crystallization kinetics of iPP in block copolymers. The results of Self-Nucleation (SN) experiments are illustrated in Chapter 9 and unveil the self-nucleation behavior of iPP, PE and LLDPE blocks in the BCPs. Moreover, the copolymers have been thermally fractionated with experiments of Successive Self-Nucleation and Annealing (SSA). The main conclusions of this work are presented in Chapter 10.

References

1) Bates, F. S.; Fredrickson, G. H. Block Copolymer Thermodynamics: Theory and Experiment. *Annual Review of Physical Chemistry* **1990**, *41*, 525–557.

2) Fasolka, M. J.; Mayes, A. M. Block Copolymer Thin Films: Physics and Applications. *Annual Review of Materials Research* **2001**, *31*, 323–355.

3) Hamley, I. W. The Physics of Block Copolymers. Oxford University Press 1998.

4) Hamley, I. W. Developments in Block Copolymer Science and Technology. *John Wiley & Sons, Ltd* **2004**.

5) Leibler, L. Theory of Microphase Separation in Block Copolymers. *Macromolecules* **1980**, *13*, 1602-1617.

6) Park, M.; Harrison, C. K.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. Block Copolymer Lithography: Periodic Arrays of ~10¹¹ Holes in 1 Square Centimeter. *Science* **1997**, *276*, 1401-1404.

7) Park, C.; Yoon, J.; Thomas, E. L. Enabling nanotechnology with self-assembled block copolymer patterns. *Polymer* **2003**, *44*, 6725-6760.

8) Lazzari, M.; De Rosa, C. Method for alignment and large area-scale ordering of block copolymer morphology. In Block Copolymers in Nanoscience. Lazzari, M.; Liu, G.; Lecommandoux S. Eds., *Wiley-VCH*, Weinheim, **2006**, 191-231.

9) Hamley, I. W. Crystallization in Block Copolymers. *Advances in Polymer Science* **1999**, *148*, 113–137.

10) Loo, Y. L.; Register, R. A. Crystallization Within Block Copolymer Mesophases. In Development in Block Copolymer Science and Technology. Hamley, I.W. Ed., *John Wiley & Sons Ltd.*, Chichester, **2004**, 213–243.

11) Ryan, A. J.; Hamley, I. W.; Bras, W.; Bates, F. S. Structure Development in Semicrystalline Diblock Copolymers Crystallizing from the Ordered Melt. *Macromolecules* **1995**, *28*, 3860–3868.

12) Loo, Y. L.; Register, R. A.; Ryan, A. J. Modes of Crystallization in Block Copolymer Microdomains: Breakout, Templated, and Confined. *Macromolecules* **2002**, *35*, 2365–2374.

13) Nojima, S.; Kato, K.; Yamamoto, S.; Ashida, T. Crystallization of Block Copolymers. 1. Small-Angle x-Ray Scattering Study of a Epsilon-Caprolactone-Butadiene Diblock Copolymer. *Macromolecules* **1992**, *25*, 2237–2242.

14) Nojima, S.; Nakano, H.; Ashida, T. Crystallization Behaviour of a MicrophaseSeparated Diblock Copolymer. *Polymer* **1993**, *34*, 4168–4170.

15) Quiram, D. J.; Register, R. A.; Marchand, G. R.; Adamson, D. H. Chain Orientation in Block Copolymers Exhibiting Cylindrically Confined Crystallization. *Macromolecules* **1998**, *31*, 4891–4898.

16) Rangarajan, P.; Register, R. A.; Fetters, L. J.; Bras, W.; Naylor, S.; Ryan, A. J. Crystallization of a Weakly Segregated Polyolefin Diblock Copolymer. *Macromolecules* **1995**, *28*, 4932-4938.

17) Li, S.; Register, R. A.; Landes, B. G.; Hustad, P. D.; Weinhold, J. D. Crystallization in Ordered Polydisperse Polyolefin Diblock Copolymers. *Macromolecules* **2010**, *43*, 4761–4770.

18) Sun, L.; Liu, Y.; Zhu, L.; Hsiao, B. S.; Avila-Orta, C. A. Self-assembly and crystallization behavior of a double-crystalline polyethylene-block-poly(ethylene oxide) diblock copolymer. *Polymer* **2004**, *45*, 8181-8193.

19) Castillo, R. V.; Muller, A. J.; Lin, M. C.; Chen, H. L.; Jeng, U. S.; Hillmyer, M. A. Confined crystallization and morphology of melt segregated PLLA-*b*-PE and PLDA-*b*-PE diblock copolymers. *Macromolecules* **2008**, *41*, 6154-6164.

20) Myers, S. B.; Register, R. A. Crystalline-Crystalline Diblock Copolymers of Linear Polyethylene and Hydrogenated Polynorbornene. *Macromolecules* **2008**, *41*, 6773-6779.

21) Castillo, R. V.; Müller, A. J.; Raquez, J. M.; Dubois, P. Crystallization kinetics and morphology of biodegradable double crystalline PLLA-*b*-PCL diblock copolymers. *Macromolecules* **2010**, *43*, 4149–4160.

22) Müller, A. J.; Albuerne, J.; Esteves, L. M.; Marquez, L.; Raquez, J. M.; Degee, P.; Dubois, P.; Collins, S.; Hamley, I. W. Confinement Effects on the Crystallization Kinetics and Self-Nucleation of Double Crystalline Poly(ρ-Dioxanone)-*b*-Poly(ε-Caprolactone) Diblock Copolymers. *Macromolecular Symposia* **2004**, *215*, 369–382.

23) Castillo, R. V.; Müller, A. J.; Lin, M. C.; Chen, H. L.; Jeng, U. S.; Hillmyer, M. A. Confined crystallization and morphology of melt segregated PLLA-*b*-PE and PLDA-*b*-PE diblock copolymers. *Macromolecules* **2012**, *45*, 4254–4261.

24) Müller, A. J.; Lorenzo, A. T.; Castillo, R. V.; Arnal, M. L.; Boschetti-de-Fierro, A.; Abetz, V. Crystallization kinetics of homogeneous and melt segregated PE containing diblock copolymers. *Macromolecular Symposia* **2006**, *245-246*, 154–160.

25) Huang, L.; Kiyofuji, G.; Matsumoto, J.; Fukagawa, Y.; Gong, C.; Nojima, S. Isothermal crystallization of poly (β -propiolactone) blocks starting from lamellar microdomain structures of double crystalline poly (β -propiolactone)-block-polyethylene copolymers. *Polymer* **2012**, *53*, 5856–5863.

26) Cohen, R. E.; Cheng, P. L.; Douzinas, K. C.; Kofinas, P.; Berney, C. V. Path-dependent morphologies of a diblock copolymer of polystyrene/hydrogenated polybutadiene. *Macromolecules*, **1990**, *23*, 324-327.

27) Douzinas K. C.; Cohen, R. E. Chain folding in ethylene-butylene-ethylethylene semicrystalline diblock copolymers. *Macromolecules* **1992**, *25*, 5030-5035.

28) De Rosa, C.; Park, C.; Thomas, E. L.; Lotz, B. Microdomain patterns from directional eutectic solidification and epitaxy. *Nature* **2000**, *405*, 433-437.

29) De Rosa, C.; Park, C.; Lotz, B.; Wittmann, J. C.; Fetters, L. J.; Thomas, E. L. Control of Molecular and Microdomain Orientation in a Semicrystalline Block Copolymer Thin Film by Epitaxy. *Macromolecules* **2000**, *33*, 4871-4876.

30) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. New Bis(salicylaldiminato) Titanium Complexes for Ethylene Polymerization. *Chemistry Letters* **1999**, 1065-1066.

31) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. Living Polymerization of Ethylene Catalyzed by Titanium Complexes Having Fluorine-Containing Phenoxy–Imine Chelate Ligands. *Journal of the American Chemical Society* **2002**, *124*, 3327-3336.

32) Mason, A. F.; Coates, G. W. New Phenoxyketimine Titanium Complexes: Combining Isotacticity and Living Behavior in Propylene Polymerization. *Journal of the American Chemical Society* **2004**, *126*, 16326-16327.

33) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. A *C*₂-Symmetric, Living α-Diimine Ni(II) Catalyst: Regioblock Copolymers from Propylene. *Journal of the American Chemical Society* **2005**, *127*, 13770-13771.

34) Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Togrou, M. The First Molecularly Characterized Isotactic Polypropylene-block-polyethylene Obtained via "Quasi-Living" Insertion Polymerization. *Macromolecules* **2003**, *36*, 3806-3808.

35) Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Talarico, G.; Togrou, M.; Wang, B. Block Copolymers of Highly Isotactic Polypropylene via Controlled Ziegler–Natta Polymerization *Macromolecules* **2004**, *37*, 8201-8203.

36) Coates, G. W. PCT Int. Appl. WO2008/112133.

37) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining polyethylene and polypropylene: Enhanced performance with PE/iPP multiblock polymers. *Science* **2017**, *355*, 814-816.

38) Xu, J.; Eagan, J. M.; Kim, S.-S.; Pan, S.; Lee, B.; Klimovica, K.; Jin, K.; Lin, T.-W.; Howard, M. J.; Ellison, C. J.; LaPointe, A. M.; Coates G. W.; Bates, F. S. Compatibilization of Isotactic Polypropylene (iPP) and High-Density Polyethylene (HDPE) with iPP–PE Multiblock Copolymers. *Macromolecules* **2018**, *51*, 8585-8596.

39) Ruokolainen, J.; Mezzenga, T.; Fredrickson, G. H.; Kramer, E. J.; Hustad, P. D.; Coates, G. W. Morphology and Thermodynamic Behavior of Syndiotactic Polypropylene–Poly(ethylene-*co*-propylene) Block Polymers Prepared by Living Olefin Polymerization. *Macromolecules* **2005**, *38*, 851-860.

40) De Rosa, C.; Auriemma, F.; Di Girolamo, R.; Aprea R.; Thierry, A. Selective gold deposition on a nanostructured block copolymer film crystallized by epitaxy. *Nano Research* **2011**, *4*, 241-248.

41) De Rosa, C.; Di Girolamo, R.; Auriemma, F.; D'Avino, M.; Talarico, G.; Cioce, C.; Scoti, M.; Coates, G. W.; Lotz, B. Oriented Microstructures of Crystalline–Crystalline Block Copolymers Induced by Epitaxy and Competitive and Confined Crystallization. *Macromolecules* **2016**, *49*, 5576-5586.

42) De Rosa, C.; Di Girolamo, R.; Auriemma, F.; Talarico, G.; Scarica, C.; Malafronte, A.; Scoti, M. Controlling Size and Orientation of Lamellar Microdomains in Crystalline Block Copolymers. *ACS Applied Material & Interfaces* **2017**, *9*, 31252-31259.

43) De Rosa, C.; Malafronte, A.; Di Girolamo, R.; Auriemma, F.; Scoti, M.; Ruiz de Ballesteros, O.; Coates, G. W. Morphology of Isotactic Polypropylene–Polyethylene Block Copolymers Driven by Controlled Crystallization. *Macromolecules* **2020**, *53*, 10234-10244.

44) De Rosa, C.; Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M. Double Crystallization and Phase Separation in Polyethylene—Syndiotactic Polypropylene Di-Block Copolymers. *Polymers* **2021**, *13*, 2589.

45) Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M.; De Stefano, F.; Giordano, A.; Malafronte, A.; De Rosa, C. Structure and Morphology of Crystalline Syndiotactic Polypropylene-Polyethylene Block Copolymers. *Polymers* **2022**, *14*, 1534.

46) Yang, F.; Wang, X.; Ma, Z.; Wang, B.; Pan, L.; Li, Y. Copolymerization of Propylene with Higher α-Olefins by a Pyridylamidohafnium Catalyst: An Effective Approach to Polypropylene-Based Elastomer. *Polymers* **2020**, *12*, 89.

47) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M.; Lund, C.; Murphy, V.; Shoemaker, J. A. W.; Tracht, U.; Turner, H.; Zhang, J.; Uno, T.; Rosen, R. K.; Stevens, J. C. A Fully Integrated High-Throughput Screening Methodology for the Discovery of New Polyolefin Catalysts: Discovery of a New Class of High Temperature Single-Site Group (IV) Copolymerization Catalysts. *Journal of the American Chemical Society* **2003**, *125*, 4306–4317.

48) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization. *Science* **2006**, *312*, 714–719.

49) De Rosa, C.; Di Girolamo, R.; Talarico, G. Expanding the Origin of Stereocontrol in Propene Polymerization Catalysis. *ACS Catalysis* **2016**, *6*, 3767–3770.

50) Domski, G. J.; Eagan, J. M.; De Rosa, C.; Di Girolamo, R.; LaPointe, A. M.; Lobkovsky, E. B.; Talarico, G.; Coates, G. W. Combined Experimental and Theoretical Approach for Living and Isoselective Propylene Polymerization. *ACS Catalysis* **2017**, *7*, 6930-6937.

2. Materials and Methods

2.1 BCPs comprising an iPP block

Samples of BCPs of isotactic polypropylene-*block*-polyethylene (iPP-*b*-PE), isotactic polypropylene-*block*-ethylene *block*-linear low-density polyethylene (iPP-*b*-LLDPE), isotactic polypropylene-*block*-ethylene-propylene rubber (iPP-*b*-EPR), as well as a sample of homopolymer of iPP, were synthesized by living polymerization using an organometallic catalyst. The employed catalyst was based on the pyridylamidohafnium complex reported in Figure 2.1 activated with $B(C_6F_5)_3$.^{1,2}



Figure 2.1 Structure of the hafnium complex used as catalyst for the preparation of the iPP, iPP-*b*-PE, iPP-*b*-LLDPE and iPP-*b*-EPR samples.

The molecular characteristics of the iPP-*b*-PE, iPP-*b*-LLDPE and iPP-*b*-EPR BCPs are reported in Tables 2.1, 2.2 and 2.3, respectively. The samples are characterized by different block lengths with total molecular masses ranging from 113 to 211 kDa. The LLDPE block in iPP-*b*-LLDPE samples corresponds to a random ethylene-1-octene copolymer with 1-octene concentration of 1-2 mol% (Table 2.2), whereas the EPR block in iPP-*b*-EPR samples corresponds to a random ethylene-propylene copolymer with ethylene concentration of 12-22 mol% (Table 2.3).

Gel permeation chromatography (GPC) experiments confirmed that the molecular masses of synthesized BCPs are almost monodispersed as indicated by polydispersity indexes (M_w/M_n) between 1.19-1.3. ¹³C NMR analysis revealed that the iPP chains in both the homopolymer and BCPs are not characterized by high isotacticity, with a concentration of the fully isotactic pentad *mmmm* of 91%, and presence of defects of stereoregularity represented by *rr* triads.¹ Moreover, the presence of 2% of defects of regioregularity represented by secondary 2,1 propene units has been detected.¹

Table 2.1. Code of iPP homopolymer and iPP-*b*-PE copolymers; total molecular mass (M_n) ; polydispersity (M_w/M_n) ; molecular masses of iPP $(M_n (iPP))$ and PE $(M_n (PE))$ blocks; weight fraction (w_{iPP}) and volume fraction (f_{iPP}) of the iPP block.

Code	M _n ^a (kDa)	$M_{ m w}/M_{ m n}{}^{ m a}$	M _{n (iPP)} ^a (kDa)	M _{n (PE)} ^b (kDa)	W _{iPP} ^c (wt%)	fipp ^d (v/v%)
RDG-1-41	139.8	1.29	139.8	_	100	100
RDG-1-91	140.1	1.23	103.4	36.7	74	74
RDG-1-127	158.0	1.27	105.3	52.7	72	68
RDG-1-138	144.7	1.30	94.6	50.1	69	65
RDG-1-166	180.6	1.26	94.6	86	64	52
RDG-1-132	113.5	1.3	61.5	52	54	54
RDG-1-88	163.5	1.19	64.6	98.9	52	40

a. From GPC analysis; b. estimated from total M_n and $M_{n (iPP)}$ such as $M_{n (PE)} = M_n M_{n (iPP)}$; c. determined from ¹³C NMR spectrum; d. calculated as $f_{iPP} = (M_{n (iPP)}/\rho_{iPP})/(M_{n (iPP)}/\rho_{iPP} + M_{n (PE)}/\rho_{PE})$ where $\rho_{iPP} = 0.850$ g cm⁻³ and $\rho_{PE} = 0.853$ g cm⁻³ are the densities of amorphous iPP and PE, respectively.

Table 2.2. Code of iPP-*b*-LLDPE copolymers; total molecular mass (M_n) ; polydispersity (M_w/M_n) ; molecular masses of iPP $(M_n (_{\text{ILDPE}}))$ and LLDPE $(M_n (_{\text{ILDPE}}))$ blocks; weight fraction (w_{iPP}) and volume fraction (f_{iPP}) of the iPP block; molar concentration of 1-octene in LLDPE block ([1-oct]).

Code	Mn ^a (kDa)	$M_{ m w}/M_{ m n}{}^{ m a}$	M _{n(iPP)} ^a (kDa)	$M_{n(LLDPE)}^{b}$ (kDa)	WiPP ^c (wt%)	fipp ^d (v/v%)	[1-oct] ^e (mol%)
JME-V-54	155	1.3	120	35	77	77	1.5
JME-IV-133	158	1.3	76	82	48	48	0.9
JME-IV-148	152	1.3	68	84	45	45	1.5
JME-IV-149	137	1.3	64	72	47	47	1.9
JME-V-256	211	1.3	31	180	15	15	1.5

a. From GPC analysis; b. estimated from total M_n and $M_n_{(iPP)}$ such as $M_n_{(LLDPE)} = M_n M_n_{(iPP)}$; c. estimated from total M_n and $M_n_{(iPP)}$ such as $w_{iPP} = M_n_{(iPP)}/M_n$; d. calculated as $f_{iPP} = (M_n_{(iPP)}/\rho_{iPP})/(M_n_{(iPP)}/\rho_{iPP} + M_n_{(LLDPE)}/\rho_{PE})$ where $\rho_{iPP} = 0.850$ g cm⁻³ and $\rho_{PE} = 0.853$ g cm⁻³ are the densities of amorphous iPP and PE, respectively; e. determined from ¹³C NMR spectrum.

Table 2.3. Code of iPP-*b*-EPR copolymers; total molecular mass (M_n) ; polydispersity (M_w/M_n) ; molecular masses of iPP $(M_{n (\text{IPP})})$ and EPR $(M_{n (\text{EPR})})$ blocks; weight fraction (w_{iPP}) and volume fraction (f_{iPP}) of the iPP block; molar concentration of ethylene in EPR block ([E]).

Code	M ^a (kDa)	$M_{ m w}/M_{ m n}^{ m a}$	$M_{n(iPP)}{}^{a}$ (kDa)	$M_{n(EPR)}^{b}$ (kDa)	WiPP ^c (wt%)	fipp ^d (v/v%)	[E] ^e (mol%)
RDG-1-149	178.22	1.17	67.8	110.4	38	38	22
RDG-1-147	161.2	1.26	64.4	96.8	40	40	12

a. From GPC analysis; b. estimated from total M_n and $M_{n (iPP)}$ such as $M_{n (EPR)} = M_n - M_{n (iPP)}$; c. estimated from total M_n and $M_{n (iPP)}$ such as $w_{iPP} = M_{n (iPP)}/M_n$; d. calculated as $f_{iPP} = (M_{n (iPP)}/\rho_{iPP})/(M_{n (iPP)}/\rho_{iPP} + M_{n (EPR)}/\rho_{EPR})$ where $\rho_{iPP} = 0.850$ g cm⁻³ and $\rho_{EPR} = 0.855$ g cm⁻³ are the densities of amorphous iPP and EPR, respectively; e. determined from ¹³C NMR spectrum.

2.2 BCPs comprising PE and sPP blocks

Samples of BCPs of polyethylene-*block*-ethylene-propylene rubber (PE-*b*-EPR), syndiotactic polypropylene-*block*-ethylene-propylene rubber (sPP-*b*-EPR), polyethylene-*block*-syndiotactic polypropylene (PE-*b*-sPP), as well as PE and sPP homopolymers, were synthesized by living polymerization using the organometallic catalyst based on the bis[N-(3-tert-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride complex of Figure 2.2, activated with methylalumoxane (MAO).^{3,4}



Figure 2.2 Structure of the titanium complex used as catalyst for the preparation of PE, sPP, PE-*b*-EPR, PE-*b*-sPP and sPP-*b*-EPR samples.

The PE-*b*-EPR samples, reported in Table 2.4, are characterized by different weight fractions of PE block (69 and 45wt%) and distinct ethylene concentrations in EPR block (24.1 and 37.7mol%). The synthesized sPP-*b*-EPR copolymer (Table 2.5) presents a preponderance of EPR block, as the weight fraction of sPP is only 13wt%. Two sets of PE-*b*-sPP copolymers have been synthesized. In Table 2.6 the samples of PE-*b*-sPP BCPs with higher molecular mass are reported ($M_n \sim 140$ kDa), whereas Table 2.7 summarizes the characteristics of PE-*b*-sPP samples with lower molecular mass ($M_n \sim 40$ kDa). Each set features samples with different block lengths. ¹³C NMR experiments performed on

sPP homopolymer and PE-*b*-sPP copolymers prepared with the same catalyst and in the same experimental conditions revealed a concentration of the *rrrr* pentad in the sPP chains of 91%. A chain-end mechanism of control of stereoregularity is operative, producing mainly *m* dyads stereodefects.^{5,6}

Table 2.4 Code of PE homopolymer and PE-*b*-EPR copolymers; total molecular mass (M_n) ; polydispersity (M_w/M_n) ; molecular masses of PE $(M_n (PE))$ and EPR $(M_n (EPR))$ blocks; weight fraction (w_{PE}) and volume fraction (f_{PE}) of PE block; molar concentration of ethylene in EPR block ([E]).

Code	M _n ^a (kDa)	$M_{ m w}/M_{ m n}{}^{ m a}$	$M_{n (PE)}{}^{a}$ (kDa)	M _{n (EPR)} ^b (kDa)	w _{PE} ^c (wt%)	f _{PE} ^d (v/v%)	[E] ^e (mol%)
PE_21-09-20	67.0	1.2	67.0	-	100	100	-
RDG-1-161	87.7	1.27	60.8	26.2	69	70	24.1
RDG-1-159	139.9	1.44	63.3	76.6	45	45	37.7

a. From GPC analysis; b. estimated from total M_n and $M_{n (PE)}$ such as $M_{n (EPR)} = M_n - M_n (PE)$; c. estimated from total M_n and $M_{n (PE)}$ such as $w_{PE} = M_n (PE)/M_n$; d. calculated as $f_{PE} = (M_n (PE)/\rho_{PE})/(M_n (PE)/\rho_{PE} + M_n (EPR)/\rho_{PPR})$ where $\rho_{PE} = 0.853$ g cm⁻³ and $\rho_{EPR} = 0.855$ g cm⁻³ are the densities of amorphous PE and EPR, respectively; e. determined from ¹³C NMR spectrum.

Table 2.5 Code of sPP homopolymer and sPP-*b*-EPR copolymer; total molecular mass (M_n); polydispersity (M_w/M_n); molecular masses of sPP (M_n (sPP)) and EPR (M_n (EPR)) blocks, weight fraction (w_{sPP}) and volume fraction (f_{sPP}) of sPP block; molar concentration of ethylene in EPR block [E].

