PPL – Polymer Physics and Macromolecular Chemistry

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Group X page: https://x.com/ppl_naples?s=11&t=G5CZrE2NCczAdg7jxwfLwQ

Research topics

Synthesis of novel polymeric materials and study of their crystallization behavior, crystal structure and physical and mechanical properties. Molecular catalysis as a tool for the development of polymers with tailored properties.

Study of nanostructures formed by crystallization and phase separation of semicrystalline block copolymers

Catalyst Design through an integrated theoretical and experimental investigation spanning from functionalized polyolefins to biodegradable and chemically recyclable materials.

The Polymer Physics Laboratory (PPL) group carries out research in various fields of polymer chemistry including the synthesis and the characterization of the structure and of the physical and mechanical properties of polymeric materials, in particular polyolefins and copolymers of olefins, and polymer composites. The Group has expertise in the synthesis of stereoregular polyolefins by Ziegler-Natta and organometallic catalysts and in the study of the structure of crystalline polymers. Structural studies are conducted at the highest levels of specialization using all the techniques of characterization of the solid state of materials, from wide and small angle X-ray diffraction to electron microscopy, and solid state nuclear magnetic resonance. The dominant motive of the research activities is the study of the relationships between the molecular structure, the crystalline structure and the physical properties of crystalline polymers.
PPL researchers have concerned the study of the crystalline structures and physical and mechanical properties of new stereoregular polymers and copolymers prepared with novel organometallic catalysts. The development of homogeneous organometallic catalysts for the polymerization of olefins has allowed the preparation of many new polymers in the last twenty years, some of which have also proved to be of great industrial interest. The properties of these materials have been interpreted on the basis of structural studies and possible practical applications have been identified. These studies have reaffirmed the long tradition of the Italian school in the field of the structural study of polyolefins. The relevant aspect of these structural studies has been the analysis of the structural disorder that is often present in the crystalline phases of polymers and of the molecular organization of the mesomorphic modifications of many polymers. The description of the structural disorder has allowed a better interpretation of the mechanical properties of polymers at molecular level.
The ultimate goal of these studies is the complete understanding of the relationships between the structure of the catalyst used for the preparation of polymers, the molecular structure of the produced macromolecules (that is, stereoregularity, regioregularity, distribution of defects and molecular masses), the crystalline structure of the polymers and the physical and mechanical properties of the produced materials (Figure 1).

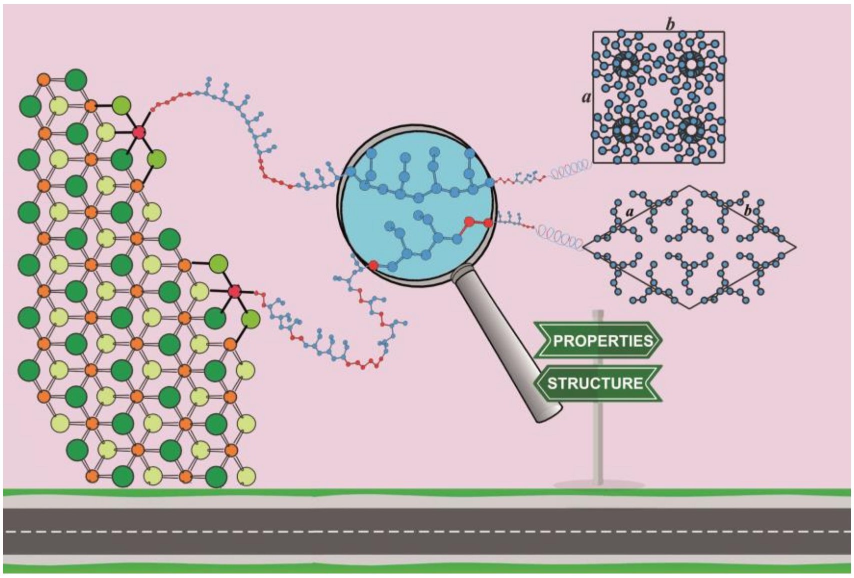

Figure 1

All this knowledge allows for the design of materials with targeted physical properties through the "design" of the catalyst. For example, the study of the influence of the presence of microstructural defects on the structure and properties of isotactic and syndiotactic polypropylene and isotactic polybutene have allowed to modulate and control the physical properties of materials through the targeted introduction of steric and constitutional defects, by means of a suitable choice of the metallocene catalyst. One of the results of scientific and industrial importance has been the development of innovative flexible and elastomeric materials based on isotactic polypropylene and its copolymers with controlled stereo-regularity (Figure 2), and of a new class of elastomers of controlled stiffness, defined as "crystalline elastomers" based on syndiotactic polypropylene and its copolymers with other olefins.