Code	M _n ^a (kDa)	$M_{w}/M_{ m n}^{ m a}$	M _{n (sPP)} ^a (kDa)	$M_{n (EPR)}{}^{b}$ (kDa)	w _{sPP} c (wt%)	fspp ^d (v/v%)	[E] ^e (mol%)
RDG-1-1	33.7	1.09	33.7	-	100	100	-
RDG-1-6	331.5	1.22	42.0	289.5	13	13	65

a. From GPC analysis; b. estimated from total M_n and $M_{n (sPP)}$ such as $M_{n (EPR)} = M_n - M_n (sPP)$; c. estimated from total M_n and $M_{n (sPP)}$ such as $w_{sPP} = M_n (sPP)/M_n$; d. calculated as $f_{sPP} = (M_n (sPP)/\rho_{sPP})/(M_n (sPP)/\rho_{sPP} + M_n (EPR)/\rho_{EPR})$ where $\rho_{sPP} = 0.850$ g cm⁻³ and $\rho_{EPR} = 0.855$ g cm⁻³ are the densities of amorphous sPP and EPR, respectively; e. determined from ¹³C NMR spectrum.

Table 2.6 Code of PE-*b*-sPP copolymers with higher molecular mass; total molecular mass (M_n); polydispersity (M_w/M_n); molecular masses of PE (M_n (PE) and sPP (M_n (SPP) blocks; weight fraction of PE (w_{PE}) and sPP (w_{SPP}) blocks; volume fraction of PE block (f_{PE}).

Code	M _n ^a (kDa)	$M_{w}/M_{ m n}^{ m a}$	$M_{n (PE)}{}^{a}$ (kDa)	$M_{n (sPP)}{}^{b}$ (kDa)	w _{PE} ^c (wt%)	w _{sPP} ^c (wt%)	f _{РЕ} ^d (v/v%)
RDG-1-164	135.6	1.29	52.6	83.0	39	61	39
RDG-1-167	151.1	1.26	80.6	70.5	53	47	53

a. From GPC analysis; b. estimated from total M_n and M_n (PE) such as M_n (sPP) = M_n - M_n (PE); c. estimated from total M_n and M_n (PE) such as $w_{PE} = M_n$ (PE)/ M_n ; d. calculated as $f_{PE} = (M_n (PE)/\rho_{PE})/(M_n (PE)/\rho_{PE} + M_n (SPP)/\rho_{SPP})$ where $\rho_{PE} = 0.853$ g cm⁻³ and $\rho_{SPP} = 0.850$ g cm⁻³ are the densities of amorphous PE and sPP, respectively.

Table 2.7 Code of PE-*b*-sPP copolymers with lower molecular mass; total molecular mass (M_n); polydispersity (M_w/M_n); weight fraction of PE block (w_{PE}); molecular masses of PE ($M_{n (PE)}$) and sPP ($M_{n (sPP)}$) blocks; volume fraction of PE block (f_{PE}).

Code	Mn ^a (kDa)	M_{w}/M_{n}^{a}	wpe ^b (wt%)	M _{n (PE)} ^c (kDa)	M _{n (sPP)} ^c (kDa)	fре ^d (v/v%)
FI-2	20.0	1.24	49	9.8	10.2	49
FI-6	64.0	1.2	27	17.3	46.7	27
FI-5	22.0	1.2	14	3.1	18.9	14

a. From GPC analysis; b. determined from ¹³C NMR spectrum; c. estimated from total M_n and w_{PE} such as $M_n_{(PE)} = M_n$ w_{PE} and $M_n_{(sPP)} = M_n - M_n_{(PE)}$ d. calculated as $f_{PE} = (M_n_{(PE)}/\rho_{PE})/(M_n_{(PE)}/\rho_{PE} + M_n_{(sPP)}/\rho_{sPP})$ where $\rho_{PE} = 0.853$ g cm⁻³ and $\rho_{sPP} = 0.850$ g cm⁻³ are the densities of amorphous PE and sPP, respectively.

2.3 Wide Angle X-ray Scattering

X-ray powder diffraction (WAXS) profiles have been recorded in a θ - θ reflection geometry (with θ the halved scattering angle) using an automatic PANalytical Empyrean Diffractometer equipped with a PIXcel^{3D} detector and Ni filtered CuK α radiation ($\lambda = 1.5418$ Å).

Diffraction profiles were also recorded in situ at different temperatures during heating and cooling from the melt at approximately 10°C/min using an attached TTK non-ambient stage (Anton Paar KG, Graz, Austria). The samples have been heated from 25°C up to the melt at 150°C at nearly 10°C/min and the diffraction profiles have been recorded every 5 degrees starting from 105°C up to 150°C. Then, the samples have been cooled from the melt at 150°C down to 25°C, still at 10°C/min, and the diffraction profiles have been recorded every 5 degrees during cooling. The temperature was kept constant while recording each diffraction profile during both heating and cooling.

The degree of crystallinity x_c has been evaluated, after subtraction of the background approximated by a straight line, as the ratio between the crystalline diffraction area A_c and the total area of the diffraction profile A_t : $x_c = A_c/A_t$. The crystalline diffraction area A_c has been obtained by subtracting the diffraction halo of the amorphous phase A_a from the total area of the diffraction profile ($A_c = A_t - A_a$).

2.4 Temperature and time resolved Wide-Angle X-ray Scattering

Simultaneous temperatures and time resolved Wide-Angle X-ray Scattering (WAXS) experiments have been performed on station BM26B (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. A modified DSC Linkam hot stage has been employed that allows the transmission of X-rays through Kapton windows. The samples have been heated from 25 to 180°C at 30°C/min, kept at 180°C for 1 min, then cooled from 180 to 25°C at 10°C/min, heated again from 25

to 180°C at 10°C/min and finally cooled to 25°C at 30°C/min. An acquisition time of 6 s, a delay time of 6 or 0 s and a wavelength of 1.0402 Å have been used to acquire the data. The sample holder scattering has been subtracted from each scan.

2.5 Differential Scanning Calorimetry

Calorimetric measurements have been performed with a differential scanning calorimeter Mettler Toledo DSC-822, in a flowing N₂ atmosphere at scan rates of 10°C/min or 2°C/min. About 3 mg of sample were used after encapsulation in standard aluminium pans. The samples have been first heated up to melting from 25°C to 180°C (first heating scan), then cooled from 180°C to 25°C (cooling scan) and finally heated again from 25°C to 180°C (second heating scan). Alternatively, samples of BCPs featuring an EPR block were analysed with Mettler-Toledo DSC/1 using liquid nitrogen to reach temperatures below -60°C, in order to allow the determination of glass transition phenomena far below room temperature. The samples have been first heated up to melting from -100°C to 180°C, then cooled from 180°C to -100°C, and finally heated again from -100°C to 180°C. The glass transition temperatures (T_g) ware determined from the second heating scan.

Self-Nucleation (SN) and Successive Self-nucleation and Annealing (SSA) experiments have been performed with the DSC-822 calorimeter.

The SN protocol is characterized by the following steps according to Ref. 7: each sample is firstly (a) heated up to 180°C and kept at this temperature for 5 min, and then (b) cooled down until 25°C at 10°C/min to give it an initial crystalline "standard" state. Afterwards (c) the sample is heated at 10°C/min to a seeding temperature (T_s) and kept at this temperature for 5 min. Again (d) the sample is cooled from T_s to 25°C at 10°C/min. At this point step (a) and (b) are repeated, in order to erase the thermal history of the sample each time and to create a "standard" thermal history respectively, before taking the sample to a lower T_s . The adopted SN protocol is shown in Scheme 2.1. From SN experiments it was possible to determine the ideal seeding temperature, $T_{s, ideal}$, for each sample, that is the temperature corresponding to the maximum self-nucleation density without the occurrence of annealing. The criterion for the selection of the $T_{s, ideal}$ was the occurrence of the annealing peak is detected in the endotherm of step (a) at a certain T_s , the immediately preceding self-seeding temperature is selected as T_s *ideal*.



Scheme 2.1 SNA protocol adopted in the present thesis work.

The SSA experiments were performed following the protocol described in Ref. 8 and 9: each sample is (a) heated up to 180°C at 10°C/min and held at this temperature for 5 min. The sample is then (b) cooled down to 25°C at 10°C/min, creating a "standard" crystalline state. At this point the sample is (c) heated to the ideal self-seeding temperature ($T_{s,ideal}$) at 10°C/min and kept for 5 min at this temperature. The sample is finally (d) cooled to 25°C at 10°C/min; steps (c) and (d) are repeated for increasingly lower T_s covering the whole melting range. At the end of the thermal fractionation, a melting scan is performed at 10°C/min up to 180°C. The fractionation window, that is the interval between the employed seeding temperatures, was 5°C or 7.5°C, depending on the sample. The adopted SSA thermal protocol is shown in Scheme 2.2.



Scheme 2.2 SSA protocol adopted in the present thesis work.

A Perkin Elmer DSC 8500 calorimeter with an Intracooler III (cooling device) was employed to perform isothermal crystallization experiments, in the laboratories of Polymat Institute in Donostia-San Sebastiàn under the supervision of Prof. Alejandro J. Müller. Indium and tin standards were used for calibration.

The determination of the minimum crystallization temperature, $T_{c,min}$, was done by trial and error following the procedure in Ref. 10: the sample is (a) held at 180°C for 5 min to erase the thermal history. Afterwards the sample (b) is fastly cooled at 60°C/min to a selected crystallization temperature (T_c) and then (c) immediately heated at 20°C/min to 180°C. The protocol is shown in Scheme 2.3. Steps (a)-(c) are cyclically repeated for increasingly higher T_c starting from the onset crystallization temperature ($T_{c,onset}$) obtained during the non-isothermal cooling scans, until no melting enthalpy is found in the reheating scan.



Scheme 2.3 Protocol adopted for the determination of the minimum crystallization temperature ($T_{c,min}$).

After the T_c range was determined, the isothermal crystallization experiments were performed following the protocol described in Ref. 10 and pictured in Scheme 2.4: the sample is (a) held at 180°C for 5 min to erase the thermal history and then (b) fastly cooled at 60°C/min to a $T_c \ge T_{c,min}$. The sample is (c) held at T_c for a crystallization time t_c , high enough to achieve the saturation of the crystallization. The sample is (d) subsequently heated at 20°C/min to 180°C to record the melting behaviour of the crystals formed in step (c). The steps (a)-(d) are repeated for as many T_c as possible. The obtained experimental data were analysed with the Avrami theory^{11,12} and the Lauritzen and Hoffman theory¹³.



Scheme 2.4 Isothermal crystallization protocol adopted in the present thesis work.

The equilibrium melting temperature (T_m^0) of each material was calculated with the Hoffman-Weeks extrapolation;¹⁴ in order to avoid lamellar thickening, however, the apparent melting temperatures (T_m) after the isothermal crystallization at T_c were provided by other experiments in which the samples were not crystallized completely, but until the peak time $(t_c=t_p)$. These data were fitted to a straight line of positive slope in a graph of T_m versus T_c , where the line is extrapolated to its intersection with the line $T_m = T_c$. The temperature at this intersection is T_m^0 .

2.6 Polarized Optical Microscopy

Polarized Optical Microscopy (POM) experiments have been performed on thin films of block copolymers. Thin films (20-50 μ m thick) of the samples have been prepared by melting small amounts of the powder samples sandwiched between glass coverslips. The films were melted at \approx 180 °C and then crystallized by slow cooling to room temperature at 10°C/min, or 2.5°C/min in a Linkam THMS600 hot stage connected to liquid nitrogen to facilitate the cooling steps and to provide an atmosphere of ultrapure nitrogen to protect the sample. Optical microphotographs of the samples have been recorded at room temperature in polarized light using a Zeiss Axioskop 40.

POM micrographs have been acquired also during cooling of the samples from the melt at 2°C/min with an Olympus BX51 polarized light optical microscope equipped with a Linkam THMS600 hot stage in the laboratories of Polymat Institute in Donostia-San Sebastiàn under the supervision of Prof. Alejandro J. Müller. Furthermore, isothermal experiments have been performed keeping the samples at selected crystallization temperatures until the whole microscope field was covered with crystals before applying a cooling scan at 5°C/min. The obtained micrographs were analysed with ImageJ, an image processing software. The light intensity that passes through the cross polarizers in a sample was recorded, and an increase in that intensity indicates that the crystal content in the sample is increasing. This allowed to follow the crystallization process by means of intensity changes in function of temperature or of time.

2.7 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) analysis has been carried out on thin films of uniform thickness (50-70 nm), prepared by drop-casting 0.5wt% solutions of the polymer samples in *p*-xylene on glass slides. The so obtained films, after solvent evaporation, were then quenched from the melt, or crystallized at a cooling rate of 10° C/min, or epitaxially crystallized onto selected substrates. Epitaxial crystallizations were performed using as substrates crystals of *p*-terphenyl (3Ph) and benzoic acid (BA), following procedures described in the literature.^{15,16}

Single crystals of 3Ph were produced independently by slow cooling of a boiling solution of acetone. A drop of the suspension was deposited onto the polymer film at room temperature. After evaporation of the solvent, flat crystals of the substrate delimited by large top and bottom (001) surfaces remained on the polymer film. This composite material was heated to $\approx 180^{\circ}$ C to melt the polymer for a short time in order to limit sublimation of the substrate, and then recrystallized by slow cooling to room temperature. During cooling the polymer crystallizes epitaxially at the interface with the 3Ph crystals. The substrate crystals are subsequently dissolved with hot acetone.

In the case of BA, the BA powder was spread on the polymer films, which were melted along with BA (melting temperature of 123° C) at $\approx 180^{\circ}$ C to melt both the polymer and BA, and then the mixture was crystallized by moving the slide slowly down the temperature gradient of a hot bar. On cooling, the BA substrate crystals grow first through directional crystallization forming elongated, large, and flat crystals aligned with the *b* axis parallel to growth front direction. Then, the polymer epitaxially crystallizes at lower temperatures onto the (001) exposed face of BA crystals. These crystals of BA were subsequently dissolved with hot ethanol.

In all cases, the polymer films on the glass slides were covered with carbon, floated on distilled water, and transferred to grids for TEM analysis. Staining procedures were employed in order to reveal the morphological features; in particular, the grids were exposed to vapours of RuO₄ to stain the amorphous regions. Another strategy employed to improve the visualization on the crystalline lamellae was the shadowing with platinum, where the metal was evaporated at an oblique angle to the sample. To improve contrast in the epitaxially crystallized films, these were eventually decorated with gold nanoparticles by vacuum evaporation and condensation; after evaporation, gold condensates and deposits mainly at amorphous-crystalline interface of the semicrystalline lamellae allowing better visualization of crystalline phases.¹⁷ The resulting grids were analysed with a FEI TECNAI G2 200 kV TEM apparatus equipped with a 4K Eagle CCD Camera operated at 120kV.

2.8 Preparation of polymer blends

Polymer blends with a 50:50 ratio have been prepared by dissolving certain amounts of selected samples in xylene at its boiling temperature under stirring. Once the solution appeared clear, after about 3 hours, it was rapidly quenched to 25°C in methanol to allow polymer coagulation and then filtered (method 1) or it was poured in an aluminium dish to allow solvent evaporation under the hood (method 2). The obtained blends were dried under vacuum-conditions at 60°C until achieving a constant weight.

References

1) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining polyethylene and polypropylene: Enhanced performance with PE/iPP multiblock polymers. *Science* **2017**, *355*, 814-816.

2) Domski, G. J.; Eagan, J. M.; De Rosa, C.; Di Girolamo, R.; LaPointe, A. M.; Lobkovsky, E. B.; Talarico, G.; Coates, G. W. Combined Experimental and Theoretical Approach for Living and Isoselective Propylene Polymerization. *ACS Catalysis* **2017**, *7*, 6930-6937.

3) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. New Bis(salicylaldiminato) Titanium Complexes for Ethylene Polymerization. *Chemistry Letters* 1999, 1065-1066.

4) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. Living Polymerization of Ethylene Catalyzed by Titanium Complexes Having Fluorine-Containing Phenoxy–Imine Chelate Ligands. *Journal of the American Chemical Society* **2002**, *124*, 3327-3336.

5) Tian, J.; Hustad, P. D.; Coates, G. W. A New Catalyst for Highly Syndiospecific Living Olefin Polymerization: Homopolymers and Block Copolymers from Ethylene and Propylene. *Journal of the American Chemical Society* **2001**, *123*, 5134-5135.

6) De Rosa, C.; Circelli, T.; Auriemma, F.; Mathers, R. T.; Coates, G. W. Structure and Physical Properties of Syndiotactic Polypropylene from Living Polymerization with Bis(phennoxyimine)-Based Titanium Catalysts. *Macromolecules* **2004**, *37*, 9034-9047.

7) Fillon, B.; Wittmann, J. C.; Lotz, B.; Thierry, A. Self-Nucleation and Recrystallization of Isotactic Polypropylene (α Phase) Investigated by Differential Scanning Calorimetry. *Journal of Polymer Science Part B: Polymer Physics* **1993**, *31*, 1383–1393.

 Müller, A. J.; Hernández, Z. H.; Arnal, M. L.; Sánchez, J. J. Successive Self-Nucleation/Annealing (SSA): A Novel Technique to Study Molecular Segregation during Crystallization. *Polymer Bulletin* 1997, *39*, 465–472.

9) Müller, A. J.; Michell, R.M.; Pérez, R.A.; Lorenzo, A.T. Successive Self-nucleation and Annealing (SSA): Correct design of thermal protocol and applications. *European Polymer Journal* **2015**, *65*, 132-154.

10) Pérez-Camargo, R.A.; Liu, GM.; Wang, DJ; Müller, A. J. Experimental and Data Fitting Guidelines for the Determination of Polymer Crystallization Kinetics. *Chinese Journal of Polymer Science* **2022**, *40*, 658–691.

11) Avrami, M., Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III. *The Journal of Chemical Physics* **1941**, *9*, 177-184.

12) Avrami, M., Kinetics of Phase Change. I General Theory. *The Journal of Chemical Physics* 1939, 7, 1103-1112.

13) Lauritzen, J. I., Jr.; Hoffman, J. D., Theory of Formation of Polymer Crystals with Folded Chains in Dilute Solution. *Journal of Research of the National Bureau of Standards* **1960**, 64A, 73-102.

14) Hoffman, J. D.; Weeks, J. J., Melting process and the equilibrium melting temperature of polychlorotrifluoroethylene. *Journal of Research of the National Bureau of Standards* **1962**, *66*, 13-28.

15) Wittmann, J. C.; Hodge, A. M.; Lotz, B. Epitaxial Crystallization of Polymers Onto Benzoic Acid: Polyethylene and Paraffins, Aliphatic Polyesters, and Polyamides. *Journal of Polymer Science: Polymer Physics Edition* **1983**, *21*, 2495-2509.

16) Wittmann, J.C.; Lotz, B. Epitaxial crystallization of polyethylene on organic substrates: A reappraisal of the mode of action of selected nucleating agents. *Journal of Polymer Science: Polymer Physics Edition* **1981**, *19*, 1837–1851.

17) Bassett, G. A. New Technique for Decoration of Cleavage and Slip Steps on Ionic Crystal Surfaces. *The Philosophical Magazine* **1958**, *3*, 1042-1045.

3. Structural and Thermal Characterization

3.1 iPP-b-PE copolymers

The X-ray powder diffraction profiles of as-prepared samples of the iPP and PE homopolymers and of iPP-*b*-PE copolymers are reported in Figure 3.1A. They clearly show that both blocks in the BCPs are crystalline,¹ and the iPP homopolymer and the iPP block in the BCPs are crystallized in the α form, as indicated by the presence of the $(130)_{\alpha}$ reflection at $2\theta = 18.6^{\circ}$.² On the other hand, PE homopolymer and PE block in the BCPs are crystallized in the orthorhombic form, as indicated by the presence of the $(130)_{\text{PE}}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° , respectively.³ The relative amount of PE crystallinity increases with increasing the PE weight fraction in the BCPs.



Figure 3.1 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of iPP and PE homopolymers and iPP-*b*-PE copolymers. The $(130)_{\alpha}$ and $(117)_{\gamma}$ reflections of α and γ forms of iPP respectively, and $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE are indicated. The weight fractions of the iPP block (*w*_{iPP}) are also reported.

The X-ray powder diffraction profiles of samples crystallized by cooling the melt (≈ 15 °C/min) to room temperature (Figure 3.1B) show that the iPP homopolymer, also in this case, crystallizes mainly in α form. In fact, the (130)_{α} reflection at 2 θ = 18.6° is observed in the X-ray diffraction profile of sample RDG-1-41 of Figure 3.1B. However, a diffraction peak with lower intensity is also detected

at $2\theta = 20.0^{\circ}$ corresponding to the $(117)_{\gamma}$ reflection of the γ form. Therefore, a small portion of crystals in γ form or in a disordered modification of α and γ forms is also present.²

The X-ray diffraction profiles of the melt–crystallized compression molded films of iPP-*b*-PE copolymers (Figure 3.1B) show a diffuse scattering at $2\theta \approx 14^{\circ}$ around the $(110)_{\alpha}$ and $(111)_{\gamma}$ reflections, and the presence with low intensities of the $(130)_{\alpha}$ and $(117)_{\gamma}$ reflections at $2\theta = 18.6^{\circ}$ and 20.0° indicating that also in the BCPs a small portion of crystals of iPP is in γ form or in a disordered modification of α and γ forms.² The crystallization of γ form in the BCPs samples and in the iPP homopolymer is explained by the not high isotacticity of the iPP chains in both the BCPs and the homopolymer determined by the used catalyst.^{4,5}

The intensities of the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° of the orthorhombic form of the PE, increase with increasing the length of the PE block and also a slight increase of the crystallinity degree is observed in samples with higher weight fraction of the PE block. Crystallization from the melt of the BCPs, therefore, produces development of three crystalline forms, the stable orthorhombic form of PE and the α and γ forms of iPP that mutually interact during crystallization, through reciprocal nucleating effect.

The values of the degree of crystallinity calculated from the diffraction profiles of the compression molded samples are reported in Table 3.1.

Code	wiPP (wt%)	wpe (wt%)	$x_{c}(\%)$
RDG-1-41	100	0	50
RDG-1-91	74	26	50
RDG-1-127	72	28	51
RDG-1-138	69	31	52
RDG-1-166	64	36	54
RDG-1-132	54	46	55
RDG-1-88	52	48	62
PE_21-09-20	0	100	74

Table 3.1 Weight fractions of iPP (w_{iPP}) and PE (w_{PE}) blocks, crystallinity degree (x_c) of compression-molded samples of iPP and PE homopolymers and iPP-*b*-PE copolymers.

The DSC curves of iPP and PE homopolymers and iPP-PE BCPs, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 3.2. The values of melting and crystallization temperatures and enthalpies are reported in Table 3.2.

The DSC heating curves of the sample of iPP homopolymer display a melting peak at temperature of $\approx 135^{\circ}$ C consistent with a concentration of the isotactic pentad *mmmm* of 91% (determined by solution ¹³C NMR), very similar to the melting temperature of the PE homopolymer.⁴ As the Hf-based post-metallocene catalyst used for the synthesis of the iPP homopolymer was employed also for the synthesis of all the BCPs comprising an iPP block, similar isotacticity of iPP block when linked to PE is expected.

The DSC thermograms of iPP-b-PE samples show in the heating and cooling curves only one broad peak, due to the overlapping of PE and iPP melting and crystallization processes. All samples, regardless of the block length, show a melting temperature ($T_{\rm m}$) at $\approx 130^{\circ}$ C, slightly lower than that of iPP and PE homopolymers. The lower melting temperatures of PE and iPP blocks with respect to the homopolymers are probably due to confinement phenomena, that is, melting of PE and iPP crystals confined within BCP domains or within crystalline lamellae of the other crystalline form.^{6,7} However, all samples of BCPs, except for samples with lowest iPP content (RDG-1-88 and RDG-1-132), present shoulders at a temperature higher ($T \approx 135^{\circ}$ C) than that of the main melting peak, indicating that these endothermic phenomena are probably due to the melting of crystals of the iPP block. In particular, the shoulder at higher temperature may correspond to the melting of the α form of iPP and the melting of γ form probably occurs at lower temperatures hidden by the melting of PE.^{8,9} The crystallization temperatures (T_c) of the BCPs are higher than that of iPP homopolymer (102°C) and increase with increasing the PE block length. These data suggest that PE crystallizes first and the crystallization of the BCPs is driven by the nucleation effect of PE on iPP block.¹ In particular, the cooling curves of the samples RDG-1-88 and RDG-1-132, the ones with the lowest weight fractions of iPP block, show exothermic peaks at ≈ 113 and 112° C respectively, with a shoulder at lower temperature (at \approx 106 and 107°C respectively). The peaks at higher temperature correspond, mainly, to the crystallization of PE block, whereas the shoulder is probably due to the crystallization of fractions of iPP crystals. For the BCPs samples presenting iPP weight fraction higher than 54%, the crystallization of the two blocks seems to take place simultaneously.¹



Figure 3.2. DSC curves recorded at 10° C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of iPP and PE homopolymers and iPP-*b*-PE copolymers. The weight fraction of iPP block (w_{iPP}) and the values of crystallization and melting temperatures are indicated.
In order to try to get additional details concerning melting and crystallization behavior, the DSC analysis of as-prepared samples of iPP and PE homopolymers and iPP-*b*-PE samples was carried out also at scanning rate of 2°C/min.

The DSC curves recorded during first heating, successive cooling from the melt and second heating of the melt-crystallized samples recorded at scanning rate of 2°C/min, are reported in Figure 3.3. The values of the melting temperatures of as-prepared samples and of the melt-crystallized samples, the crystallization temperatures and corresponding values of the enthalpies evaluated from the DSC curves recorded at 2°C/min are reported in Table 3.2

It is apparent that also in this case, the iPP and PE blocks melt and crystallize, basically, at nearly the same temperature. However, in this case, the lower scan rate allowed to better resolve the endothermic phenomena, as all heating curves of Figures 3.3A and C exhibit an endothermic peak at $T\approx130^{\circ}$ C, and a small peak at higher temperatures, associated to melting of iPP crystals. Furthermore, also the samples RDG-1-132 and RDG-1-88, with the highest weight fractions of PE, show the same melting behaviour, presenting small shoulders at high temperature.

Cooling scans (Figure 3.3B) confirm that the presence of PE block linked to iPP leads to an increase of the crystallization temperatures, probably due to a nucleation effect. The cooling curves of the samples RDG-1-91, RDG-1-127 and RDG-1-138 show exothermic peaks with shoulders at higher temperatures. In these samples, it is reasonable to consider that a small fraction of PE crystals starts to crystallize just before the crystallization of iPP block and a small exothermic phenomenon at \approx 110°C in the cooling curves is observed.

For the sample RDG-1-166 with $w_{iPP} = 64\%$, lower than samples RDG-1-91, RDG-1-127, and RDG-1-138, a single broad peak is observed.

The cooling curves of RDG-1-32 and RDG-1-88, the samples with the lowest iPP fractions (54 and 52 wt%) show a main exothermic peak at $T \approx 115^{\circ}$ C and a smaller peak at lower temperature, indicating that the PE block start to crystallize first and then, the crystallization of iPP block occurs at lower temperature.



Figure 3.3 DSC curves recorded at 2°C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of iPP and PE homopolymers and iPP-*b*-PE copolymers. The weight fractions of iPP block (w_{iPP}) and the values of crystallization and melting temperatures are indicated.

Code	WiPP (wt%)	WPE (wt%)	$T_{\rm m}^{\rm I}$ (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	Т _с (°С)	$\Delta H_{\rm c}$ (J/g)	<i>Т</i> _m ^{II} (°С)	$\Delta H_{\rm m}^{\rm I}$ (J/g)		
scan rate 10°C/min										
RDG-1-41	100	0	127.9; 134.4	-80.3	102.0	77.3	134.7	-76.6		
RDG-1-91	74	26	126.7; 133.7	-98.7	103.2	83.0	129.2; 135.2	-85.4		
RDG-1-127	72	28	125.0; 130.5	-91.3	102.2	77.7	125.9; 133.4	-77.9		
RDG-1-138	69	31	128.6; 134.2	-105.4	106.0	86.5	130.2	-89.1		
RDG-1-166	64	36	129.0	-112.3	109.2	89.1	130.0; 136.8	-92.1		
RDG-1-132	54	46	129.8	-117.8	107.4; 111.7	89.9	132.0	-102.		
RDG-1-88	52	48	129.8	-129.7	106.0; 112.6	110.1	131.9	-113.		
PE_21-09-20	0	100	139.9	-223.3	118.5	197.9	134.0	-193.		
				scan rate 2°C	/min					
RDG-1-41	100	0	134.7	-73.0	107.9	77.4	137.5	-71.8		
RDG-1-91	74	26	125.9; 134.3	-104.5	107.8; 111.3	87.6	128.7; 136.6	-82.8		
RDG-1-127	72	28	124.0; 131.0	-96.8	106.7; 109.8	79.3	125.7; 135.6	-73.9		
RDG-1-138	69	31	127.8; 134.1	-112.2	110.6	87.6	129.4; 137.2	-83.2		
RDG-1-166	64	36	128.4; 134.5	-108.9	112.2	86.0	130.1; 138.0	-84.2		
RDG-1-132	54	46	130.1; 135.7	-87.9	112.3; 115.5	106.4	132.1; 138.0	-112.		
RDG-1-88	52	48	128.8; 133.1	-140.3	109.3; 116.0	117.4	132.1; 137.5	-113.		
PE_21-09-20	0	100	132.3	-200.0	123.6	215.6	134.3	-222.		

Table 3.2. Weight fractions of the iPP (w_{iPP}) and PE (w_{PE}) blocks, melting temperature (T_m^{I}) and melting enthalpy (ΔH_m^{I}) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m^{II}) and melting enthalpy (ΔH_m^{II}) recorded during the second heating of the samples of iPP and PE homopolymers and of the iPP-*b*-PE block copolymers, evaluated evaluated from the DSC curves recorded at 10 and 2°C/min.

Simultaneous time and temperature-resolved Wide Angle X-ray Scattering (WAXS) experiments have been performed with synchrotron radiation at ESRF in Grenoble to further investigate the melting and crystallization behavior of iPP-PE di-block copolymers and to confirm the previously discussed DSC results.

The experiments were performed on iPP-*b*-PE samples with different block lengths (namely RDG-1-91, RDG-1-166 and RDG-1-88).¹ The temperature profile employed was: heating from 25 to 180°C at 30°C/min; isotherm at 180°C for 1 min; cooling to 25°C at 10°C/min, heating again to 180°C at 10 °C/min and finally, cooling from 180 to 25°C at 30°C/min.

WAXS profiles of the sample RDG-1-91 with the highest iPP weight fraction (74wt%), at selected temperatures, recorded during the cooling and heating scans at 10°C/min, are reported in Figure 3.4. The diffraction profiles recorded during cooling clearly show that, starting from the amorphous halo of the melt at 180°C (profile a of Figure 3.4A), the weak (110)_{PE} reflection of PE at $2\theta = 21.3^{\circ}$ is the first to appear during cooling at 114°C (profile b of Figure 3.4A) while no reflections of iPP can be observed at this temperature. These data indicate that the PE block crystallizes first and crystalline iPP becomes detectable only at lower temperature (109°C), as evidenced by the presence of (110)_a and (040)_a reflections of iPP in the diffraction profile d of Figure 3.4A.

The WAXS profiles of the sample RDG-1-91 recorded during heating of melt–crystallized sample (Figure 3.4B) show that the PE crystals start melting at a temperature slightly lower than that of the iPP crystals since a strong decrease of the intensity of $(110)_{PE}$ and $(200)_{PE}$ reflections of PE is observed at 130°C (profile d of Figure 3.4). In fact, PE crystallinity is no more detectable in the diffraction profile recorded at 139°C (curve f of Figure 3.4B) where only the $(110)_{\alpha}$ reflection of iPP, with low intensity, is present. These results are in agreement with the DSC heating curves (Figure 3.2C) and confirm that the small endothermic phenomenon at high temperatures is due to the melting of thicker/more perfect iPP crystals.

The same experiments have been performed also for the samples RDG-1-166 and RDG-1-88 presenting weight fractions of the iPP block of 64% and 52%, respectively. The WAXS profiles of the sample RDG-1-166, recorded during cooling and heating at 10°C/min, are reported in Figure 3.5, whereas those of the sample RDG-1-88 are shown in Figure 3.6.



Figure 3.4 WAXS profiles of the sample RDG-1-91 (w_{iPP} =74 wt%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

For the sample RDG-1-166 with $w_{iPP} = 64\%$, the WAXS profiles recorded during cooling from the melt (Figure 3.5A) show that also in this case PE crystallizes first. The iPP block starts crystallizing at lower temperature (110°C) as indicated by the increasing intensity of the (110)_a and (040)_a reflections in profile d of Figure 3.5A. The WAXS profiles recorded during heating at 10°C/min of the melt-crystallized sample evidence that both blocks melt simultaneously as shown by the progressive decrease of intensity of both PE and iPP reflections as in the case of the sample RDG-1-91 (Figure 3.5B). A weak peak, corresponding to the (110)_a reflection of iPP is still present at 138°C (profile f of Figure 3.5B) according with the shoulder evidenced in the DSC heating trace (Figure 3.2C) at the same temperature.

Similar results to those discussed for the samples RDG-1-91 and RDG-1-166 have been obtained from WAXS data acquired during cooling and successive heating at 10°C/min of the sample RDG-1-88 presenting the highest PE content (48 wt%), confirming the behaviour discussed for the other iPP-*b*-PE samples. The only difference is represented by the appearance of the (110)_{PE} and (200)_{PE} reflections of PE during cooling from the melt already at 120°C (profile b of Figure 3.6A), at a higher temperature with respect to the other BCPs.



Figure 3.5 WAXS profiles of the sample RDG-1-166 (w_{iPP} =64 wt%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.



Figure 3.6 WAXS profiles of the sample RDG-1-88 (w_{iPP} =52 wt%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

3.2 iPP-b-LLDPE copolymers

The X-ray powder diffraction profiles of as-prepared samples of the iPP homopolymer and of iPP-LLDPE BCPs are reported in Figure 3.7A. The profile of sample JME-V-256 does not appear in this plot as this sample was provided as a compression molded

Also in this case, in the diffraction profiles of the BCPs we can observe the $(130)_{\alpha}$ reflection at $2\theta=18.6^{\circ}$ of the α form of iPP,² together with the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° , respectively, of the orthorhombic form of PE,³ indicating that both iPP and PE blocks are crystalline.



Figure 3.7 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of iPP homopolymer and iPP-*b*-LLDPE copolymers. The $(130)_{\alpha}$ and $(117)_{\gamma}$ reflections of α and γ forms of iPP respectively, and $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE are indicated. The weight fractions of the iPP block (w_{iPP}) are also reported.

The X-ray powder diffraction profiles of compression-molded samples slowly crystallized from the melt ($\approx 15 \text{ °C/min}$) are reported in Figure 3.7B. The presence of the $(130)_{\alpha}$ and $(117)_{\gamma}$ reflections of α and γ form respectively both in diffraction profiles of the iPP homopolymer and of the BCPs, indicates that the iPP block crystallizes in a mixture of the two forms, as it was found when the iPP block is linked to the PE block.^{1,2}

The values of the crystallinity degree evaluated for the iPP-*b*-LLDPE compression molded films are slightly higher than those of iPP homopolymer (Table 3.3).

Code	Wipp (wt%)	[1-oct] (mol%)	xc (%)
RDG-1-41	100	_	50
JME-V-54	77	1.5	53
JME-IV-133	48	0.9	53
JME-IV-148	45	1.5	55
JME-IV-149	47	1.9	54
JME-V-256	15	1.5	39

Table 3.3. Weight fractions of the iPP block (w_{iPP}), molar concentration of 1-octene in LLDPE block ([1-oct]), crystallinity degree (x_c) of the compression-molded samples of iPP homopolymer and iPP-*b*-LLDPE copolymers.

The DSC curves of iPP homopolymer and iPP-LLDPE BCPs, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 3.8. The values of melting and crystallization temperatures and enthalpies are reported in Table 3.4.

Unlike iPP-*b*-PE BCPs, the heating curves of iPP-*b*-LLDPE samples (Figures 3.8 A and C) show two endothermic peaks; from the second heating curves we can observe that for all the samples the melting peak at higher temperature always occurs around 133°C. On the other hand, the melting peak at lower temperature occurs at different temperatures, between 101 and 113°C.

The DSC heating curves of the sample JME-V-54 with the highest weight fraction of iPP (77wt%) and concentration of 1-octene of 1.5mol% (Figure 3.8 A and C) show a main endothermic peak at 127°C or 134°C for the first and second heating scans respectively, and a small endothermic peak at lower temperatures. We can attribute the main peak at higher temperature to the melting of iPP block, whereas the small peak at lower temperature can be attributed to the melting of the LLDPE block.

The heating curves of the copolymers JME-IV-133, JME-IV-148 and JME-IV-149 (Figure 3.8 A and C) with similar lengths of the iPP and LLDPE blocks and concentration of 1-octene of 0.9, 1.5 and 1.9 mol% respectively, show two endothermic peaks, corresponding to the melting of iPP and LLDPE blocks, that are better resolved in the second heating curves (Figure 3.8C). It can be observed that the melting temperature of the LLDPE block decreases when increasing the concentration of 1-octene.



Figure 3.8 DSC curves recorded at 10° C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of iPP homopolymer and iPP*b*-LLDPE copolymers. The weight fraction of iPP block (w_{iPP}), the molar concentration of 1-octene ([1-oct]), and the values of crystallization and melting temperatures are indicated.

The heating curves of the sample JME-V-256 (Figure 3.8 A and C) with the lowest weight fraction of iPP (15wt%) show opposite behaviour with respect to the sample JME-V-54; as a matter of fact, the sample JME-V-256 displays a main endothermic peak at 106°C and a small endothermic peak at higher temperature. Furthermore, we can observe that all the BCPs with a concentration of 1-octene in LLDPE block of 1.5 mol%, regardless of iPP content, display an endothermic peak attributable to the melting of LLDPE block at 106°C.

The DSC thermograms recorded during cooling from the melt of all iPP-*b*-LLDPE samples (Figure 3.8B) show only one exothermic peak due to the overlapping of iPP and LLDPE crystallization phenomena. Only in the cooling scan of sample JME-IV-149 with w_{iPP} =47% and [1-oct]=1.9mol% we can spot a small peak at lower temperature.

Cooling scans of iPP-*b*-PE samples (Figure 3.2B) have demonstrated that the presence of the PE block linked to the iPP block produces a nucleation effect resulting in an increase of the T_c in the BCPs compared to the T_c of iPP homopolymer. Conversely, in the cooling scans of iPP-*b*-LLDPE copolymers (Figure 3.8B) we can notice a decrease in crystallization temperature of the BCPs compared to the T_c of iPP homopolymer. Probably, in these samples iPP crystallizes just before the LLDPE and no nucleation effect occurs, while the presence of the LLDPE block linked to the iPP slows down the crystallization.

The DSC curves recorded at scanning rate of 2°C/min during first heating, successive cooling from the melt and second heating of the melt-crystallized samples, are reported in Figure 3.9. The values of the melting temperatures of as-prepared samples and of the melt-crystallized samples, the crystallization temperatures and corresponding values of the enthalpies are reported in Table 3.4.

It is apparent that also in this case, the iPP and LLDPE blocks melt at different temperatures (Figure 3.9 A and C). However, the lower scan rate allowed to better resolve the exothermic phenomena (Figure 3.9B); as a matter of fact, the cooling curve of the sample JME-V-54 displays a main exothermic peak at 104.2°C and a shoulder at lower temperature that can be attributed to crystallization of iPP and LLDPE blocks, respectively.

When the fraction of LLDPE block increases, the crystallization of the two blocks during cooling at 2° C/min seems to occur at different temperatures (Figure 3.9B). In fact, the cooling scans at 2° C/min of the sample JME-IV-148 (*w*_{iPP}=45wt%, [1-oct]=1.5mol%) and JME-IV-149 (*w*_{iPP}=47wt%, [1-oct]=1.9mol%) display a main peak ascribable to the crystallization of iPP block (at 103.0 and 102.2°C respectively) and peak at lower temperatures related to the crystallization of LLDPE block (at 98.3 and 94.2°C respectively).



Figure 3.9 DSC curves recorded at 2° C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of iPP homopolymer and iPP-*b*-LLDPE copolymers. The weight fraction of iPP block (w_{iPP}), the molar concentration of 1-octene ([1-oct]), and the values of the melting and crystallization temperatures are indicated.

We can observe a decrease in T_c of the lower temperature crystallization peak with the increase of 1octene concentration in LLDPE block. Moreover, if we look closely at the cooling curves (Figure 3.10), we will notice that in the case of JME-IV-148 the peak at 98.3°C exhibits a shoulder at lower temperature. Similarly, in the cooling curve of sample JME-IV-149 we can detect another small peak at 86.5°C. This indicates that the LLDPE block in these samples is presumably constituted by different fractions that crystallize at different temperatures.

Moving on to the sample JME-IV-133 (w_{iPP} =48wt%, [1-oct]=0.9mol%), probably the 1-octene concentration in LLDPE block is too low as in this case we still observe a single crystallization peak during cooling at 103.7°C, despite the lower scan rate (Figure 3.9B). Also in the sample JME-V-256 the crystallization phenomena of the two blocks must be overlapped, as we observe a single crystallization peak at 96.6°C, very close to the T_c of LLDPE block in sample JME-IV-148 with the same 1-octene concentration (Figure 3.9B). This could indicate that, due to the very high fraction of LLDPE block, in this sample the crystallization of iPP block is delayed and the two blocks start crystallizing simultaneously.



Figure 3.10 DSC curves recorded at 2° C/min during cooling of iPP-*b*-LLDPE samples JME-IV-148 and JME-IV-149. The weight fraction of iPP block (w_{iPP}), the molar concentration of 1-octene ([1-oct]), and the values of the crystallization temperatures are indicated.

Code	WiPP (wt%)	[1-oct] (mol%)	T_{m}^{I} (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	<i>Т</i> с (°С)	$\Delta H_{\rm c}$ (J/g)	$T_{\mathbf{m}}^{\mathbf{II}}$ (°C)	$\Delta H_{\rm m}^{\rm II}$ (J/g)			
scan rate 10°C/min											
RDG-1-41	100	0	127.9; 134.4	-80.3	102.0	77.3	134.7	-76.6			
JME-V-54	77	1.5	105.5; 127.0	-94.2	98.9	76.2	106.0; 133.1	-69.6			
JME-IV-133	48	0.9	116.2; 126.2	-106.4	98.1	76.4	113.0; 133.4	-76.9			
JME-IV-148	45	1.5	109.4; 126.2	-100.4	94.2	73.4	106.2; 132.9	-65.2			
JME-IV-149	47	1.9	101.1; 126.7	-91.1	84.7; 95.7	71	101.3; 134.1	-69.0			
JME-V-256	15	1.5	106.2; 123.9	-53.6	92.6	75.5	106.0; 132.4	-55.0			
			sca	an rate 2°C/mi	n						
RDG-1-41	100	0	134.7	-73.0	107.9	77.4	126.0; 137.5	-71.8			
JME-V-54	77	1.5	107.9; 133.2	-83.8	104.2	76.4	107.4; 133.0	-75.2			
JME-IV-133	48	0.9	112.1; 133.7	-94.9	103.7	79.6	111.9; 135.0	-75.6			
JME-IV-148	45	1.5	105.9; 133.4	-87.5	98.3; 103.0	81.6	105.7; 135.3	-83.8			
JME-IV-149	47	1.9	101.1; 133.4	-81.5	94.2; 102.2	81.8	101.0; 135.3	-62.5			
JME-V-256	15	1.5	105.7; 133.9	-82.7	96.6	75.6	104.1; 134.3	-70.0			

Table 3.4 Weight fractions of the iPP block (w_{iPP}), molar concentration of 1-octene in LLDPE block ([1-oct]), melting temperature (T_m ^I) and melting enthalpy (ΔH_m ^I) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m ^{II}) and melting enthalpy (ΔH_m ^{II}) recorded during the second heating of the samples of iPP and of the iPP-*b*-LLDPE block copolymers, evaluated evaluated from the DSC curves recorded at 10 and 2°C/min.

Simultaneous time and temperature-resolved Wide Angle X-ray Scattering (WAXS) experiments have been performed with synchrotron radiation at ESRF in Grenoble to clarify the melting and crystallization behavior of iPP-*b*-LLDPE di-block copolymers and to confirm the DSC results previously discussed.

The temperature profile employed was: heating from 25 to 180°C at 30°C/min; 1 min hold at 180°C; cooling to 25°C at 10°C/min, heating again to 180°C at 10°C/min and finally, cooling from 180 to 25°C at 30°C/min.

WAXS profiles of the sample JME-V-54 with 77 wt% of iPP at selected temperatures, recorded during cooling and heating scans at 10°C/min, are reported in Figure 3.11.

It is notable that starting from an amorphous halo of the melt at 180°C (curve a of Figure 3.11A), during cooling the iPP block crystallizes first as indicated by the appearance of the weak $(110)_{\alpha}$ and $(040)_{\alpha}$ reflections of iPP at 103°C, while no reflections of LLDPE are observed (curve c of Figure 3.11A). The WAXS profiles recorded at lower temperatures show that only the crystallization of the iPP block occurs until 99°C (curves d-f of Figure 3.11A), whereas, the presence of crystals of LLDPE is detectable only at 88°C (curve e of Figure 3.11A), as indicated by the increase of the intensity of the reflection at q=15 nm⁻¹ (2 θ = 21°) due to the (110)_{PE} reflection of PE.

WAXS experiments performed during heating of the melt-crystalized sample from 25°C to 180°C at 10°C/min (Figure 3.11B), show that crystals of LLDPE melt first at a temperature lower than that of iPP crystals, confirmed by the decrease of the intensity of the reflection at $q = 15 \text{ nm}^{-1}$ ((110)_{PE} reflection of PE) during heating already at 106°C (curves a-c of Figure 3.11B); in the diffraction profiles recorded at temperatures higher than 106°C all iPP reflections are present while those of LLDPE have disappeared. A decrease of the intensities of the diffraction peaks of iPP can observed in the WAXS profiles recorded during heating of the sample up to 133°C and only an amorphous halo is shown in the profiles at 141°C and 180°C indicating that the sample is fully melted. These data are perfectly in agreement with the DSC second heating curve of this sample (Figure 3.8C) in which the two endothermic peaks at 106.0°C and 133.1°C were attributed to the melting of LLDPE and iPP crystalline domains respectively.