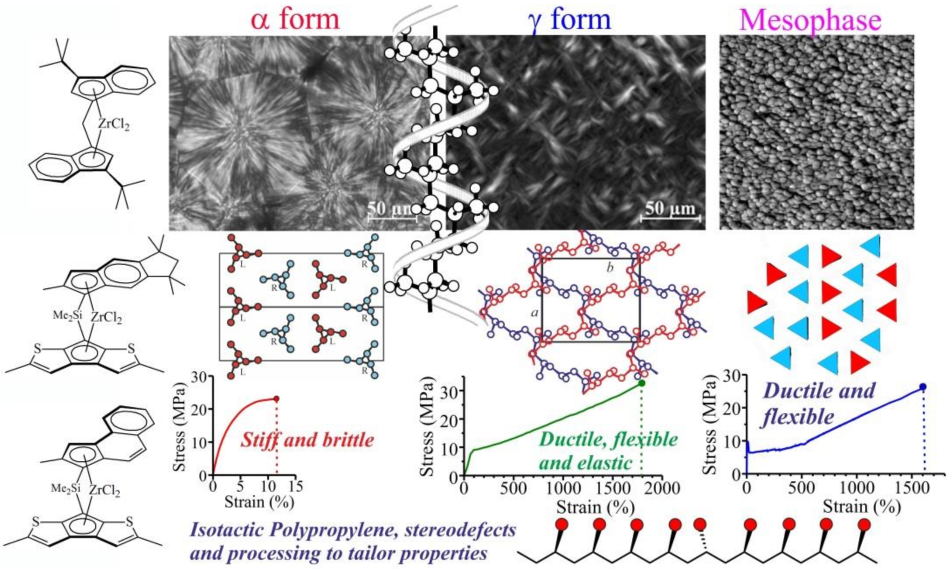

Figure 2

Another research activity concerns the study of nanostructures formed by crystallization and phase separation of semicrystalline block copolymers. Of particular importance is the discovery of a new process for the orientation of phase-separated microdomains and of crystals formed by self-assembly and crystallization, obtaining ordered nanostructures useful for applications in nanotechnologies (Figure 3). In this context, a research topic of this group consists in the preparation and characterization of hybrid organic/inorganic nano-composites by dispersing metal nanoparticles into polymeric matrices consisting of the ordered nanostructures generated in block copolymers (Figure 3). These materials can be used in many applications in microelectronics, such as support for integrated circuits, non-volatile memories, photonic crystals for the confinement of light, sensors etc. These studies have enabled the development of nanotechnologies based on the engineering of thin film surfaces for the fabrication of microelectronic devices and nanosensors.