Also in the case of the sample JME-IV-133, with weigh fraction of iPP of 48 wt% and concentration of 1-octene of 0.9 mol%, the iPP block start to crystallize at higher temperatures than the LLDPE block, according with the presence of iPP reflections and absence of those of LLDPE in the WAXS profiles recorded, by cooling from the melt, at 102°C and 100°C (curves b and c of Figure 3.12A).



Figure 3.11 WAXS profiles of the sample JME-V-54 ($w_{iPP}=77$ wt%, [1-oct]=1.5mol%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

However, crystallinity of the polyethylene phase is detected already at 98°C (curve d of Figure 3.12A) indicating that the two blocks crystallize almost simultaneously. These data are in agreement with the presence of only one exothermic peak at 98°C in the DSC cooling curve of sample JME-IV-133, recorded at the same scanning rate (Figure 3.8B).

The WAXS profiles recorded during heating at 10°C/min of the melt- crystallized sample show that, the LLDPE block is completely melted at 117°C (curve d of Figure 3.12B), whereas crystallinity of the iPP block is still present up to 135°C (curve f of Figure 3.12B), confirming the DSC data of the second heating scan (Figure 3.8C) which displays two separated melting peaks at 113°C and 133.4°C. WAXS profiles of the samples JME-IV-148 and JME-IV-149, with 45 and 47 wt% of iPP respectively, recorded during cooling and heating scans at 10°C/min, are reported in Figures 3.13 and 3.14. For these iPP-LLDPE block copolymers, characterized by same blocks lengths as sample JME-IV-133 but with higher 1-octene content, similar results were obtained. However, the crystallization behavior of these two samples is slightly different as for these two BCPs, the crystallization of the two blocks takes place at different temperatures. In particular, for the sample JME-IV-148 with 1.5 mol% of 1-octene, crystallinity of the polyethylene phase is detected at nearly 94°C (curve e of Figure 3.13A), whereas for the sample JME-IV-149, with 1.9 mol% of 1-octene, the iPP block crystallizes almost completely in the range of temperatures between 105 and 92°C and the crystallization of the LLDPE block starts only at lower temperatures (curve f of Figure 3.14A).



Figure 3.12 WAXS profiles of the sample JME-V-133 (w_{iPP} =48 wt%, [1-oct]=0.9mol%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.



Figure 3.13 WAXS profiles of the sample JME-IV-148 (w_{iPP} =45wt%, [1-oct]=1.5mol%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

Therefore, in the iPP-*b*-LLDPE copolymers, with similar block lengths, the crystallization of the LLDPE block is slower than the iPP block and becomes increasingly slower with increasing of 1-octene content. Indeed, in the sample JME-IV-133 with 0.9mol% of 1-octene the two blocks crystallize almost simultaneously, instead in the samples with the highest 1-octente content (1.5 and 1.9mol%) the crystallization of the two blocks occurs separately.



Figure 3.14 WAXS profiles of the sample JME-IV-149 (w_{iPP} =47wt%, [1-oct]=1.9mol) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

WAXS profiles of the sample JME-V-256 with 15 wt% of iPP and concentration of 1-octene of 1.5 mol% at selected temperatures, recorded during cooling and heating scans at 10°C/min, are reported in Figure 3.15. Differently from the already discussed iPP-*b*-LLDPE BCPs, in the WAXS profiles acquired during cooling from the melt (Figure 3.15A) of the sample JME-V-256 we can notice that iPP and LLDPE blocks start crystallizing simultaneously as indicated by the appearance at 99°C of both (110)_{α} and (110)_{PE} reflections of iPP and PE respectively (curve b of Figure 3.15A). Therefore, when the fraction of iPP is decreased to 15wt%, the crystallization of iPP block starts to take places at lower temperatures with respect to the other iPP-*b*-LLDPE BCPs and is simultaneous with the crystallization of LLDPE block.

The WAXS profiles recorded during heating at 10°C/min of the melt-crystallized sample (Figure 3.15B) show a melting behavior that is analogous to the other iPP-*b*-LLDPE BCPs as PE reflections are the first to lose intensity whereas crystallinity of the iPP block is still present up to 135°C (profile f of Figure 3.15B), confirming the DSC data of the second heating scan (Figure 3.8C).



Figure 3.15 WAXS profiles of the sample JME-V-256 ($w_{iPP}=15wt\%$, [1-oct]=1.5mol%) recorded during cooling (A) and heating (B) scan at 10°C/min at the indicated temperatures.

3.3 iPP-*b***-EPR copolymers**

The X-ray powder diffraction profiles of as-prepared and compression molded samples of the iPP homopolymer and of iPP-*b*-EPR BCPs are reported in Figure 3.16 and show the typical diffraction pattern of the α form of iPP.² In the copolymers, such reflections are overlapped with the amorphous halo of the EPR block. The values of the degree of crystallinity calculated from the diffraction profiles of the compression molded samples are reported in Table 3.5. Due to the presence of the EPR amorphous block, the iPP-*b*-EPR copolymers display lower crystallinity degrees with respect to the iPP homopolymer.

The DSC curves of iPP homopolymer and iPP-*b*-EPR BCPs, recorded at 10°C/min during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, are reported in Figure 3.17. The values of melting and crystallization temperatures, enthalpies and glass transition temperatures are reported in Table 3.6. From the second heating curves of Figure 3.17C we can notice that iPP block in samples RDG-1-149 and RDG-1-147 melts at temperatures slightly lower with respect to the iPP homopolymer, at 133.7 and 131.4°C respectively. When cooled from the melt (Figure 3.17B), the two samples show crystallization temperatures considerably lower than that of the iPP homopolymer, due to the presence of amorphous EPR block; in fact, the sample RDG-1-149 crystallizes at 92.5°C while the sample RDG-1-147 crystallizes at 81.9°C.



Figure 3.16 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of iPP homopolymer and iPP-*b*-EPR copolymers. The $(130)_{\alpha}$ and $(117)_{\gamma}$ reflections of α and γ forms of iPP are indicated. The weight fractions of the iPP block (w_{iPP}) and the concentration of ethylene in EPR block ([E]) are also reported.

Table 3.5 Weight fractions of the iPP block (w_{iPP}), molar concentration of ethylene in EPR block ([E]), crystallinity degree (x_c) of the compression-molded samples of iPP homopolymer and iPP-*b*-EPR copolymers.

Code	w _{iPP} (wt%)	[E] (mol%)	xc (%)
RDG-1-41	100	_	50
RDG-1-149	38	22	30
RDG-1-147	40	12	32

Moreover, as the two copolymers have very similar weight fraction of iPP, the reason for the difference of ~ 10°C in their T_c must be ascribed to the ethylene concentration in EPR block. In fact, the lower ethylene concentration of sample RDG-1-147 could result in a higher solubility between EPR and iPP blocks. This would mean that iPP block in the sample RDG-1-147 crystallizes at lower temperatures as iPP chains in the melt state are more diluted by EPR phase. The different concentration of ethylene in the iPP-*b*-EPR samples is responsible also for their different glass transition temperatures, noticeable from the second heating scans (Figure 3.17C); in fact, sample RDG-1-149 with higher concentration of E in EPR (22mol%) has a lower T_g (-42.3°C) with respect to sample RDG-1-147 (12mol% of E in EPR, T_g : -33.6°C).



Figure 3.17 DSC curves recorded at 10°C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of iPP homopolymer and iPP*b*-EPR copolymers. The weight fraction of iPP block (w_{iPP}), the concentration of ethylene in EPR block ([E]), and the values of the melting, crystallization and glass transition temperatures are indicated.

Table 3.6 Weight fractions of the iPP block (w_{iPP}), molar concentration of ethylene in EPR block ([E]), melting temperature (T_m^{I}) and melting enthalpy (ΔH_m^{I}) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m^{II}), melting enthalpy (ΔH_m^{II}) and glass transition temperature (T_g) recorded during the second heating of the samples of iPP homopolymer and of the iPP-*b*-EPR block copolymers.

Code	WiPP (wt%)	[E] (mol%)	T_{m}^{I} (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	<i>Т</i> с (°С)	$\Delta H_{\rm c}$ (J/g)	T _m ^{II} (°C)	$\Delta H_{\rm m}^{\rm II}$ (J/g)	Т _g (°С)
RDG-1-41	100	0	127.9; 134.4	-80.3	102.0	77.3	134.7	-76.6	-11.5
RDG-1-149	38.0	22	126.5; 132.7	-28.7	92.5	29.9	133.7	-30.2	-42.3
RDG-1-147	40.0	12	128.0	-49.2	81.9	32.2	131.4	-29.6	-33.6

3.4 PE-b-EPR copolymers

The X-ray powder diffraction profiles of as-prepared and compression molded samples of the PE homopolymer and of PE-*b*-EPR BCPs are reported in Figure 3.18 and exhibit the $(110)_{PE}$ and $(200)_{PE}$ reflections typical of the orthorhombic form of PE.³ In the copolymers, such reflections are overlapped with the amorphous halo of the EPR block. The values of the degree of crystallinity calculated from the diffraction profiles of the compression molded samples are reported in Table 3.7.



Figure 3.18 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of PE homopolymer and PE-*b*-EPR copolymers. The $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE are indicated. The weight fractions of the PE block (w_{PE}) and the molar concentration of ethylene in EPR block ([E]) are also reported.

The copolymers are clearly less crystalline than the PE homopolymer by virtue of the presence of EPR amorphous blocks. Moreover, the decrease of PE weight fraction results in a decrease of the crystallinity degree.

Code	w _{PE} (wt%)	[E] (mol%)	xc (%)
PE_21-09-20	100	_	74
RDG-1-161	69	24.1	55
RDG-1-159	45	37.7	37

Table 3.7 Weight fractions of PE block (w_{PE}), molar concentration of ethylene in EPR block ([E]), crystallinity degree (x_c) of the compression-molded samples of PE homopolymer and PE-*b*-EPR copolymers.

The DSC curves of PE homopolymer and PE-*b*-EPR BCPs, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 3.19. The values of melting and crystallization temperatures, enthalpies and glass transition temperatures are reported in Table 3.8.

Looking at the second heating curves of Figure 3.19C we can notice that PE block in samples RDG-1-161 and RDG-1-159 melts at temperatures very close to that of the PE homopolymer, at 132.3 and 132.7°C respectively. On the other hand, both samples, when cooled from the melt (Figure 3.19B) display crystallization temperature lower than that of the homopolymer, due to the presence of the linked EPR block. Moreover, both the weight fraction of EPR and its composition can be accounted for the difference in T_c between the two copolymers. RDG-1-161, with the highest w_{PE} (69 wt%) and the lowest [E] in EPR (24.1 mol%) crystallizes at 113.2°C, whereas sample RDG-1-159 with the lowest w_{PE} (45 wt%) and the highest [E] in EPR (37.7 mol%) crystallizes at 105.8°C.

From the second heating curves of the PE-*b*-EPR copolymers (Figure 3.19C) we can notice how the glass transition temperature decreases when increasing ethylene concentration in EPR; as a matter of fact sample RDG-1-161 with [E]=24.1mol% displays a T_g at -51.5°C, whereas sample RDG-1-159 with [E]=37.7mol% exhibits a glass transition at -56.0°C.



Figure 3.19 DSC curves recorded at 10° C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of PE homopolymer and PE*b*-EPR copolymers. The weight fraction of PE block (w_{PE}), the molar concentration of ethylene in EPR block ([E]) and the values of the melting, crystallization and glass transition temperatures are indicated.

Table 3.8 Weight fraction of PE (w_{PE}) block, molar concentration of ethylene in EPR block ([E]), melting temperature (T_m^I) and melting enthalpy (ΔH_m^I) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m^{II}), melting enthalpy (ΔH_m^{II}) and glass transition temperature (T_g) recorded during the second heating of the samples of PE homopolymer and of the PE-*b*-EPR block copolymers.

Code	w _{PE} (wt%)	[E] (mol%)	$T_{\rm m}{}^{\rm I}$ (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	<i>Т</i> с (°С)	$\Delta H_{\rm c}$ (J/g)	T _m ^{II} (°C)	$\Delta H_{\rm m}^{\rm II}$ (J/g)	Tg (°℃)
PE_21-09-20	100	0	139.9	-223.3	118.5	197.9	134.0	-193.4	-
RDG-1-161	69	24.1	137.7	-154.0	113.2	135.7	132.3	-138.4	-51.5
RDG-1-159	45	37.7	137.8	-77.6	105.8	69.8	132.7	-68.5	-56.0

3.5 PE-b-sPP block copolymers

The X-ray powder diffraction profiles of as-prepared samples of the sPP homopolymer and of PE-*b*-sPP copolymers with higher molecular masses are reported in Figure 3.20. They clearly show that both blocks are crystalline and both the sPP homopolymer and the sPP block in the BCPs are crystallized in form I of sPP, as indicated by the presence of the $(200)_{sPP}$ and $(020)_{sPP}$ reflections at $2\theta = 12.2^{\circ}$ and 16° .^{10,11} On the other hand, PE block in the BCPs crystallizes in the orthorhombic form, as indicated by the presence of the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° .³ This indicates that PE and sPP blocks crystallize in their most stable polymorphic forms. The reflections in the diffraction profiles of the melt-crystallized samples (Figure 3.20B) are sharper than those of the as-prepared samples, making visible also the $(121)_{sPP}$ reflection of form I of sPP at $2\theta = 21^{\circ}$. The values of the degree of crystallinity calculated from the diffraction profiles of the compression molded samples are reported in Table 3.9.



Figure 3.20 X-ray powder diffraction profiles of as-prepared (A) and compression-molded (B) samples of sPP homopolymer and of PE-*b*-sPP copolymers with higher molecular masses. The $(200)_{sPP}$, $(020)_{sPP}$, and $(121)_{sPP}$ reflections form I of sPP and $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE are indicated. The weight fractions of the sPP block (w_{sPP}) are also reported.

Table 3.9 Weight fractions of sPP block (w_{sPP}) and crystallinity degree (x_c) of compression-molded samples of sPP homopolymer and of PE-*b*-sPP copolymers with higher molecular masses.

Code	w _{sPP} (wt%)	<i>x</i> _c (%)
RDG-1-1	100	54
RDG-1-164	61	31
RDG-1-167	47	28

The X-ray powder diffraction profiles of as-prepared and compression molded samples of PE-*b*-sPP BCPs with the lower molecular masses are reported in Figure 3.21. Also in this case both blocks in the BCPs are crystalline, as indicated by the presence of reflections of form I of sPP and orthorhombic form of PE.¹²⁻¹⁴ From the values of the degree of crystallinity calculated from the diffraction profiles of the compression molded samples reported in Table 3.10 it is evident how the decrease in sPP weight fraction leads to an increase in the degree of crystallinity.



Figure 3.21 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of PE-*b*-sPP copolymers with lower molecular masses. The $(200)_{sPP}$, $(020)_{sPP}$ and $(121)_{sPP}$ reflections form I of sPP and $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE are indicated. The weight fractions of the sPP block (w_{sPP}) are also reported.

Table 3.10	Weight fractions	of sPP bloc	k (w _{sPP}) an	d crystallinity	degree (x_c)) of compre	ssion-molded	samples o	of PE-b-
sPP copoly	mers with lower n	nolecular m	asses.						

Code	wspp (wt%)	<i>x</i> c (%)
FI-5	86	26
FI-6	73	41
FI-2	51	49

The DSC curves of the sPP homopolymer and PE-sPP BCPs with higher molecular masses, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 3.22. The values of melting and crystallization temperatures and enthalpies are reported in Table 3.11. The DSC heating curves of sPP homopolymer, sample RDG-1-1 (Figure 3.22 A and C), display two melting peaks, at 132.1 and 143.2°C in second heating scan, that can be attributed to melting and recrystallization phenomena of less stable crystals. The melting temperature of the sPP homopolymer of 143.2°C is consistent with a concentration of the syndiotactic pentad *rrrr* of 91%. Only one crystallization peak at $T_c=95.2°C$ can be observed in the cooling scan (Figure 3.22B).



Figure 3.22 DSC curves recorded at 10°C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of sPP homopolymer and of PE-*b*-sPP copolymers with higher molecular mass. The weight fraction of sPP block (w_{sPP}) and the values of the melting and crystallization temperatures are indicated.

The DSC heating thermograms of PE-b-sPP samples (Figure 3.22 A and C) show only one broad peak due to the overlapping of PE and sPP melting processes at T~132°C. Since a similar stereoregularity is expected for sPP both in the homopolymer and in PE-b-sPP copolymers, the lower melting temperatures are not correlated with a decrease of stereoregularity but are probably due to confinement phenomena. On the other hand, as evident from the cooling thermograms (Figure 3.22 B), the crystallization of the two blocks takes place at different temperatures. The assignment of the crystallization peaks can be done by comparison with the T_c of sPP and PE homopolymers. We remind that PE homopolymer during the cooling scan at 10°C/min (Figure 3.2B) exhibited a crystallization peak at 118.5°C, at temperatures higher compared to sPP homopolymer ($T_c=95.2$ °C). For this reason, in the DSC cooling scans of PE-b-sPP copolymers we can attribute the peak occurring at higher temperature to the crystallization of PE crystals, and the one at lower temperature to the crystallization of sPP block. In fact, the cooling curve of sample RDG-1-164 with higher w_{sPP} displays a main exothermic peak a 96°C and a peak with lower enthalpy at higher temperature (109°C). On the contrary, the sample RDG-1-167, with lower w_{sPP} , is characterized by a main crystallization peak a 113°C and by a peak with lower enthalpy at lower temperature (99°C). These results confirm that in these BCPs PE block crystallizes first during cooling.

Table 3.11 Weight fraction of sPP block (w_{sPP}), melting temperature (T_m^I) and melting enthalpy (ΔH_m^I) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m^{II}) and melting enthalpy (ΔH_m^{II}) recorded during the second heating of the samples of sPP homopolymer and PE-*b*-sPP copolymers with higher molecular mass.

Code	WsPP (wt%)	<i>T</i> _m ^I (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	Tc (°C)	⊿ <i>H</i> c (J/g)	T _m ^Π (°C)	$\Delta H_{\rm m}^{\rm II}$ (J/g)
RDG-1-1	100	116.2; 145.0	-69.7	95.2	23.0	132.1; 143.2	-51.7
RDG-1-164	61	135.0	-112	96.7; 109.3	73.3	131.0	-75.7
RDG-1-167	47	136.0	-134.5	99.1; 113.0	94.7	133.3	-98.3

The DSC curves of PE-*b*-sPP BCPs with lower molecular masses, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 3.23. The values of melting and crystallization temperatures and enthalpies are reported in Table 3.12.



Figure 3.23 DSC curves recorded at 10° C/min during first heating (A), successive cooling (B) and second heating scans (C) of as-prepared samples of PE-*b*-sPP copolymers with lower molecular mass. The weight fraction of sPP block (w_{sPP}) and the values of the melting and crystallization temperatures are indicated.

The DSC thermograms of PE-*b*-sPP sample with lowest weight fraction of sPP (FI-2, with w_{sPP} = 51wt%) show only one broad peak in the heating and cooling curves (Figure 3.23 A,C), due to the overlapping of PE and sPP melting and crystallization processes.^{12,13} When w_{sPP} is increased to 73wt%, as in sample FI-6, the crystallization phenomena are still overlapped (Figure 3.23B), however in the second heating scans (Figure 3.23C) it is possible to observe a melting peak at 126°C with a shoulder at higher temperature at 137.1°C.^{12,13} Finally, in the sample FI-5, with the highest sPP content (86wt%), the heating scans are characterized by two distinct melting endotherms (at 121.3 and 136.3°C in the second heating curve), where the one occurring at higher temperature can be attributed to the melting of sPP block.¹⁴

Table 3.12 Weight fraction of sPP block (w_{sPP}), melting temperature (T_m^I) and melting enthalpy (ΔH_m^I) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), melting temperature (T_m^{II}) and melting enthalpy (ΔH_m^{II}) recorded during the second heating of the samples of PE-*b*-sPP copolymers with lower molecular mass.

Codo	WsPP	$T_{ m m}{}^{ m I}$	$\Delta H_{\rm m}{}^{\rm I}$	Tc	∆Hc		$\varDelta H_{ m m}^{ m II}$
Coue	(wt%)	(°C)	(J /g)	(°C)	(J/g)	Im (C)	(J/g)
FI-5	86	123.8; 136.1	-62.0	97.9	41.7	121.3; 136.3	-49.9
FI-6	73	128.1	-84.6	109.6	69.7	126.0; 128.3; 137.1	-74.5
FI-2	51	136.2	-131.1	113.6	124.0	134.4	-127.5

The X-ray diffraction profiles of the samples FI-5, FI-6, FI-2 recorded at different temperatures during heating and cooling from the melt down to room temperature, are reported in Figures 3.24-3.26. Each sample was heated from 25°C up to the melt at 150°C at nearly 10°C/min and the diffraction profiles were recorded every 5 degrees starting from 105°C up to 150°C. Then, the sample was cooled from the melt at 150°C down to 25°C still at 10°C/min and the diffraction profiles were recorded every 5 degrees during cooling. The temperature was kept constant during recording of each diffraction profile during both heating and cooling.



Figure 3.24 X-ray powder diffraction profiles of the sample FI-5 with $w_{sPP} = 86wt\%$ recorded at different temperatures during first heating of the as-prepared sample up to the melt (A), during cooling from the melt to room temperature (B) and during successive heating of the melt-crystallized sample up to the melt (C). The $(200)_{sPP}$, $(020)_{sPP}$, $(211)_{sPP}$ and $(121)_{sPP}$ reflections of form I of sPP at $2\theta = 12.2^{\circ}$, 16° , 18.8° and 20.7° and the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° of the orthorhombic form of PE are indicated.



Figure 3.25 X-ray powder diffraction profiles of the sample FI-6 with $w_{sPP} = 73$ wt% recorded at different temperatures during first heating of the as-prepared sample up to the melt (A), during cooling from the melt to room temperature (B) and during successive heating of the melt-crystallized sample up to the melt (C). The $(200)_{sPP}$, $(020)_{sPP}$, $(211)_{sPP}$ and $(121)_{sPP}$ reflections of form I of sPP at $2\theta = 12.2^{\circ}$, 16° , 18.8° and 20.7° and the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° of the orthorhombic form of PE are indicated.



Figure 3.26 X-ray powder diffraction profiles of the sample FI-2 with $w_{sPP} = 51$ wt% recorded at different temperatures during first heating of the as-prepared sample up to the melt (A), during cooling from the melt to room temperature (B) and during successive heating of the melt-crystallized sample up to the melt (C). The $(200)_{sPP}$, $(020)_{sPP}$ and $(211)_{sPP}$ reflections of form I of sPP at $2\theta = 12.2^{\circ}$, 16° , 18.8° and the $(110)_{PE}$ and $(200)_{PE}$ reflections at $2\theta = 21.4^{\circ}$ and 23.9° of the orthorhombic form of PE are indicated.

From X-ray diffraction patterns recorded at different temperatures it is possible to gain more information about the melting and crystallization behavior of PE-sPP di-block copolymers and to confirm the DSC results previously discussed. For all the samples it was not possible to properly resolve the melting process of the two blocks during the first melting (Figure 2.24A, 2.25A, 2.26A). On the other hand, during the melting of the crystallized samples (Figure 2.24C, 2.25C, 2.26C) it is possible to observe that the PE block melts first. In fact, it is evident how the intensity of diffraction peaks associated to PE crystals rapidly decreases when increasing the temperature, while the intensity of sPP reflections remains almost constant until 140°C. For all the samples, except FI-5, during cooling from the melt, the (110)_{PE} and (200)_{PE} reflections appear first already at $T \sim 130^{\circ}$ C, indicating that PE block in these samples crystallizes before sPP block.^{12,13} For what concerns sample FI-5, with the highest w_{sPP} = 86wt%, when cooling, the (200)_{sPP}, (020)_{sPP} and (121)_{sPP} reflections of sPP appear first, already at 120°C, before the (110)_{PE} and (200)_{PE} reflections of PE, that are well visible only at 115°C.¹⁴

3.6 sPP-b-EPR copolymer

The X-ray powder diffraction profiles of as-prepared and compression molded samples of sPP-*b*-EPR block copolymer RDG-1-6 (with w_{sPP} = 13wt% and [E]=65mol%) are reported in Figure 3.27. Only the weak (200)_{sPP} reflection at 20 \approx 12° of form I of sPP can be observed as the diffraction pattern is mainly characterized by the amorphous halo, in agreement with the high fraction of the amorphous EPR block (w_{EPR} = 87wt%).



Figure 3.27 X-ray powder diffraction profiles of as prepared (A) and compression molded (B) samples of sPP-*b*-EPR copolymer RDG-1-6. The $(200)_{sPP}$ reflection of form I of sPP is indicated. The weight fraction of the sPP block (w_{sPP}) is also reported.

The DSC curves of the sPP-*b*-EPR copolymer recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized sample, all recorded at 10°C/min, are reported in Figure 3.28.

The first heating thermogram displays two peaks at 114.6 and 132.2°C that can be only attributed to melting and recrystallization of sPP crystals. The same melting behaviour was exhibited also by sPP homopolymer (Figure 3.22A). In the second heating curve we can observe a single melting peak at 130.4°C, preceded by a cold crystallization peak at 32.8°C. Due to the high fraction of EPR, the DSC curves display a very clear glass transition. From the second heating curve it was possible to evaluate the $T_{\rm g}$ = -51.5°C



Figure 3.28 DSC curves of the sample RDG-1-6 with $w_{sPP} = 13$ wt% recorded at scanning rate of 10°C/min during heating of the as-prepared sample, cooling from the melt to room temperature and successive heating of the melt-crystallized sample. The values of crystallization, melting and glass transition temperatures are indicated.

References

1) Di Girolamo, R.; Santillo, C.; Malafronte, A.; Scoti, M.; De Stefano, F.; Talarico, G.; Coates, G.W.; De Rosa, C. Structure and morphology of isotactic polypropylene-polyethylene block copolymers prepared with living and stereoselective catalyst. *Polymer Chemistry* **2022**, *13*, 2950–2963.

2) De Rosa, C.; Scoti, M.; Di Girolamo, R.; Ruiz de Ballesteros, O.; Auriemma, F.; Malafronte, A. Polymorphism in polymers: A tool to tailor material's properties. *Polymer Crystallization* **2020**, *3*, e10101.

3) Bunn, C. W. The crystal structure of long-chain normal paraffin hydrocarbons. The "shape" of the <CH₂ group. *Transactions of Faraday Society* **1939**, *35*, 482-491.

4) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining polyethylene and polypropylene: Enhanced performance with PE/iPP multiblock polymers. *Science* **2017**, *355*, 814-816.

5) Xu, J.; Eagan, J. M.; Kim, S.-S.; Pan, S.; Lee, B.; Klimovica, K.; Jin, K.; Lin, T.-W.; Howard, M. J.; Ellison, C. J.; LaPointe, A. M.; Coates, G. W.; Bates, F. S. Compatibilization of Isotactic Polypropylene (iPP) and High-Density Polyethylene (HDPE) with iPP–PE Multiblock Copolymers. *Macromolecules* **2018**, *51*, 8585-8596.

6) De Rosa, C.; Di Girolamo, R.; Auriemma, A.; D'Avino, M.; Talarico, G.; Cioce, C.; Scoti, M.; Coates, G. W.; Lotz, B. Oriented Microstructures of Crystalline–Crystalline Block Copolymers Induced by Epitaxy and Competitive and Confined Crystallization. *Macromolecules* **2016**, *49*, 5576.

7) De Rosa, C.; Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M. Double Crystallization and Phase Separation in Polyethylene-Syndiotactic Polypropylene Di-Block Copolymers. *Polymers* **2021**, *13*, 2589.

8) Alamo, R. G.; Kim, M. H.; Galante, M. J.; Isasi, J. R.; Mandelkern, L. Structural and Kinetic Factors Governing the Formation of the γ Polymorph of Isotactic Polypropylene. *Macromolecules* **1999**, *32*, 4050-4064.
9) De Rosa, C.; Auriemma, F.; Di Capua, A.; Resconi, L.; Guidotti, S.; Camurati, I.; Nifant'ev, I. E.; Laishevtsev, I. P. Structure–Property Correlations in Polypropylene from Metallocene Catalysts: Stereodefective, Regioregular Isotactic Polypropylene. *Journal of the American Chemical Society* **2004**, *126*, 17040-17049.

10) De Rosa, C.; Corradini, P. Crystal Structure of Syndiotactic Polypropylene. *Macromolecules* **1993**, *26*, 5711–5718.

11) Lotz, B.; Lovinger, A. J.; Cais, R.E. Crystal structure and morphology of syndiotactic polypropylene single crystals. *Macromolecules* **1988**, *21*, 2375-2382.

12) De Rosa, C.; Di Girolamo, R.; Auriemma, F.; D'Avino, M.; Talarico, G.; Cioce, C.; Scoti, M.; Coates, G.W. Lotz, B. Oriented Microstructures of Crystalline-Crystalline Block Copolymers Induced by Epitaxy and Competitive and Confined Crystallization. *Macromolecules* **2016**, *49*, 5576–5586.

13) Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M.; De Stefano, F.; Giordano, A.; Malafronte, A.; De Rosa, C. Structure and Morphology of Crystalline Syndiotactic Polypropylene-Polyethylene Block Copolymers. *Polymers* **2022**, *14*, 1534.

14) De Rosa, C.; Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M. Double Crystallization and Phase Separation in Polyethylene-Polypropylene Di-Block Copolymers. *Polymers* **2021**, *13*, 2589.

<u>4. Bulk Morphology</u>

The morphology of bulk crystallized samples of BCPs at micrometer length scales has been carried out by Polarized Optical Microscopy (POM). The samples have been crystallized by cooling the melt from 180°C to room temperature at scan rates of 10 or 2°C/min. The thickness of the polymer films is \approx 100µm.

4.1 iPP and PE homopolymers

POM images of samples of iPP and PE homopolymers crystallized from the melt at cooling rate of 10°C/min are shown in Figure 4.1.

The image of Figure 4.1A of the sample RDG-1-41 shows the presence of bundle-like entities, organized in a nearly 90° texture that are typical of samples of iPP in which crystals of α and γ forms can be present simultaneously.¹ Space-filled spherulites are, indeed, not observed in stereoirregular iPPs and the size of bundle crystals decreases with decreasing stereoregularity, up to the formation of small, elongated needle-like crystals.¹

On the other hand, the morphology of the homopolymer of PE (Figure 4.1B) exhibits small banded spherulites with concentric dark and light rings, which is a structure typical of PE, indicating radiating twisted crystalline lamellae.²⁻⁵





Figure 4.1 Polarized optical microscope images (crossed polars) recorded at room temperature of iPP homopolymer RDG-1-41 (A) and of PE homopolymer PE_21-09-20 (B), crystallized from the melt by cooling at 10°C/min to room temperature.

4.2 iPP-b-PE copolymers

Similar bundle-like crystals as those displayed by the sample RDG-1-41 are observed in the POM images of the iPP-PE block copolymers with the highest iPP weight fractions (samples RDG-1-91 and RDG-1-127 with 74 and 72wt% of iPP respectively) of Figures 4.2A,B.⁶ The temperature and time resolved WAXS experiments have demonstrated that for all iPP-*b*-PE copolymers PE block crystallizes first (Figures 3.4 to 3.6). However, in these samples the fraction of PE that crystallizes first is not sufficient to define the morphology. Moreover, it is apparent that the crystalline structures observed for the block copolymers are less defined than those of the iPP homopolymer crystallized in the same conditions.

When the weight fraction of iPP is decreased the morphology changes, as displayed by the POM images of sample RDG-1-138 ($w_{iPP} = 69wt\%$) featuring bundle crystals together with banded spherulites (Figure 4.2C). A further decrease of the length of iPP block, as in the samples RDG-1-166 with $w_{iPP} = 64$ wt% (Figure 4.2D), RDG-1-132 with $w_{iPP} = 54$ wt% (Figure 4.2E) and RDG-1-88 with $w_{iPP} = 52wt\%$ (Figure 4.2F), leads to the disappearance of iPP crystalline entities as the morphology is uniquely defined by the crystallization of banded spherulites of PE block.⁶ The crystallization of iPP block must occur inside the preformed spherulites in a templated fashion.



C) RDG-1-138, $w_{iPP} = 69 \text{ wt\%}$



B) RDG-1-127, $w_{iPP} = 72 \text{ wt\%}$



D) RDG-1-166, $w_{iPP} = 64 \text{ wt\%}$



E) RDG-1-132, $w_{iPP} = 54 \text{ wt\%}$

F) RDG-1-88, $w_{iPP} = 52 \text{ wt\%}$



Figure 4.2 Polarized optical microscope images (crossed polars) recorded at room temperature of iPP-*b*-PE copolymers RDG-1-91 (A), RDG-1-127 (B), RDG-1-138 (C), RDG-1-66 (D), RDG-1-132 (E) and RDG-1-88 (F), crystallized from the melt by cooling at 10°C/min to room temperature.

4.3 iPP-b-LLDPE copolymers

POM images of samples of iPP-*b*-LLDPE BCPs crystallized from the melt at cooling rate of 10°C/min are shown in Figure 4.3.

The POM images of all the samples, except for sample JME-V-256, reveal the presence of bundlelike entities typical of iPP crystals in a disordered modification intermediate between α and γ forms.¹ The same crystalline supramolecular structure is observed, indeed, also for the iPP homopolymer (Figure 4.1A) confirming that this morphology is given mainly by the iPP block that is crystallizing first. On the other hand, the POM morphology obtained when cooling sample JME-V-256 with *w*_{iPP} = 15wt% seems to be a mixture of small spherulites and bundle-like entities. This result agrees with time and temperature resolved WAXS profiles, which displayed the simultaneous appearance of both iPP and PE reflections while cooling from the melt (Figure 3.15).







B) JME-IV-133, $w_{iPP} = 48 \text{ wt\%}$









Figure 4.3 Polarized optical microscope images (crossed polars) recorded at room temperature of iPP-*b*-LLDPE copolymers JME-V-54 (A), JME-IV-133 (B), JME-IV-148 (C), JME-IV-149 (D) and JME-V-256 (E) crystallized from the melt by cooling at 10°C/min to room temperature.

Samples of iPP-*b*-LLDPE copolymers have been crystallized also at lower cooling rate (2°C/min) with the aim to separate the crystallization events of the two blocks. The DSC curves of iPP-*b*-LLDPE BCPs cooled at 2°C/min in most cases revealed that the iPP and LLDPE blocks crystallize at different temperatures, with the iPP block crystallizing first (Figure 3.9B). Therefore, POM micrographs have been acquired continuously during the cooling from the melt to observe the evolution of the morphology, and, in particular, to try to detect a change in morphology as the block of LLDPE begins crystallizing.

POM images of samples of iPP homopolymer and iPP-*b*-LLDPE copolymers acquired during cooling from the melt at rate of 2°C/min are shown in Figures 4.4 to 4.8. For each sample the first image reported is that acquired at the appearance of the first crystalline entities. In Figure 4.9 the POM images acquired at room temperature after cooling at 2°C/min of the iPP homopolymer and of the iPP-*b*-LLDPE samples are reported.



Figure 4.4 Polarized optical microscope images (crossed polars) recorded at different temperatures during cooling from the melt at 2°C/min of iPP homopolymer RDG-1-41.



Figure 4.5 Polarized optical microscope images (crossed polars) recorded at different temperatures during cooling from the melt at 2° C/min of sample JME-V-54 with $w_{iPP}=77$ wt% and [1-oct]=1.5mol%.



Figure 4.6 Polarized optical microscope images (crossed polars) recorded at different temperatures during cooling from the melt at 2° C/min of sample JME-IV-133 with w_{iPP} =48wt% and [1-oct]=0.9mol%.



Figure 4.7 Polarized optical microscope images (crossed polars) recorded at different temperatures during cooling from the melt at 2° C/min of sample JME-IV-148 with w_{iPP} =45wt% and [1-oct]=1.5mol%.



Figure 4.8 Polarized optical microscope images (crossed polars) recorded at different temperatures during cooling from the melt at 2°C/min of sample JME-IV-149 with w_{iPP} =47wt% and [1-oct]=1.9mol%.



Figure 4.9 Polarized optical microscope images (crossed polars) recorded at room temperature of iPP homopolymer RDG-1-41 (A) and of iPP-*b*-LLDPE copolymers JME-V-54 (B), JME-IV-133 (C), JME-IV-148 (D), JME-IV-149 (E), crystallized from the melt by cooling at cooling rate of 2°C/min to room temperature.

The POM images of Figure 4.4 acquired during cooling of the sample of iPP homopolymer show the appearance of the first birefringent entities at T=118°C (Figure 4.4A). As the temperature decreases (Figure 4.4B) these crystalline entities grow and reveal a bundle-like morphology. When further

decreasing temperature, the film is progressively saturated with crystals, as we can observe in the images acquired at 111°C and finally at room temperature (Figure 4.4C, D).

The POM images of the BCP samples show a similar behavior that can be described considering the micrographs acquired for the sample JME-IV-148 ($w_{iPP}=45\%$, [1-oct]=1.5mol%) reported in Figure 4.7. The DSC cooling thermogram of this sample recorded at 2°C/min displayed two separate exothermic peaks, indicating that the crystallization of LLDPE block starts only once the crystallization of iPP block is completed (Figure 3.9B). The POM images acquired during cooling at the same rate show the appearance at $T=111^{\circ}C$ (Figure 4.7A) of the first birefringent entities, that should correspond to nuclei of iPP block. As the temperature decreases these entities become bigger and, also in this case, reveal a bundle-like morphology. At $T=102^{\circ}C$ (Figure 4.7E) the film appears completely saturated with crystals, although at this temperature, according to the DSC cooling curve, the crystallization of LLDPE block has not begun yet. Comparing the images acquired at 102°C and 25°C (Figures 4.7E,F) we cannot observe any change in morphology, suggesting that the crystallization of LLDPE block must occur in a templated fashion inside the preformed crystals of iPP. However, the last two mentioned images show an increased brightness in the micrograph acquired at room temperature. Such increase in the light intensity indicates that the crystal content in the sample has increased. To better visualize and quantify this increase in brightness and thus of crystalline content, for each sample, all the POM images were processed to get a mean value of light intensity. The values of the POM intensity for the iPP homopolymer and all BCP samples are plotted versus the temperature in Figures 4.10-4.14.



Figure 4.10 Values of the POM normalised intensity corresponding to the micrographs of Figure 4.4 of iPP homopolymer RDG-1-41 as a function of temperature during cooling from the melt.

Starting from the molten state at $T=120^{\circ}$ C, the plot of iPP homopolymer sample RDG-1-41 (Figure 4.10) exhibits a sharp increase of light intensity from $T=114^{\circ}$ C until $T=106^{\circ}$ C and a successive slower increase until $T=90^{\circ}$ C up to achieve a plateau, indicating that crystallization is completed.

The plot of iPP-*b*-LLDPE sample JME-V-54 ($w_{iPP}=77wt\%$, [1-oct]=1.5mol%), reported in Figure 4.11, displays the same sharp increase, although located at a slightly lower temperature ($T=111^{\circ}C$). The intensity seems to reach a plateau, however at 98°C a further small increment is observed probably related to the crystallization of the LLDPE block. In fact, the DSC cooling thermogram of this sample recorded at 2°C/min displayed a crystallization peak attributable to iPP block at 104.2°C and a shoulder at lower temperatures (Figure 3.9B).



Figure 4.11 Values of the POM normalised intensity corresponding to the micrographs of Figure 4.5 of iPP-*b*-LLDPE sample JME-V-54 as a function of temperature during cooling from the melt.

The DSC cooling curve of sample JME-IV-133 (w_{iPP} =48wt%, [1-oct]=0.9mol%) recorded at 2°C/min only showed a single crystallization peak denoting that the two blocks crystallize simultaneously (Figure 3.9B). Such behaviour can be appreciated also from the plot of the POM intensity as a function of the temperature of Figure 4.12 obtained for this sample. The plot features two increases in intensity, the first fast increase at 112°C, and a second slower increase from 106 to 80°C. The absence of a plateau between the two increments suggests that the crystallization of iPP block is not already completed when the crystallization of LLDPE block starts, confirming the results obtained with DSC.



Figure 4.12 Values of the POM normalised intensity corresponding to the micrographs of Figure 4.6 of iPP-*b*-LLDPE sample JME-IV-133 as a function of temperature during cooling from the melt.

When the weight fraction of iPP block is kept constant and the concentration of 1-octene in the LLDPE block is increased, as in samples JME-IV-148 and JME-IV-149 with 1.5 and 1.9mol% of 1-octene respectively, it is possible to clearly distinguish the crystallization events of the two blocks, as it occurred in the DSC cooling scans at 2°C/min (Figure 3.9B). The plot of the POM intensity obtained for the sample JME-IV-148 with 45 wt% of iPP, reported in Figure 4.13, exhibits a first fast increase at $T=109^{\circ}$ C related to the crystallization of the block of iPP and a plateau at $T=102^{\circ}$ C, corresponding to a value of normalized intensity of ~0.6. At $T=96^{\circ}$ C a further slower increase of intensity is observed as the LLDPE block crystallizes, up to achieve a second plateau around $T\sim65^{\circ}$ C. The same trend has also been observed for the sample JME-IV-149 (Figure 4.14), however in this case the plot is slightly shifted at lower temperatures. Moreover, for both samples when the light increases for the crystallization of the second block, the plot seems to exhibit a double bump that could be related to the two overlapped crystallization peaks observed at lower temperatures in the DSC cooling scans at 2°C/min (Figure 3.10).



Figure 4.13 Values of the POM normalised intensity corresponding to the micrographs of Figure 4.7 of iPP-*b*-LLDPE sample JME-IV-148 as a function of temperature during cooling from the melt.



Figure 4.14 Values of the POM normalised intensity corresponding to the micrographs of Figure 4.8 of iPP-*b*-LLDPE sample JME-IV-149 as a function of temperature during cooling from the melt.

A comparison of the values of the POM light intensity as a function of the temperature during crystallization of the iPP homopolymer and the iPP-*b*-LLDPE BCPs is reported in Figure 4.15. It is apparent that the temperature at which the crystallization starts decreases with decreasing iPP weight fraction. Moreover, also the value of normalized light intensity that is reached after the first sharp increase due to the crystallization of iPP block decreases with decreasing iPP weight fraction.



Figure 4.15 Values of the POM normalised intensity corresponding to the micrographs of iPP homopolymer and iPP-*b*-LLDPE samples as a function of temperature during cooling from the melt.

4.4 PE-b-sPP copolymers

The POM images recorded at room temperature of PE-*b*-sPP block copolymers RDG-1-164 and RDG-1-167 (with 39 and 53wt% of PE, respectively) crystallized at 2.5°C display in both cases morphologies dictated by the crystallization of PE banded spherulites.²⁻⁵ This result is in agreement with the interpretation of the DSC cooling scans, showing two exothermic peaks, with the one at higher temperature belonging to crystallization of PE block (Figure 3.22B). The crystallization of sPP block must take place at lower temperatures inside the preformed spherulites.



Figure 4.16 Polarized optical microscope images (crossed polars) recorded at room temperature of PE-*b*-sPP copolymers RDG-1-164 (A) and RDG-1-167 (B), crystallized from the melt by cooling at 2.5°C/min to room temperature.

4.5 iPP-b-EPR copolymers

POM images of samples of iPP-*b*-EPR block copolymers RDG-1-149 and RDG-1-147 (with 38 and 40wt% of iPP respectively) crystallized from the melt at cooling rate of 2.5°C/min are shown in Figure 4.17. They are characterized in both cases by bundles of elongated crystals organized in a texture with different bundles tilted 90° apart, typical of samples of iPP in which crystals of α and γ forms can be present simultaneously.¹ Moreover, the different concentration of ethylene in EPR block does not seem to affect the morphology.



Figure 4.17 Polarized optical microscope images (crossed polars) recorded at room temperature of iPP-*b*-EPR copolymers RDG-1-149 (A) and RDG-1-147 (B), crystallized from the melt by cooling at 2.5°C/min to room temperature.

4.6 PE-*b*-EPR copolymers

POM images of samples of PE-*b*-EPR block copolymers RDG-1-161 and RDG-1-159 (with 69 and 45wt% of PE respectively) crystallized from the melt at cooling rate of 10°C/min are shown in Figure 4.18. Clearly, both copolymers display the typical morphology exhibited by PE samples characterized by banded spherulites.²⁻⁵



Figure 4.18 Polarized optical microscope images (crossed polars) recorded at room temperature of PE-*b*-EPR copolymers RDG-1-161 (A) and RDG-1-159 (B), crystallized from the melt by cooling at 10°C/min to room temperature.

4.7 sPP homopolymer and sPP-b-EPR copolymer

The POM images of sPP homopolymer RDG-1-1 and of sPP-*b*-EPR block copolymer RDG-1-6 with w_{sPP} =13wt% cooled from the melt at 10°C/min are reported in Figure 4.19. In both cases the morphology is characterized by a dense pattern of bundle-like crystals, as expected for samples of sPP with concentration of the *rrrr* pentad in the sPP chains of 91%.⁷



Figure 4.19 Polarized optical microscope images (crossed polars) recorded at room temperature of sPP homopolymer sample RDG-1-1 (A) and sPP-*b*-EPR copolymer RDG-1-6 (B), crystallized from the melt by cooling at 10°C/min to room temperature.

References

1) De Rosa, C.; Auriemma, F.; Di Girolamo, R.; Ruiz de Ballesteros, O.; Pepe, M.; Tarallo, O.; Malafronte, A. Morphology and Mechanical Properties of the Mesomorphic Form of Isotactic Polypropylene in Stereodefective Polypropylene. *Macromolecules* **2013**, *46*, 5202-5214.

2) Geil, P. H. Polymer Single Crystals. John Wiley and Sons Inc., NewYork, 1963.

3) Gedde, U. W. Polymer Physics. Chapman & Hall, London, 1995.

4) Keith, H. D.; Padden, F. J. A Phenomenological Theory of Spherulitic Crystallization. *Journal of Applied Physics* **1963**, *34*, 2409-2421.

5) Keith, H. D.; Padden, F. J. The optical behavior of spherulites in crystalline polymers. Part I. Calculation of theoretical extinction patterns in spherulites with twisting crystalline orientation. *Journal of Polymer Science* **1959**, *39*, 101-122.

6) Di Girolamo, R.; Santillo, C.; Malafronte, A.; Scoti, M.; De Stefano, F.; Talarico, G.; Coates, G.W.; De Rosa, C. Structure and morphology of isotactic polypropylene-polyethylene block copolymers prepared with living and stereoselective catalyst. *Polymer Chemistry* **2022**, *13*, 2950–2963.

7) Scoti, M. PhD thesis: Novel polyolefin based elastomers with tailored stiffness from metallorganic catalysis: the crystalline elastomers. **2019**.

5. Thin Film Morphology

pag. 85 – pag. 100 under embargo

6. Morphology of Epitaxially Crystallized Thin Films

The presence of crystallizable components in the BCPs was exploited to induce crystal orientation in thin polymer films by epitaxial crystallization on suitable crystalline substrates. This is a well-established method used to induce preferred orientation of crystals and/or to drive crystallization of a particular polymorph.¹⁻⁸ This method allowed producing oriented nanostructures with highly aligned microdomains in BCPs comprising blocks of iPP, PE and sPP, as a consequence of the orientation of the crystalline phases. Thin films of BCPs samples were epitaxially crystallized onto crystals of *p*-terphenyl (3Ph) and benzoic acid (BA) (Figure 6.1) and the resulting morphologies have been characterized with TEM.



Figure 6.1 Polarized optical microscope images of directionally crystallized flat BA crystals (A) and of a flat crystal of 3Ph with exposed (001) face (B). BA crystals are elongated and aligned with the *b* axis parallel to growth front direction. BA single crystals with various thicknesses lead to different colours under polarized light.

The interest was focused on the nanostructures that can be obtained when only one block in the BCPs displays epitaxial relationship with the substrate, and when both blocks can be oriented by the substrate. Moreover, the change in morphology with the change of volume fraction of the blocks was also investigated.

To improve contrast, the thin films were decorated with gold nanoparticles by vacuum evaporation and condensation. After evaporation, gold condensates and deposits mainly at amorphous–crystalline interface of the semicrystalline lamellae, allowing better visualization of crystalline phases.⁹ The periodicity of the lamellar nanostructures in the BCPs has also been estimated as the separation of the parallel adjacent dark lines of gold.

6.1 Epitaxial crystallization of PE, iPP and sPP homopolymers onto BA

The crystal structure of BA is characterized by a monoclinic unit cell with parameters a = 5.510 Å, b = 5.157 Å, c = 21.973 Å, $\beta = 97.41^{\circ}$, and space group $P2_{1/c}$.¹⁰ Epitaxy of PE onto BA crystals is

related to the crystallographic similarity between the PE interchain distance (the *b* axis of PE equal to 4.93 Å)¹¹ and the *b* axis periodicity of the BA crystal (5.157 Å),⁴ and between the *c* axis periodicity of PE (2.53 Å)¹¹ and the *a* axis of BA (5.510 Å).⁴ This produces the crystallization of PE onto the (001)_{BA} exposed face of BA with PE lamellae standing edge-on, that is, perpendicular to the (001)_{BA} plane of the BA crystal, and oriented as shown in the scheme of Figure 6.2A, with the PE chain axis (*c*_{PE}) aligned parallel to the *a* axis of BA (*a*_{BA}), and the *b* axis of PE (*b*_{PE}) aligned parallel to the *b* axis of BA (*a*_{BA}), and the *b* axis of PE (*b*_{PE}) aligned parallel to the *b* axis of BA (*b*_{BA}).⁴ The (100)_{PE} lattice plane of PE is in touch with the (001)_{BA} exposed face of BA. The epitaxial relationships between BA and PE are, therefore: $(100)_{PE}/(001)_{BA}$ and *b*_{PE}//*b*_{BA}, and *c*_{PE}//*a*_{BA}.⁴



Figure 6.2 Schematic diagrams showing how crystals of PE (A) and of α form of iPP (B) are oriented onto the (001) exposed face of BA crystals after epitaxial crystallization.

Epitaxy of iPP onto BA is more complex^{5,6} and is strictly related to the periodicities arising in the (010)_{iPP} crystallographic planes (the *ac* faces) of the monoclinic unit cell of the α form of iPP,^{12,13} as shown in the scheme of Figure 6.2B.^{5,6} In particular, epitaxy is due to the similarity of the iPP periodicity of 5.07 Å perpendicular to the short diagonal of the (010)_{iPP} faces, which corresponds to the spacing of the ($\overline{101}$) planes in the α form of iPP, and the *b* axis periodicity of 5.16 Å of BA. Correspondingly, iPP crystallizes onto BA in such a way that the *b* axis of BA is perpendicular to the ($\overline{101}$) plane of the α form of iPP directed along the spacing *d*($\overline{101}$) of the ($\overline{101}$) planes, and the *a* axis of BA is aligned along the short diagonal of the *ac* face (the ($\overline{101}$) plane) of iPP, that is, the [101] direction. The *c* axis of iPP may be aligned parallel to both the two edges of the *ac* face (*c*_{1(iPP)} and *c*_{2(iPP)} in Figure 6.2B). Therefore, epitaxy generates two families of iPP lamellae aligned with their *c* axes along the two edges of the (010)_{iPP} plane, more precisely along two directions tilted 50° away from the short diagonal of the *ac* plane (the [101] direction) and from the *a* axis of BA. These two families of iPP lamellae are consequently 80° apart ($180^\circ - (2 \times 50^\circ)$) and inclined by about ±50° to the *a* axis of BA (Figure 6.2B). The epitaxial relationships between BA and iPP are, therefore: (010)_{iPP}/((001)_{BA}, *a*_{BA}//[101]_{iPP}, and *b*_{BA} $\approx d(\overline{101}$)_{iPP}.

The TEM images of thin films of the sample of iPP homopolymer epitaxially crystallized onto BA (Figure 6.3) confirm the presence of two families of edge-on iPP crystalline lamellae, generated by epitaxy, highly aligned along two directions $\approx 60-70^{\circ}$ apart with their chain axes c ($c_{1(iPP)}$ and $c_{2(iPP)}$ in Figure 6.2B) inclined by about $\pm 50^{\circ}$ to the a axis of BA, which is parallel to the [101] crystallographic direction of the α form of iPP.¹⁴ Both the families of lamellae display thickness of about 10 nm.



Figure 6.3 BF-TEM images of gold-decorated films of iPP homopolymer RDG-1-41 epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of the iPP lamellae.

Conversely, no epitaxy exists for crystallization of sPP onto BA substrate. In fact, in the BF-TEM images of gold-decorated films of sPP homopolymer crystallized onto BA (Figure 6.4), crystalline lamellae are visible, but they do not show any preferential orientation.



Figure 6.4 BF-TEM images of gold-decorated films of sPP homopolymer crystallized onto BA crystals.

6.2 Epitaxial crystallization of PE, iPP and sPP homopolymers onto 3Ph

For what concerns epitaxial crystallization of PE onto 3Ph, two different equivalent orientations of PE crystalline lamellae are generated by crystallization onto the (001) face of 3Ph.² The (110) plane of PE is in contact with the (001) plane of 3Ph.³ The PE lamellae stand edge-on with the chain axes oriented parallel to the [110] and [110] directions of the 3Ph crystal about 74° apart, as shown in the scheme of Figure 6.5A.



Figure 6.5 Schemes of the double orientations of PE lamellae (A) and single orientation of crystalline lamellae of sPP (B) onto the (001) face of 3Ph induced by epitaxial crystallization.

This epitaxy and the selection of the (110) plane as contact plane with the (001) plane of 3Ph is due to the matching between the 4.45 Å interchain distance in the (110) plane of PE and the 4.60 Å interplanar distance of the {110} planes of 3Ph.³ The epitaxial relationships between PE and 3Ph crystals are, therefore: $(110)_{PE}/(001)_{3Ph}$, $c_{PE}/[110]_{3Ph}$ and/ $[1\overline{10}]_{3Ph}$. The TEM images of thin films of PE homopolymer epitaxially crystallized onto 3Ph (Figure 6.6) confirm the presence of two families of edge-on PE crystalline lamellae, about 21 nm thick and generated by epitaxy, highly aligned along two directions $\approx 74^{\circ}$ apart.



Figure 6.6 BF-TEM images of gold-decorated films of PE homopolymer PE_21-09-20 epitaxially crystallized onto the (001) surface of 3Ph crystals. White arrows show the two different directions of alignment of the two families of the PE lamellae.

Also sPP displays epitaxial relationships for crystallization on crystals of 3Ph. The (100) plane of crystals of form I of sPP is in contact with the (001) plane of 3Ph; therefore, the crystalline sPP lamellae stand edge-on on the substrate surface, oriented with the *b* and *c* axes of sPP parallel to the *b* and *a* axes of 3Ph, respectively (Figure 6.5B).¹⁵ The chain axis of the crystalline sPP lamellae lies flat on the substrate surface and oriented parallel to the *a* axis of 3Ph crystals. This epitaxy is well explained in terms of the crystal structures of 3Ph (unit cell with a = 8.05Å, b = 5.55 Å, c = 13.59 Å, $\beta = 91.9^{\circ}$)¹⁵ and form I of sPP (orthorhombic unit cell with axes a = 14.5 Å, b = 5.6 Å or 11.2 Å, c = 7.4 Å)^{16,17} and matching of the $a_{3Ph} = 8.05$ Å and $b_{3Ph} = 5.55$ Å axes of 3Ph with the c = 7.4 Å and b = 5.6 Å axes, respectively, of form I of sPP.¹⁵ The epitaxial relationships between sPP and 3Ph crystals are, therefore: $(100)_{sPP}/(001)_{3Ph}$, $b_{sPP}//b_{3Ph}$ and $c_{sPP}//a_{3Ph}$. The orientation of sPP lamellae induced by epitaxy can be easily observed in the TEM images of gold-decorated films of sPP epitaxially crystallized on 3Ph (Figure 6.7). The thickness of the aligned lamellae was evaluated to be about 9 nm.



Figure 6.7 BF-TEM images of gold-decorated films of sPP homopolymer RDG-1-1 epitaxially crystallized onto the (001) surface of 3Ph crystals.

On the other hand, no epitaxial relationships between iPP and 3Ph are reported. In fact, in the TEM images of gold-decorated films of iPP crystallized onto 3Ph (Figure 6.8) no apparent orientation of lamellae can be evidenced.



Figure 6.8 BF-TEM images of gold-decorated films of iPP homopolymer RDG-1-41 crystallized onto the (001) surface of 3Ph crystals.

In addition to epitaxies on crystalline substrates as BA and 3Ph considered so far, possible polymer–polymer heteroepitaxies between PE and iPP and between PE and sPP have been reported in the literature.¹⁸⁻²¹ As well as in iPP/BA epitaxy, the $(010)_{iPP}$ plane of iPP is involved in iPP/PE epitaxy, the $(100)_{PE}$ plane of PE and the $(010)_{iPP}$ plane of iPP being the contact planes.^{18,19} The *b* axis of α form crystals of iPP (*b*_{iPP}) and the *a* axis of PE (*a*_{PE}) are perpendicular to the touch plane, and the

chain axis of PE is aligned along the [101] direction of iPP in the α form (the short diagonal of the *ac* face). Therefore, the chain axis of PE c_{PE} is tilted to about 50° to the chain axis of iPP c_{iPP} .¹⁹

Moreover, Petermann et al.²⁰ have crystallized sPP on a uniaxially oriented film of PE and report about sPP lamellae oriented at about 53° to the PE stretching direction (forming an angle of 37° between chain axes of sPP and PE), with the (100) plane of sPP as the probable sPP contact face.²⁰ The epitaxial relationship could not be determined as the fiber-like structure of PE gives no clue about the PE contact plane. This epitaxy has been instead analyzed with PE evaporated and condensed on an exposed (100) face of sPP generated first by epitaxial crystallization on 3Ph.²¹ The PE/sPP heteroepitaxy is therefore: (100)_{sPP} //(110)_{PE}, c_{PE} /[021]_{sPP}.²¹

6.3 Epitaxial crystallization of BCPs comprising an iPP block

Thin films of BCPs comprising iPP block were epitaxially crystallized on BA. We remind that in iPP*b*-EPR BCPs only iPP block can be oriented by BA, whereas in iPP-*b*-PE and iPP-*b*-LLDPE copolymers both blocks display epitaxial relationships with the substrate.

6.3.1 iPP-b-EPR copolymers

TEM bright field images of gold-decorated films of iPP-*b*-EPR sample RDG-1-149, with f_{iPP} =38%, epitaxially crystallized onto BA are reported in Figure 6.9. iPP block of the BCP is oriented by BA substrate as we can distinguish two families of crystalline lamellae, about 10 nm thick, highly aligned along two directions $\approx 60-70^{\circ}$ apart. The same alignments were exhibited also by the thin films of iPP homopolymer epitaxially crystallized onto BA. However, in the images obtained with the iPP homopolymer (Figure 6.3) bigger domains featuring longer lamellae with single orientation are present, whereas in the iPP-*b*-EPR BCP, lamellae with different orientations are more interbred and definitely shorter.



Figure 6.9 BF-TEM images of gold-decorated films of iPP-*b*-EPR sample RDG-1-149 with f_{iPP} =38% epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of the iPP lamellae.

6.3.2 iPP-b-PE copolymers

For what concerns iPP-*b*-PE copolymers, two samples were selected for epitaxial crystallization on BA, that are RDG-1-91 ($f_{iPP}=74\%$) and RDG-1-132 ($f_{iPP}=54\%$). The BF-TEM images show more complex morphologies (Figures 6.10 and 6.11) compared to those obtained with iPP and iPP-*b*-EPR samples, resulting from the reciprocal influence of all three involved components (iPP, PE, and BA).



Figure 6.10 BF-TEM images of gold-decorated films of iPP-*b*-PE sample RDG-1-91 with $f_{iPP}=74\%$ epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of the iPP lamellae, whereas the red arrow indicates the unique direction of the alignment of PE lamellae.



Figure 6.11 BF-TEM images of gold-decorated films of iPP-*b*-PE sample RDG-1-132 with $f_{iPP}=54\%$ epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of the iPP lamellae, whereas the red arrow indicates the unique direction of the alignment of PE lamellae.

The TEM images of the samples RDG-1-91 and RDG-1-132 show regions where the thinner crystalline lamellae are aligned along two directions and regions where the thicker crystalline lamellae are aligned along a unique direction.¹⁴ In the regions with a double orientation, the lamellae are aligned along two directions $\approx 60^{\circ}$ apart, similarly to the arrangement seen in Figures 6.3 and 6.9 for the iPP homopolymer and iPP-*b*-EPR copolymer, respectively. This suggests that the thinner crystalline lamellae with a double orientation are the iPP lamellae. Considering that the epitaxy of PE onto BA produces the alignment of the PE lamellae along one direction as shown in Figure 6.2A, in the TEM images of Figures 6.10 and 6.11 of the iPP-*b*-PE BCPs, the thicker crystalline lamellae aligned along one direction are the PE lamellae.¹⁴ The thickness of PE lamellae with a single orientation was estimated to be 15 and 18 nm in samples RDG-1-91 and RDG-1-132, respectively. The evaluated thickness of iPP lamellae with double orientation, 10 and 8 nm in samples RDG-1-91 and RDG-1-132 respectively, is quite lower compared to PE lamellae. A scheme of the final orientations of iPP and PE lamellae onto BA is represented in Figure 6.12A.¹⁴



Figure 6.12. (A) Scheme of the alignment of PE and iPP lamellae epitaxially crystallized onto BA crystals in iPP–PE BCPs. (B) Scheme of the revealed alignment of PE and iPP lamellae defined by the ED.

The attribution of PE and iPP blocks based on lamellar orientation is confirmed by the observation that the regions containing lamellae with a unique orientation become larger with increasing the length and the volume fraction of the PE block. These regions are, indeed, very small for the sample RDG-1-91 with $f_{iPP}=74\%$ (Figure 6.10) but are much larger and interconnected for the sample RDG-1-132 with $f_{iPP}=54\%$, as shown in Figure 6.11. Moreover, the distribution of domains with different lamellar alignments in sample RDG-1-132 (Figure 6.11) reminds the phase separated morphology observed in the quenched films of the same sample (Figure 5.2). The morphology obtained by epitaxial crystallization on BA could be explained in terms of a simultaneous crystallization of PE and iPP blocks in segregated microdomains present in the melt due to phase separation.

An alternative explanation for the obtained nanostructure could be that in the regions of the films showing the single lamellar orientation (Figure 6.10 and 6.11), the morphology is dictated by PE as it probably crystallizes before iPP. In these regions iPP may crystallize after PE and its double alignment may not be seen in the BF-TEM images as iPP crystallizes after PE between its oriented lamellae. This was confirmed by electron diffraction (ED) experiments performed in the area where a single lamellar orientation was observed.¹⁴ The ED patterns showed simultaneously a unique alignment of PE lamellae, and a double alignment of iPP lamellae suggesting that in these regions there are trapped iPP lamellae, parallel to PE but with the c_{iPP} axes tilted to the basal fold surface and tilted about 50° to the c_{PE} axis (Figure 6.12B).¹⁴

pag. 111 – pag. 113 under embargo

6.4 Epitaxial crystallization of BCPs comprising a sPP block

6.4.1 PE-b-sPP copolymers

Similarly to iPP-*b*-PE copolymers, also PE-*b*-sPP samples were epitaxially crystallized on a substrate that displays lattice matching with both blocks, and on a substrate that is capable of aligning crystalline lamellae only of one block.

The TEM bright fields images of gold-decorated films of PE-*b*-sPP samples FI-2, FI-6 and FI-5, with volume fractions of PE equal to 49, 27 and 14% respectively, epitaxially crystallized onto the (001) surface of 3Ph are reported in Figures 6.17-6.19. The complex morphologies generated in this process result from interactions between all three components involved, sPP, PE, and 3Ph.

The nanostructure obtained with the epitaxially crystallized films of the sample FI-2 (Figure 6.17) shows regions where thinner crystalline lamellae, about 8 nm thick, are aligned along one direction and regions where thicker crystalline lamellae, 16 nm thick, are aligned along two directions $\approx 70^{\circ}$ apart. Taking into account the epitaxial relationships described between PE and 3Ph³ and between sPP and 3Ph¹⁵, we can state that the lamellae aligned along a single direction belong to sPP block, whereas the lamellae aligned along two directions are of PE.²²



Figure 6.17 BF-TEM images of gold-decorated films of PE-*b*-sPP sample FI-2 with f_{PE} =49% epitaxially crystallized onto 3Ph crystals. Red arrows show the two different directions of alignment of the two families of the PE lamellae, whereas the white arrow indicates the unique direction of the alignment of sPP lamellae.

On the other hand, when the volume fraction of PE is decreased, as in samples FI-6 and FI-5 (Figures 6.18 and 6.19) a single set of parallel lamellae of sPP about 9 and 15 nm thick, respectively, can be observed, and must have the *c* axis parallel to the *a* axis of 3Ph.^{22,23} However, the diffraction patterns acquired on samples FI-6 indicate a single orientation of sPP lamellae and a double orientation of PE

lamellae with their chain axes oriented along two directions 74° apart and symmetrically tilted by about 37° relative to the chain axis of sPP.^{22,23} As none of the expected PE lamellae with two different orientations 74° apart is visible, PE must crystallize after sPP in the confined interlamellar regions prescribed by the oriented sPP lamellae (Figure 6.20A). These trapped, rather short and thin PE lamellae are hardly visualized by the gold decoration. The final morphology is, therefore, driven by the crystallization of sPP, in agreement with the fact that the sPP block is longer than the PE block.^{22,23}



Figure 6.18 BF-TEM images of gold-decorated films of PE-*b*-sPP sample FI-6 with $f_{PE}=27\%$ epitaxially crystallized onto 3Ph crystals. The white arrow indicates the unique direction of the alignment of sPP lamellae.



Figure 6.19 BF-TEM images of gold-decorated films of PE-*b*-sPP sample FI-5 with $f_{PE}=14\%$ epitaxially crystallized onto 3Ph crystals. The white arrow indicates the unique direction of the alignment of sPP lamellae.



Figure 6.20 Models of the structures and morphologies that develop upon epitaxial crystallization of PE-*b*-sPP copolymers onto the (001) surfaces of crystals of 3Ph when sPP block crystallizes first (A) and on BA (B). In (A) sPP crystallizes first onto 3Ph, forming lamellae aligned with the *c* and *b* axes of sPP parallel to the *a* and *b* axes of 3Ph. PE crystallizes after sPP in the confined inter-lamellar regions prescribed by the oriented sPP lamellae. In (B) PE crystallizes after PE in the confined inter-lamellar regions prescribed by the oriented PE lamellae.

Sample FI-5 was epitaxially crystallized also onto BA and the obtained TEM images are reported in Figure 6.21.²³ Also in this case, the obtained morphology is characterized by crystalline lamellae about 9 thick aligned along a single direction. Although very similar to the morphology observed after epitaxial crystallization on the (001) surface of 3Ph, in this case the orientation is induced by BA on PE lamellae, as only this block displays lattice matching with the substrate. In fact, according to the epitaxy of PE with BA, PE lamellae must have a single orientation with the *c* and *b* axes parallel to the *a* and *b* axes of BA, respectively.^{4,11}. The crystallization of the PE block defines the overall morphology of the whole epitaxially crystallized film. This may be explained considering that the PE block must have crystallized first in the presence of BA, or nearly contemporarily to the sPP block. Therefore, sPP crystallizes after PE (or with PE) in the confined inter-lamellar regions prescribed by the oriented PE lamellae (Figure 6.20B).²³



Figure 6.21 BF-TEM images of gold-decorated films of PE-*b*-sPP sample FI-5 with f_{PE} =14% epitaxially crystallized onto BA crystals. The white arrow indicates the unique direction of the alignment of PE lamellae. The image on the right was acquired on the edge of the crystal footprint, thus it is possible to notice on one side the aligned lamellae and on the other side the unoriented film.

Thanks to the use of different substrates, the images of Figures 6.19 and 6.21, although very similar in terms of induced single orientation of crystalline lamellae (sPP and PE), reveal the different sequence of crystallization events during cooling from the melt and what is the dominant event that drives the final morphology.

Also thin films of the sample RDG-1-167 with $f_{PE}=53\%$ of PE-*b*-sPP BCP were epitaxially crystallized onto 3Ph and BA, as this PE-*b*-sPP sample was used for the preparation of the polymer blends. The TEM images of sample RDG-1-167 epitaxially crystallized onto the (001) surface of preformed crystals of 3Ph are reported in Figure 6.22. As well as sample FI-2, the obtained morphology shows regions where thinner sPP crystalline lamellae, about 8 nm thick, are aligned along one direction and regions where thicker PE crystalline lamellae, 15 nm thick, are aligned along two directions $\approx 70^{\circ}$ apart. Since the DSC cooling thermogram of the sample RDG-1-167 (Figure 3.22B) displayed two almost separate crystallization peaks, with the one occurring at higher temperatures related to crystallization on PE crystals, a morphology featuring only doubly oriented PE lamellae was expected. Conversely, crystallization of this sample of PE-*b*-sPP BCP with similar volume fractions of the two blocks (about 50%) on a substrate that is selective for both block makes their crystallization simultaneous, allowing to observe and discriminate the crystalline lamellae of the two blocks. Moreover, the regions with different orientation are homogenously distributed with no preponderance of one over the other and their distribution reminds the arrangement of domains in phase-separated quenched films (Figure 5.18).



Figure 6.22 BF-TEM images of gold-decorated films of PE-*b*-sPP sample RDG-1-167 with f_{PE} =53% epitaxially crystallized onto 3Ph crystals. Red arrows show the two different directions of alignment of the two families of the PE lamellae, whereas the white arrow indicates the unique direction of the alignment of sPP lamellae.

On the other hand, when the sample RDG-1-167 was epitaxially crystallized on BA (Figure 6.23), as only PE block exhibits lattice matching with the substrate, similarly to sample FI-5 (Figure 6.21) only PE lamellae about 13 nm thick with a single orientation can be observed.



Figure 6.23 BF-TEM images of gold-decorated films of PE-*b*-sPP sample RDG-1-167 with $f_{PE}=53\%$ epitaxially crystallized onto BA crystals. The red arrow shows the unique direction of the alignment of PE lamellae.

References

1) Wittmann, J. C.; Lotz, B. Epitaxial Crystallization of Polymers on Organic and Polymeric Substrates. *Progress in Polymer Science* **1990**, *15*, 909-948.

2) Wittmann, J. C.; Lotz, B. Epitaxial Crystallization of Polyethylene on Organic Substrates: A Reappraisal of the Mode of Action of Selected Nucleating Agents. *Journal of Polymer Science: Polymer Physics Edition* **1981**, *19*, 1837-1851.

3) Wittmann, J. C.; Lotz, B. Epitaxial Crystallization of Monoclinic and Orthorhombic Polyethylene Phases. *Polymer* **1989**, *30*, 27-34.

4) Wittmann, J. C.; Hodge, A. M.; Lotz, B. Epitaxial Crystallization of Polymers Onto Benzoic Acid: Polyethylene and Paraffins, Aliphatic Polyesters, and Polyamides. *Journal of Polymer Science: Polymer Physics Edition* **1983**, *21*, 2495-2509.

5) Mathieu, C.; Thierry, A.; Wittmann, J. C.; Lotz, B. "Multiple" nucleation of the (010) contact face of isotactic polypropylene, α phase. *Polymer* **2000**, *41*, 7241-7253.

6) Stocker, W.; Magonov, S. N.; Cantow, H. J.; Wittmann, J. C.; Lotz, B. Contact Faces of Epitaxially Crystallized α - and γ -Phase Isotactic Polypropylene Observed by Atomic Force Microscopy. *Macromolecules* **1993**, *26*, 5915-5923.

7) De Rosa, C.; Auriemma, F.; Di Girolamo, R.; Aprea, R.; Thierry, A. Selective Gold Deposition on a Nanostructured Block Copolymer Film Crystallized by Epitaxy. *Nano Research* **2011**, *4*, 241-248.

8) De Rosa, C.; Di Girolamo, R.; Auriemma, F.; Talarico, G.; Scarica, C.; Malafronte, A.; Scoti, M. Controlling Size and Orientation of Lamellar Microdomains in Crystalline Block Copolymers. *ACS Applied Materials & Interfaces* **2017**, *9*, 31252–31259.

9) Bassett, G. A. New Technique for Decoration of Cleavage and Slip Steps on Ionic Crystal Surfaces. *The Philosophical Magazine* **1958**, *3*, 1042-1045.

10) Bruno, G.; Randaccio, L. Refinement of the Benzoic Acid Structure at Room Temperature. *Acta Crystallographica Section B* **1980**, *36*, 1711-1712.

11) Bunn, C. W. The crystal structure of long-chain normal paraffin hydrocarbons. The "shape" of the <CH₂ group. *Transactions of the Faraday Society* **1939**, *35*, 482-491.

12) Natta, G.; Corradini, P. Structure and Properties of Isotactic Polypropylene. *Il Nuovo Cimento* **1960**, *15*, 40-51.
13) Auriemma, F.; De Rosa, C.; Malafronte, A.; Scoti, M.; Di Girolamo, R. Solid State Polymorphism of Isotactic and Syndiotactic Polypropylene. In Polypropylene Handbook. Karger-Kocsis, J.; Bárány, T. Eds. *Springer*, Cham, **2019**.

14) De Rosa, C.; Malafronte, A.; Di Girolamo, R.; Auriemma, F.; Scoti, M.; Ruiz de Ballesteros, O.; Coates, G.W. Morphology of Isotactic Polypropylene–Polyethylene Block Copolymers Driven by Controlled Crystallization. *Macromolecules* **2020**, *53*, 10234–10244.

15) Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J.C.; Lovinger, A.J.; Lotz, B. Direct Observation of Right and Left Helical Hands of Syndiotactic Polypropylene by Atomic Force Microscopy. *Macromolecules* **1994**, *27*, 6948–6955.

16) De Rosa, C.; Corradini, P. Crystal Structure of Syndiotactic Polypropylene. *Macromolecules* **1993**, *26*, 5711–5718.

17) Lotz, B.; Lovinger, A.J.; Cais, R.E. Crystal structure and morphology of syndiotactic polypropylene single crystals. *Macromolecules* **1988**, *21*, 2375-2382.

18) Li, H.; Yan, S. Surface-Induced Polymer Crystallization and the Resultant Structures and Morphologies. *Macromolecules* **2011**, *44*, 417-428.

19) Lotz, B.; Wittmann, J. C. Polyethylene-Isotactic Polypropylene Epitaxy: Analysis of the Diffraction Patterns of Oriented Biphasic Blends. *Journal of Polymer Science, Part B: Polymer Physics* **1987**, 25, 1079-1087.

20) Petermann, J.; Xu, Y.; Loos, J.; Yang, D. Epitaxial crystallization of syndiotactic polypropylene on uniaxially oriented polyethylene. *Polymer* **1992**, *33*, 1096-1098.

21) Schumacher, M.; Lovinger, A. J.; Agarwal, P.; Wittmann, J. C.; Lotz, B. Heteroepitaxy of Syndiotactic Polypropylene with Polyethylene and Homoepitaxy. *Macromolecules* **1994**, *27*, 6956-6962.

22) De Rosa, C.; Di Girolamo, R.; Auriemma, F.; D'Avino, M.; Talarico, G.; Cioce, C.; Scoti, M.; Coates, G.W.; Lotz, B. Oriented Microstructures of Crystalline-Crystalline Block Copolymers Induced by Epitaxy and Competitive and Confined Crystallization. *Macromolecules* **2016**, *49*, 5576–5586

23) De Rosa, C.; Di Girolamo, R.; Cicolella, A.; Talarico, G.; Scoti, M. Double Crystallization and Phase Separation in Polyethylene-Polypropylene Di-Block Copolymers. *Polymers* **2021**, *13*, 2589.

7. Blends of BCPs

In this chapter the structural, thermal, and morphological analysis of blends of block-copolymers will be reported. Blends of selected BCPs were prepared in order to study the phase-separation in blends of BCPs sharing a common block of PE or EPR.

With this aim, a 50:50 blend of iPP-*b*-PE and PE-*b*-sPP samples with similar volume fractions of PE block was prepared following the methodology described in Chapter 2 (method 1). The selected samples were RDG-1-132 (f_{PE} = 46%) and RDG-1-167 (f_{PE} = 53%), and their properties are reported in Table 7.1

Table 7.1 Total molecular mass (M_n) , polydispersity (M_w/M_n) , molecular mass of PE block $(M_{n (PE)})$ and of iPP or sPP block $(M_{n (iPP)/(sPP)})$, weight fraction (w_{PE}) and volume fraction (f_{PE}) of PE block of selected iPP-*b*-PE and PE-*b*-sPP samples for the preparation of the blend.

Code	Sample	Composition (wt%)	Mn (kDa)	$M_{ m w}/M_{ m n}$	M _{n (PE)} (kDa)	$M_{n (iPP)/(sPP)}$ (kDa)	w _{PE} (wt%)	fpe (v/v%)
RDG-1-132	iPP-b-PE	50	113.5	1.30	52	61.5	46	46
RDG-1-167	PE-b-sPP	50	151.1	1.26	80.6	70.5	53	53

Similarly, a 50:50 blend was prepared using iPP-*b*-EPR and sPP-*b*-EPR samples sharing a block of amorphous EPR block. The chosen samples were RDG-1-149 ($f_{EPR}=62\%$) and RDG-1-6 ($f_{EPR}=87\%$), and their properties are reported in Table 7.2.

Table 7.2 Total molecular mass (M_n), polydispersity (M_w/M_n), molecular mass of EPR block (M_n (EPR)) and of iPP or sPP block (M_n (iPP)/(sPP)), weight fraction (w_{EPR}) and volume fraction (f_{EPR}) of EPR block, molar concentration of ethylene in EPR block ([E]) of selected iPP-*b*-EPR and sPP-*b*-EPR samples for the preparation of the blend.

Code	Sample	Composition (wt%)	Mn (kDa)	$M_{ m w}/M_{ m n}$	M _{n (EPR)} (kDa)	M _{n (iPP)/(sPP)} (kDa)	wepr (wt%)	fepr (v/v%)	[E] (mol%)
RDG-1-149	iPP-b-EPR	50	178.2	1.17	110.4	67.8	62	62	22
RDG-1-6	sPP-b-EPR	50	331.5	1.22	289.5	42.0	87	87	65

7.1 Structural and thermal analysis

The X-ray powder diffraction profiles of as-prepared samples of selected BCPs and their blends are reported in Figure 7.1. The diffraction profile of the iPP-*b*-PE/PE-*b*-sPP blend (Figure 7.1 A) displays crystallinity of all the three crystallizable blocks as suggested by the presence of the $(110)_{\alpha}$, $(040)_{\alpha}$ and $(130)_{\alpha}$ reflections at $2\theta = 14$, 17 and 18.6° diagnostic of the α form of iPP,¹ of the $(200)_{sPP}$

reflection at $2\theta = 12.2^{\circ}$ typical of form I of sPP^{2,3} and finally of the (110)_{PE} and (200)_{PE} reflections at $2\theta = 21.4^{\circ}$ and 23.9° of orthorhombic form of PE.⁴ Moreover, we can notice the higher intensity of the reflections associated to PE as in the blend this component is the most abundant.

On the other hand, it can be observed that the X-ray diffraction profile of the iPP-*b*-EPR/sPP-*b*-EPR blend (Figure 7.1B) is mainly amorphous in agreement with the preponderance of EPR block in the constituent copolymers. However, the diffraction pattern of α form of iPP together with (200)_{sPP} reflection of form I of sPP block can be observed.



Figure 7.1 X-ray powder diffraction profiles of as prepared samples of selected iPP-*b*-PE and PE-*b*-sPP copolymers and of the corresponding 50:50 blend (A) and of selected iPP-*b*-EPR and sPP-*b*-EPR copolymers and of the corresponding 50:50 blend (B). The $(130)_{\alpha}$ reflections of α form of iPP, the $(110)_{PE}$ and $(200)_{PE}$ reflections of the orthorhombic form of PE and $(200)_{sPP}$ and $(020)_{sPP}$ reflections of form I of sPP are indicated.

The DSC curves of samples of the BCPs blends, recorded during first heating, successive cooling from the melt, and second heating of the melt-crystallized samples, all recorded at 10°C/min, are reported in Figure 7.2. The values of melting and crystallization temperatures and enthalpies of the blends are reported in Table 7.3.



Figure 7.2 DSC curves recorded at 10°C/min during first heating, successive cooling and second heating scans of asprepared iPP-*b*-PE/PE-*b*-sPP blend of samples RDG-1-132 and RDG-1-167 (A) and of iPP-*b*-EPR/sPP-*b*-EPR blend of samples RDG-1-149 and RDG-1-6 (B).

The DSC thermograms of the iPP-*b*-PE/PE-*b*-sPP blend (Figure 7.2A) show in the heating curves only one broad peak, due to the overlapping of PE, iPP and sPP melting processes. The values of melting temperatures obtained in the second heating scans for the copolymers used to prepare the blend were, indeed, very close, $T_m^{II}=132^{\circ}C$ for RDG-1-132 and $T_m^{II}=133^{\circ}C$ for RDG-1-167. On the other hand, the cooling curve exhibits a main crystallization peak at 110.4°C and a shoulder at lower temperature. The same behavior was observed also in iPP-*b*-PE and PE-*b*-sPP samples, and in both cases the peak at higher temperatures was attributed to crystallization of PE block. For this reason, we can associate the peak at higher temperature to the crystallization of PE blocks of both copolymers and the shoulder at 103.8°C to the simultaneous crystallization of iPP and sPP blocks.

For what concerns the iPP-*b*-EPR/sPP-*b*-EPR blend (Figure 7.2B), in both heating and cooling scans we can notice a single peak that we can attribute mainly to melting and crystallization processes of iPP block, as the fraction of sPP in the blend is very low. The glass transition in second heating scan occurs at -47.0°C, at a temperature that is intermediate between the T_g of the EPR blocks of the copolymers (-42.3°C for RDG-1-149 and -51.5°C for RDG-1-6). This confirms that solubilization of EPR blocks in the blend has effectively occurred.

Table 7.3 Melting temperature (T_m^{I}) and melting enthalpy (ΔH_m^{I}) recorded during the first heating, crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) , melting temperature (T_m^{II}) , melting enthalpy (ΔH_m^{II}) and glass transition temperature (T_g) recorded during the second heating of samples of iPP-*b*-PE/PE-*b*-sPP and iPP-*b*-EPR/sPP-*b*-EPR blends.

Blend	T ^m I (°C)	$\Delta H_{\rm m}^{\rm I}$ (J/g)	Т _с (°С)	Δ <i>H</i> _c (J/g)	T _m ^{II} (°C)	$\Delta H_{\rm m}^{\rm II}$ (J/g)	Т _g (°С)
iPP-b-PE/PE-b-sPP	129.5	-79.3	103.8; 110.4	79.5	131.1	-81.2	-
iPP-b-EPR/sPP-b-EPR	132.9	-22.7	96.3	14.9	133.9	-20.3	-47.0

7.2 Thin film morphology

The morphology of thin films of the BCPs blends characterized above has been investigated with TEM microscopy in order to study the effect of blending on the phase-separation and dimensions of the microdomains. All samples of blends have been subjected to fast cooling from the melt, with the aim to freeze the phase separated structure eventually existing in the melt, and to slow cooling at 10°C/min, in order to observe the eventual change in morphology dictated by crystallization.

7.2.1 iPP-b-PE/PE-b-sPP blend

TEM bright field images of thin films of the 50:50 blend iPP-*b*-PE/PE-*b*-sPP of samples RDG-1-132 and RDG-1-167 rapidly quenched from the melt and stained with RuO₄ are reported in Figures 7.3.



Figure 7.3 BF-TEM images of thin films stained with RuO₄ of iPP-*b*-PE/PE-*b*-sPP 50:50 blend of samples RDG-1-132 and RDG-1-167 crystallized by quenching from the melt in liquid nitrogen.

Both copolymers, when quenched, revealed a phase-separated morphology (Figures 5.2 and 5.18) probably caused by incompatibility between iPP and PE, and sPP and PE blocks in the melt. The equal distribution of dark and bright domains is clearly ascribable to the symmetry of the di-blocks, as both copolymers are characterized by volume fraction of PE very close to 50% (f_{PE} =46% in RDG-1-132, and 53% in RDG-1-167). The same structure, with no prevalence of dark and bright domains, can be observed also in the TEM images of the blend of these copolymers (Figure 7.3) and indicates that the PE blocks of the iPP-*b*-PE and PE-*b*-sPP copolymers are soluble and segregated in dark domains, characterized by width of 56 nm and containing thin lamellae 14 nm thick. At the same time, we cannot distinguish iPP and sPP blocks as both of them in the TEM images of the copolymers appeared as bright domains with no apparent lamellae. This result could be interpreted as the hypothetical formation of a tri-block copolymer with a central PE block linking iPP and sPP blocks (iPP-*b*-PE-*b*-sPP). Considering this model, the molecular mass of the tri-block and the corresponding volume fraction of PE block resulting from the blending of the PE blocks of the single copolymers are reported in Table 7.4.

Table 7.4 Total molecular mass (M_n) of the hypothetical iPP-*b*-PE-*b*-sPP tri-block copolymer formed by blending the two samples iPP-*b*-PE RDG-1-132 and PE-*b*-sPP RDG-1-167, calculated as the sum of the molecular masses of the copolymers (Table 7.1), molecular mass of iPP block $(M_n_{(iPP)})$ and sPP block $(M_n_{(sPP)})$, molecular mass of PE block $(M_n_{(PE)})$ calculated as the sum of the molecular masses of PE blocks of the copolymers, volume fraction of PE block (f_{PE}) calculated as $f_{PE} = (M_n_{(PE)}/\rho_{PE})/(M_n_{(PE)}/\rho_{PE} + M_n_{(iPP)}/\rho_{iPP} + M_n_{(sPP)}/\rho_{sPP})$, where ρ_{PE} , ρ_{iPP} and ρ_{sPP} are the densities of amorphous PE, iPP and sPP blocks equal to 0.853 g cm⁻³, 0.850 g cm⁻³ and 0.850 g cm⁻³, respectively.

blend	Mn	M _{n (iPP)}	M _{n (sPP)}	M _{n (PE)}	fpe
	(kDa)	(kDa)	(kDa)	(kDa)	(v/v%)
iPP-b-PE/PE-b-sPP	264.6	61.5	70.5	132.6	50

When the thin films of the iPP-*b*-PE/PE-*b*-sPP blend are slowly crystallized from the melt the morphology changes (Figure 7.4) as crystalline lamellae 19 nm tick are no longer confined into domains but spread all over the film. However, it is not possible to distinguish whether such lamellae belong to iPP, sPP or PE blocks.



Figure 7.4 BF-TEM images of thin films stained with RuO₄ of iPP-*b*-PE/PE-*b*-sPP 50:50 blend of samples RDG-1-132 and RDG-1-167 crystallized by slow cooling from the melt at 10°C/min.

7.2.2 iPP-b-EPR/sPP-b-EPR blend

For what concerns the iPP-*b*-EPR/sPP-*b*-EPR blend, TEM bright field images of thin films of the blend of samples RDG-1-149 and RDG-1-6 rapidly quenched from the melt and stained with RuO₄ are reported in Figures 7.5.



Figure 7.5 BF-TEM images of thin films stained with RuO_4 of iPP-*b*-EPR/sPP-*b*-EPR 50:50 blend of samples RDG-1-149 and RDG-1-6 crystallized by quenching from the melt in liquid nitrogen.

In the images of iPP-*b*-EPR sample RDG-1-149 rapidly quenched from the melt (Figure 5.16), no phase-separation was observed, and this was attributed to the possible miscibility between iPP block and an EPR block containing 22 mol% of ethylene. A homogeneous morphology was also observed

in the quenched films of sPP-*b*-EPR sample RDG-1-6 (Figure 5.20), due in this case to the very low volume fraction of the sPP block (13%). The TEM images obtained with the 50:50 blend of these copolymers of Figure 7.5 surprisingly exhibit a phase-separated morphology characterized by bright domains segregated from a dark matrix. Such bright domains are almost circular and are arranged in an approximately ordered structure with distorted pseudo-hexagonal symmetry. Crystalline lamellae seem to be more confined in the bright domains even though lamellae crossing the bright domains are also visible.

Considering that RuO₄ stains preferably the amorphous phase and that the sPP crystalline block is a very minor part of the sample sPP-*b*-EPR RDG-1-6 (volume fraction of sPP of 13%), the dark matrix in the TEM image of Figure 7.5 corresponds to the prevailing amorphous EPR phase, whereas the bright spherical domains correspond to the more crystalline iPP blocks. It cannot be distinguished whether the sPP block is segregated together with iPP in the bright domains or it is hidden in the EPR matrix. This observed phase separated structure, probably existing in the melt, is possibly due to the increased incompatibility between iPP block and EPR phase arising from the increased concentration of ethylene in the EPR domains of the blend. In fact, the two EPR blocks of the two components, the sample iPP-*b*-EPR RDG-1-149 (with [E]=22mol% in the EPR) and the sample sPP-*b*-EPR RDG-1-6 (with [E]=65mol% in the EPR), are miscible and form a hypothetical EPR block with ethylene concentration higher than that of the sample RDG-1-149. Therefore, also in this case, the phase separated morphology of Figure 7.5 could be interpreted as the hypothetical formation of a tri-block copolymer with a central EPR block linking iPP and sPP blocks (iPP-*b*-EPR-*b*-sPP). Considering this model, the molecular mass of the tri-block and the corresponding volume fraction of the EPR block resulting from the blending of EPR blocks of the single copolymers are reported in Table 7.5.

Table 7.5 Total molecular mass (M_n) of the hypothetical iPP-*b*-EPR-*b*-sPP tri-block copolymer formed by blending the two samples iPP-*b*-EPR RDG-1-149 and sPP-*b*-EPR RDG-1-6, calculated as the sum of the molecular masses of the two block copolymer components (Table 7.2), molecular mass of iPP block (M_n (iPP)) and of sPP block (M_n (sPP)), molecular mass of EPR block (M_n (EPR)) calculated as the sum of the molecular masses of EPR blocks of the copolymers, volume fraction of EPR block (f_{EPR}) calculated as $f_{EPR} = (M_n (EPR)/\rho_{EPR})/(M_n (EPR)/\rho_{EPR} + M_n (iPP)/\rho_{iPP} + M_n (sPP)/\rho_{sPP})$, where ρ_{EPR} , ρ_{iPP} and ρ_{sPP} are the densities of the EPR, iPP and sPP blocks equal to equal to 0.855 g cm⁻³, 0.850 g cm⁻³ and 0.850 g cm⁻³, respectively.

blend	Mn	M _{n(iPP)}	M _{n(sPP)}	M _{n(EPR)}	fepr
	(kDa)	(kDa)	(kDa)	(kDa)	(v/v%)
iPP-b-EPR/sPP-b-EPR	509.8	67.8	42.0	400.0	78

When thin films of the iPP-*b*-EPR/sPP-*b*-EPR blend were slowly cooled from the melt at 10°C/min and stained with RuO₄ the obtained morphology shown in Figure 7.6 still features bright circular

domains surrounded by a daker matrix. The crystalline lamellae are no longer confined inside the bright domains but they are visible all over the film, passing through the bright domains. We can notice that the arrangement of the crystalline lamellae is the same exhibited by sample RDG-1-149 (Figure 5.17) and corresponds to the cross-hatched texture typical of iPP with lamellae arranged at 80°.^{5,6} Therefore, iPP lamellae depart from iPP crystalline bright domains and spread in the EPR matrix.



Figure 7.6 BF-TEM images of thin films stained with RuO₄ of iPP-*b*-EPR/sPP-*b*-EPR 50:50 blend of samples RDG-1-149 and RDG-1-6 crystallized by slow cooling from the melt at 10°C/min.

7.3 Morphology of epitaxially crystallized films

Research activities were also focused on investigating the nanostructures obtained by epitaxial crystallization in blends of BCPs. Therefore, thin films of the blends described above have been epitaxially crystallized on the surface of the two selected single crystal substrates, that are benzoic acid (BA) and *p*-terphenyl (3Ph), already described in Chapter 6.

7.3.1 iPP-b-PE/PE-b-sPP blend

TEM bright field images of gold-decorated films of the iPP-*b*-PE/PE-*b*-sPP blend of samples RDG-1-132 and RDG-1-167 epitaxially crystallized onto BA are reported in Figure 7.7. We recall that iPP and PE crystallize epitaxially onto BA, whereas no epitaxy exists for crystallization of sPP onto BA. As in the sample iPP-*b*-PE RDG-1-132 crystallized onto BA (Figure 6.11), we can note an heterogenous morphology featuring regions with PE lamellae aligned along a single direction, where PE probably crystallizes first, and regions with the double orientation of crystalline iPP lamellae, where iPP probably crystallizes first. On the other hand, the sample PE-*b*-sPP RDG-1-167 epitaxially crystallized onto BA (Figure 6.23) gives a morphology defined by the PE block with a single orientation of crystalline PE lamellae, as no epitaxial relationships exist between sPP and BA. Therefore, in the morphology of Figure 7.7, the sPP block presumably crystallizes in a confined fashion inside interlamellar regions defined by the aligned lamellae of PE and iPP. As observed in iPP-*b*-PE and PE-*b*-sPP copolymers epitaxially crystallized onto BA, the PE lamellae display higher thickness (16 nm) compared with doubly oriented iPP lamellae (8 nm). The obtained morphology is displayed by the whole polymer film, and this is a further proof of the miscibility of PE blocks in the iPP-*b*-PE/PE-*b*-sPP blend, which behaves as a triblock copolymer.



Figure 7.7 BF-TEM images of gold-decorated films of iPP-*b*-PE/PE-*b*-sPP 50:50 blend of samples RDG-1-132 and RDG-1-167 epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of iPP lamellae, whereas the red arrow indicates the unique direction of the alignment of PE lamellae.

7.3.2 iPP-b-EPR/sPP-b-EPR blend

Thin films of the iPP-*b*-EPR/sPP-*b*-EPR blend of samples RDG-1-149 and RDG-1-6 were also epitaxially crystallized onto crystals of BA. In this blend only iPP block displays lattice matching with BA and the epitaxially crystallized film exhibits a morphology with lamellae highly aligned along two directions $\approx 60-70^{\circ}$ apart (Figure 7.8).



Figure 7.8 BF-TEM images of gold-decorated films of iPP-*b*-EPR/sPP-*b*-EPR 50:50 blend of samples RDG-1-149 and RDG-1-6 epitaxially crystallized onto BA crystals. White arrows show the two different directions of alignment of the two families of iPP lamellae.

For what concerns the epitaxial crystallization onto crystals of 3Ph, TEM bright field images of golddecorated films of the iPP-*b*-PE/PE-*b*-sPP blend of samples RDG-1-132 and RDG-1-167 epitaxially crystallized onto the (001) surface of 3Ph crystals are reported in Figure 7.9.



Figure 7.9 BF-TEM images of gold-decorated films of iPP-*b*-PE/PE-*b*-sPP 50:50 blend of samples RDG-1-132 and RDG-1-167 epitaxially crystallized onto the (001) surface of 3Ph crystals. Red arrows show the two different directions of alignment of the two families of the PE lamellae, whereas the white arrow indicates the unique direction of the alignment of sPP lamellae.

The resulting morphology is complex and is similar to that displayed by epitaxially crystallized films of the PE-*b*-sPP sample RDG-1-167 (Figure 6.22). In fact, it is possible to distinguish regions where

thinner sPP crystalline lamellae, about 9 nm thick, are aligned along one direction and regions where thicker PE crystalline lamellae, 16 nm thick, are aligned along two directions $\approx 70^{\circ}$ apart.

Finally, the TEM image of films of the iPP-*b*-EPR/sPP-*b*-EPR blend of samples RDG-1-149 and RDG-1-6 epitaxially crystallized onto 3Ph crystals are shown in Figure 7.10. It is apparent that a single orientation of crystalline lamellae, corresponding to sPP lamellae, is present. In fact, since only sPP block in the blend displays epitaxial relationships with the substrate, the aligned lamellae 8 nm thick must be sPP lamellae. Although sPP block corresponds to only ~8% in volume fraction of the blend, surprisingly the epitaxy is capable to induce orientation over the whole film.



Figure 7.10 BF-TEM images of gold-decorated films of iPP-*b*-EPR/sPP-*b*-EPR 50:50 blend of samples RDG-1-149 and RDG-1-6 epitaxially crystallized onto the (001) surface of 3Ph crystals. The white arrow indicates the unique direction of the alignment of sPP lamellae.

References

1) De Rosa, C.; Scoti, M.; Di Girolamo, R.; Ruiz de Ballesteros, O.; Auriemma, F.; Malafronte, A. Polymorphism in polymers: A tool to tailor material's properties. *Polymer Crystallization* **2020**, *3*, e10101.

2) De Rosa, C.; Corradini, P. Crystal Structure of Syndiotactic Polypropylene. *Macromolecules* **1993**, *26*, 5711–5718.

3) Lotz, B.; Lovinger, A.J.; Cais, R.E. Crystal structure and morphology of syndiotactic polypropylene single crystals. *Macromolecules* **1988**, *21*, 2375-2382.

4) Bunn, C. W. The crystal structure of long-chain normal paraffin hydrocarbons. The "shape" of the <CH₂ group. *Transactions of the Faraday Society* **1939**, *35*, 482-491.

5) Padden, F. J.; Keith, H.D. Crystallization in Thin Films of Isotactic Polypropylene. *Journal of Applied Physics* **1966**, *37*, 4013-4020.

6) Lovinger, A.J. Microstructure and unit-cell orientation in α-polypropylene. *Journal of Polymer Science: Polymer Physics Edition* **1983**, *21*, 97-110.

8. Crystallization Kinetics

pag. 133 – pag. 201 under embargo

9. Self-Nucleation Behavior and Thermal Fractionation

pag. 202 – pag. 256 under embargo

10. Conclusions

The present work aimed at exploring the properties of a novel class of semicrystalline BCPs composed of crystallizable blocks of stereoregular polyolefins synthesized with a pyridylamidohafnium catalyst in living and stereoselective polymerization. The interest towards these systems is driven by the possibility of creating nanostructured materials with high temperature melting crystalline domains. Moreover, the orientation of such domains can be controlled through the control of the crystallization, affording ordered patterns on thin polymer films. However, for this class of semi-crystalline BCPs a complex solid-state morphology is expected due to the interplay between the phase separation of incompatible blocks and the crystallization. Moreover, as polyolefin-based BCPs have been synthesized only recently, their complexity has not been fully clarified to date. Within this framework, research activities have been focused on the systematic characterization of BCPs containing crystallizable isotactic or syndiotactic polypropylene linked to amorphous blocks of random propene-ethylene copolymers or to crystalline PE and LLDPE blocks. The influence of the different compositions and block lengths on the crystallization behavior and morphology on different length scales of these systems has been examined.

In particular, the studies have been focused on crystalline-crystalline BCPs, such as isotactic polypropylene-*block*-polyethylene (iPP-*b*-PE), isotactic polypropylene-*block*-linear low-density polyethylene (iPP-*b*-LLDPE), polyethylene-*block*-syndiotactic polypropylene (PE-*b*-sPP) copolymers, and crystalline-amorphous BCPs, such as isotactic polypropylene-*block*-ethylene-propylene rubber (iPP-*b*-EPR), polyethylene-*block*-ethylene-propylene rubber (PE-*b*-EPR), and syndiotactic polypropylene-*block*-ethylene-propylene rubber (sPP-*b*-EPR) copolymers.

In all iPP-*b*-PE samples the PE block crystallizes from the melt in the stable orthorhombic form and the iPP block crystallizes in mixtures of α and γ forms, in agreement with the not high isotacticity of iPP, determined by the used catalyst (with [*mmmm*] = 91%). Because of the imperfect isotacticity, the iPP block melts at low temperature of 135°C, close to that of the PE block. Therefore, PE and iPP blocks crystallize and melt almost in the same temperature range and all DSC thermograms showed only one broad peak either in the heating scans or cooling curves, due to the overlapping of PE and iPP melting and crystallization phenomena. The crystallization temperatures of the iPP-*b*-PE samples are higher than that of the iPP homopolymer and increase with increasing the PE block length, suggesting that PE crystallizes first, and the crystallization of the block copolymers is driven by the nucleation effect of PE on the crystallization of iPP block. Temperature and time resolved WAXS profiles recorded during cooling from the melt confirmed that PE block crystallizes first upon cooling.

In the case of iPP-*b*-LLDPE samples, the presence of the comonomer (1-octene) reduces the melting temperature of the LLDPE block that results lower than that of the iPP block and two separated melting peaks were present in the DSC heating curves of these copolymers. The crystallization temperatures are lower than that of iPP homopolymer and decrease with decreasing the iPP weight percentage. Temperature and time resolved WAXS experiments demonstrated that crystallization of the LLDPE block occurs at temperatures lower than that of the iPP block. Moreover, a decrease of both melting and crystallization temperatures of polyethylene domain with increasing 1-octene content was observed.

The iPP-*b*-EPR copolymers displayed lower crystallization temperatures with respect to that of the iPP homopolymer. Moreover, a decrease of the ethylene concentration in EPR block resulted in a further decrease of crystallization temperature due to the higher solubility between iPP and EPR blocks. Similarly, the lower crystallization temperatures of PE block in PE-*b*-EPR samples with respect to the PE homopolymer were attributed to the presence of the attached EPR block and on its ethylene concentration.

In the PE-*b*-sPP copolymers, the sPP block crystallizes in the stable form I and the PE block crystallizes in the orthorhombic form. The DSC heating thermograms of PE-*b*-sPP samples with higher molecular masses showed only one broad endothermic peak due to the overlapping of PE and sPP melting processes at T~132°C. However, as evident from the cooling thermograms, the crystallization of the two blocks takes place at different temperatures, and the peak occurring at higher temperature was attributed to the crystallization of PE block. The DSC cooling thermograms of the PE-*b*-sPP copolymers with lower molecular masses featured only one broad peak. The crystallization behavior of these samples was clarified by the X-ray diffraction profiles recorded during cooling, which indicated that PE block in these samples crystallizes before sPP block. The diffraction pattern of the sPP-*b*-EPR sample is mainly characterized by the amorphous halo, in agreement with the high fraction of the amorphous EPR block ($w_{EPR}= 87wt\%$).

The POM analysis of melt-crystallized samples of iPP-*b*-PE copolymers has shown the presence of bundle-like crystals in the samples with longer iPP blocks and of small banded spherulites in the samples with longer PE block. The observation of banded spherulites typical of PE indicated that the crystallization of PE is not influenced by the phase-separated melt structure and determines the final morphology, confirming that crystallization of PE occurs first upon cooling from the melt. The POM images of all the iPP-*b*-LLDPE samples revealed the presence of bundle-like entities typical of iPP crystals in a disordered modification intermediate between α and γ forms, confirming that in these

samples iPP block crystallizes first upon cooling from the melt. POM micrographs have been acquired continuously during the cooling at 2°C/min from the melt of iPP-*b*-LLDPE samples to observe the evolution of the morphology, and, in particular, to try to detect a change in morphology as the block of LLDPE begins crystallizing. No change in morphology was observed, but only an increased brightness, suggesting that the crystallization of LLDPE must occur in a templated fashion inside the preformed crystals of iPP. Moreover, when the values of the POM normalised intensity were plotted as a function of temperature during cooling from the melt, it was possible to distinguish two increments related to the crystallization events of the two blocks.

The POM images recorded at room temperature of samples of iPP-*b*-EPR and PE-*b*-EPR copolymers displayed the typical morphologies of iPP and PE homopolymers, that are axialites and banded spherulites, respectively. Banded spherulites were observed also in the POM images of PE-*b*-sPP BCPs, confirming that in these samples PE block crystallizes first upon cooling. The sPP homopolymer and the sPP-*b*-EPR copolymer displayed the same morphology characterized by a dense pattern of bundle-like crystals, as expected for samples of sPP with not high syndiotacticity ([*rrrr*]=91%).

The TEM analysis allowed to image the microdomain structure probably existing in the melt in thin films of iPP-*b*-PE and iPP-*b*-LLDPE copolymers rapidly cooled from the melt by quenching in liquid nitrogen and stained with RuO₄. The thin films exhibited a morphology characterized by dark and bright domains about 50 nm wide that were attributed to PE (or LLDPE) and iPP domains, respectively. Inside the dark PE domains thin white lamellae were observed, whereas crystals of iPP were instead not visible, probably because quenching produces formation of very small crystals with a non-lamellar morphology. The different volume fractions of the blocks in the copolymers resulted in different repartitions of dark and bright domains. The phase-separated morphology seemed to be partially retained even when the thin films were crystallized by slow cooling from the melt, however in this case thin crystalline lamellae randomly oriented and homogeneously distributed were also observed.

Thin films of an iPP-*b*-EPR sample rapidly quenched from the melt did not display any phase separated domains and crystalline lamellae were not clearly visible. This was ascribed to the presence of a homogeneous melt due to the partial miscibility of iPP and EPR blocks. When the sample was crystallized by slow cooling from the melt, a morphology characterized by the cross-hatched texture typical of iPP was obtained. The TEM images of films of a PE-*b*-sPP BCP quenched from the melt exhibited a segregated morphology very similar to that obtained by quenching an iPP-*b*-PE sample with similar weight fraction. Also in this case, when the sample was crystallized by slow cooling

from the melt the crystalline lamellae were no longer confined inside the dark domains, but they were distributed over the whole film, passing through both the dark and bright domains. The absence of a phase-separated morphology in the quenched films of sPP-*b*-EPR was ascribed to very small volume fraction of sPP block. Sporadic lamellae were visible in TEM images of the slowly crystallized films.

The presence of crystallizable components in the BCPs was exploited to induce crystal orientation in thin polymer films by epitaxial crystallization on suitable crystalline substrates. Thin films of BCPs samples have been epitaxially crystallized onto crystals of *p*-terphenyl (3Ph) and benzoic acid (BA) and the resulting morphologies were characterized with TEM. To improve contrast, the thin films were decorated with gold nanoparticles by vacuum evaporation and condensation. The iPP block of iPP-*b*-EPR samples was oriented by the BA substrate, as two families of crystalline lamellae highly aligned along two directions $\approx 60^{\circ}$ apart were observed. The same alignments were exhibited also by thin films of iPP homopolymer epitaxially crystallized onto the same substrate. The TEM images of iPP-*b*-PE BCPs epitaxially crystallized onto BA showed regions where the thicker crystalline lamellae of PE were aligned along a unique direction and regions where thinner iPP crystalline lamellae were aligned along two directions $\approx 60^{\circ}$ apart. It was found that in the regions containing lamellae with a unique orientation the morphology is dictated by PE as it probably crystallizes first, and the double alignment could not be seen as in these regions iPP crystallizes after PE between its oriented lamellae.

The nanostructure obtained when thin films of an iPP-*b*-LLDPE sample were epitaxially crystallized onto BA displayed regions where lamellae were aligned along two directions and regions where crystalline lamellae were aligned along one direction, similarly to iPP-*b*-PE samples. However, the boundaries of the regions with the lamellae aligned along a single direction were less evident, as the presence of 1-octene in LLDPE chains makes the lamellae thinner compared to PE lamellae. When crystallized onto 3Ph, all the iPP-*b*-PE samples showed the pattern with double orientation typical of PE epitaxy onto 3Ph, with lamellae with their chain axes oriented along two directions 74° apart. Even though only PE block presents lattice matching with this substrate, no random lamellae orientation was observed, and a large-scale oriented nanostructure was obtained. These results suggested that PE crystallized first onto 3Ph crystals defining the whole morphology, and iPP probably crystallized after in the confined inter-lamellar PE regions. The decrease in iPP volume fraction in the BCPs led to an increase in the thickness of PE lamellae and resulted in more ordered nanostructures.

The morphologies obtained with PE-*b*-sPP films epitaxially crystallized onto 3Ph showed regions where thinner sPP crystalline lamellae were aligned along one direction and regions where thicker PE crystalline lamellae were aligned along two directions \approx 70° apart. On the other hand, when the volume fraction of PE was decreased to ~30%, a single set of sPP parallel lamellae was be observed, indicating that PE must crystallize after sPP in the confined interlamellar regions. The final morphology is, therefore, driven by the crystallization of sPP, in agreement with the fact that the sPP block is longer than the PE block. When a PE-*b*-sPP sample with PE volume fraction lower than 30% was epitaxially crystallized onto BA, the obtained morphology was very similar to that observed after epitaxial crystallization on 3Ph, however in this case the single orientation is induced by BA on PE lamellae, as only this block displays lattice matching with the substrate. The use of different substrates revealed the sequence of crystallization events during cooling from the melt and which is the dominant event that drives the final morphology.

Blends of selected BCPs have been prepared in order to study the phase-separation in blends of BCPs sharing a common block of PE or EPR. With this aim, a 50:50 blend of iPP-*b*-PE and PE-*b*-sPP samples with similar volume fractions of PE block, as well as a 50:50 blend of iPP-*b*-EPR and sPP-*b*-EPR samples sharing a block of amorphous EPR block have been prepared. TEM images of thin films of the iPP-*b*-PE/PE-*b*-sPP blend rapidly quenched from the melt displayed a phase-separated morphology indicating that the PE blocks of the iPP-*b*-PE and PE-*b*-sPP copolymers are soluble and segregated in the same domains. This result could be interpreted as the hypothetical formation of a tri-block copolymer with a central PE block linking iPP and sPP blocks. The TEM images obtained with the iPP-*b*-EPR/sPP-*b*-EPR blend surprisingly exhibited a morphology characterized by bright domains, probably of iPP, segregated from a dark matrix of EPR. This observed phase-separated structure probably existing in the melt could possibly be due to the increased incompatibility between iPP block and the EPR phase arising from the increased concentration of ethylene in the EPR domains of the blend. Therefore, also in this case, the phase-separated morphology may be interpreted as the hypothetical formation of a tri-block copolymer with a central EPR block linking iPP and sPP blocks.

DSC experiments of isothermal crystallization have been performed on the BCPs, allowing to understand how the different blocks mutually influence their crystallization rates. The kinetic data have been processed with Avrami and Lauritzen-Hoffman models. The equilibrium melting temperatures of iPP and PE blocks in the BCPs have been estimated with the Hoffman-Weeks extrapolation and their values are very close to those of the homopolymers. It was found that the presence of a linked amorphous EPR block drastically reduces the overall crystallization rate of the iPP block, with respect to the homopolymer. Furthermore, a higher concentration of propylene in EPR phase determines a higher solubility between the blocks, resulting in a greater slowdown of the crystallization kinetics of iPP. Similar diluent effect was observed in iPP-*b*-LLDPE copolymers, where the crystallization rate of iPP block is reduced by the attached molten LLDPE block. Increasing LLDPE content led to a larger decrease in crystallization rate. However, it was found that, at the same iPP weight fraction in the BCP, the melt LLDPE block has a lower influence on the crystallization kinetics of iPP, than the EPR block.

For what concerns the BCPs comprising a block of PE, the presence of a linked amorphous EPR block resulted in a slow down of the crystallization of PE, and the crystallization rate seemed to decrease with increasing the EPR weight fraction or the concentration of ethylene in EPR phase. Finally, it was possible to observe that the crystallization rates of iPP-*b*-PE copolymers are lower than that of the PE homopolymer, but faster compared to iPP homopolymer. The linked iPP block, which remains in the melt state or crystallizes partially, slows down the crystallization kinetics of PE, in contrast to what happens in a iPP/PE blend, where the crystallization kinetics of PE is not affected by the presence of iPP.

Self-Nucleation experiments have been performed in order to investigate the SN behavior of iPP, PE and LLDPE in block copolymers. This technique allows to define the temperature ranges for which the molten state of a polymer is a homogeneous melt (Domain I), is a melt containing self-nuclei or self-seeds (Domain IIa or IIb), or it is a melt containing unmolten crystal fragments (Domain III). The iPP homopolymer, as well as iPP blocks of iPP-b-EPR and iPP-b-LLDPE BCPs displayed a wide Domain IIa and a narrow Domain IIb. This was addressed to the not high isotacticity of the iPP chains, and thus to the presence of stereodefects. When iPP is linked to an amorphous block (EPR) or to a block that crystallizes at lower temperatures (LLDPE), higher temperatures with respect to the homopolymer are necessary to obtain an isotropic melt. The increase in the extension of *Domain II* with the decrease of the iPP weight fraction was addressed uniquely to the widening of Domain IIa, as the extension of Domain IIb remained unchanged. The decrease of ethylene content in iPP-b-EPR copolymers and the decrease of iPP fraction in iPP-b-LLDPE copolymers resulted in greater increments of the crystallization temperature in Domain II with respect to the homopolymer of iPP. On the other hand, almost no increase in the T_c of LLDPE block was observed. When iPP is linked to a PE block, which crystallizes before iPP and acts as a nucleating agent, lower temperatures are needed in order to allow the self-nucleation of iPP block. This results also in a lower increment of the $T_{\rm c}$ with respect to the homopolymer, and to a complete absence of *Domain II* when the $w_{\rm iPP}$ is lower than 50wt%. The nature of the block linked to iPP did not seem to affect its $T_{\rm s \ ideal}$, which is about 139°C in all the BCPs. Knowing the values of the $T_{s ideal}$ of iPP, PE and LLDPE blocks, it was possible to perform the thermal fractionations of the BCPs following the SSA protocol. Successive steps of self-nucleation and annealing allowed to thermally fractionate the iPP-*b*-PE copolymers helping to partially resolve the melting phenomena of PE and iPP blocks. In fact, for all samples it was possible to obtain a high temperature fraction related to the melting of only iPP crystals. However, it was not possible to adequately fractionate the lower part of the melting endotherm as PE block probably does not fractionate, similarly to the homopolymer. Moreover, the low resolution of the obtained melting peaks could be ascribed to the overlapping of PE with iPP fractions that melt at lower temperatures. In iPP-*b*-LLDPE copolymers it was possible to fractionate the melting peaks of both blocks and most of the fractions found in the homopolymer of iPP could be obtained. The decrease of iPP weight fraction of iPP block. For what concerns the LLDPE block, it was observed that increasing the 1-octene concentration caused the most abundant fraction of LLDPE to occur at lower temperatures. Additionally, the increase in 1-octene led to a higher number of more resolved fractions.

Concluding, this thesis work has contributed to expand the knowledge in the field of semi-crystalline block-copolymers. The systematic characterization conducted on polyolefin-based BCPs revealed that the presence of an attached crystalline or amorphous block to iPP, sPP or PE blocks does not influence their melting behavior, affording in all the cases BCPs with high melting temperature domains. However, it leads to substantial variations in the crystallization behavior, that is crystallization temperature, crystallization rate, self-nucleation and morphology. Varying the length and the composition of the blocks as well as the crystallization conditions it is possible to modulate the final properties of the block-copolymers, affording materials with nanostructured morphologies, due to microphase separation of incompatible blocks, or via epitaxial crystallization onto suitable substrates.