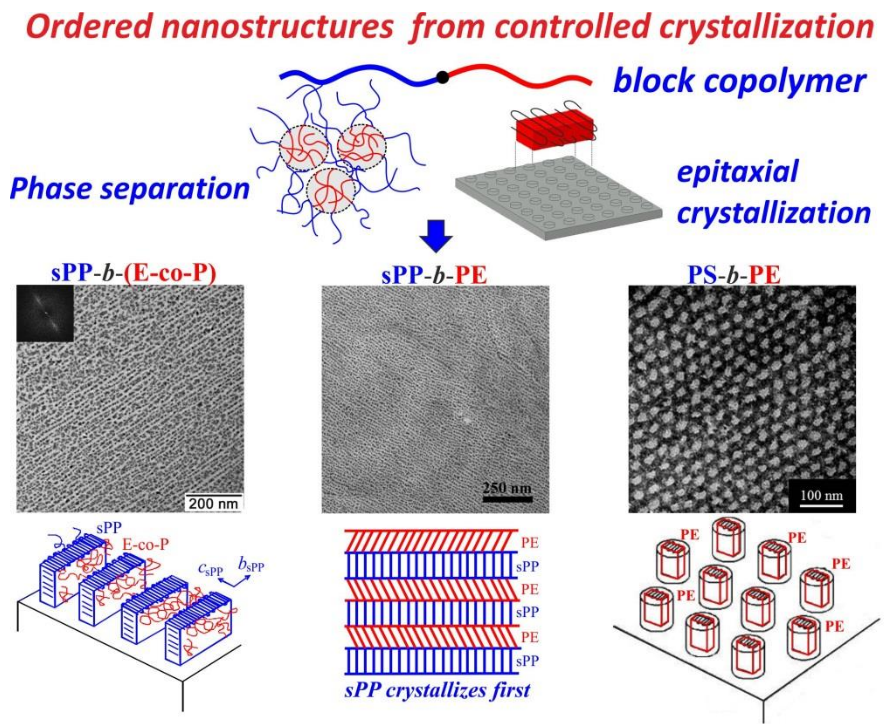

Figure 3

Our group is actively extending its research into the field of biodegradable, stereocomplexable and chemically recyclable materials, particularly focusing on polyesters and polycarbonates. These materials are synthesized through Ring-Opening Polymerization (ROP) and Ring-Opening Copolymerization (ROCOP), using an integrated theoretical and experimental approach.
A central goal of our work is the development and optimization of catalysts for ROP and ROCOP, with particular attention to improving catalytic activity as well as stereo- and regioselectivity. Our methodology is largely computational, driven by structure–activity relationships that guide the rational design of catalysts. While stereoselective catalysis in olefin polymerization is well understood-thanks to established links between catalyst structure and polymer microstructure- such connections are still poorly defined in ROP and ROCOP systems. This is primarily due to the increased complexity of their mechanisms. One of our key research objectives is to uncover these missing correlations, particularly the relationship between ligand structure and resulting polymer microstructure.
Building on insights from our computational investigations, we aim to design next-generation ROP and ROCOP catalysts to advance the development of novel sustainable polymers (Figure 4).

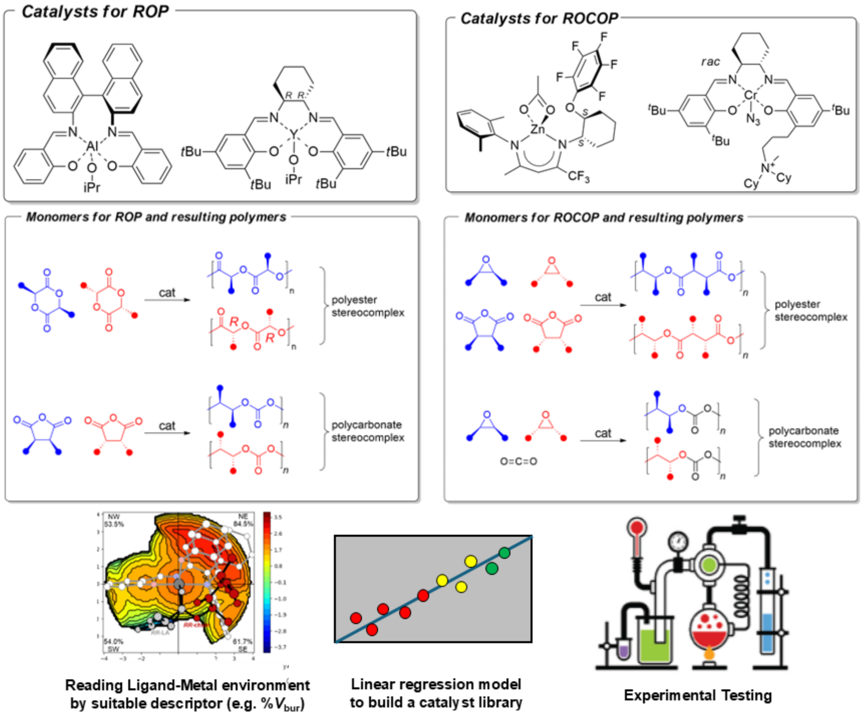

Figure 4

The resolution of the crystal structures of these innovative sustainable polymers developed by ROP and ROCOP is the key for understanding the relationships between catalyst structure, molecular microstructure, crystallization behavior and physical properties. In particular, the determination of the crystal structures of chiral polymers having the property to be chemically recyclable to their monomers, in particular polyesters and polycarbonates, carried out by our group shed light on to the comprehension of the physical properties of these innovative materials, which are candidates to replace polyolefins in a perspective of a perfect circular economy of plastics. Thanks to the deeply rooted tradition in the resolution of the crystal structure of stereoregular polymers, which dates back to our mentor Prof. Paolo Corradini, our group has explained the tacticity-independent crystallization phenomenon shown by many chiral chemically recyclable polymers through the resolution of their crystal structures by using X-ray and electron diffraction and computational methods of conformational analysis and simulation of diffraction patterns. The resolutions of the crystal structures of new isotactic and atactic dimethylated poly-3-hydroxybutyrates (Figure 5) and chiral polythioesters are exemplary cases.
In many chiral polyesters and polycarbonates the crystallization of stereocomplexes between enantiopure polymers of opposite configurations has demonstrated to be a route to improve properties.

The case of the stereocomplex of polylactide (PDLA/PLLA) that melts at temperature higher than that of the enantiopure polymers PDLA and PLLA is well know. Our group is actively involved in the study of the phenomenon of stereocomplexation through the resolution of the crystal structures of stereocomplexes of many polyesters and polycarbonates, to understand whether the stereocomplexation is driven by the establishment in the crystals of specific interlocking interactions (dipolar interaction or hydrogen bonds) between the enantiomorphic macromolecules. Understanding what drives the crystallization of stereocomplexes may be the key to the design of new biodegradable and sustainable polyesters and polycarbonates with improved mechanical properties and thermal stability.

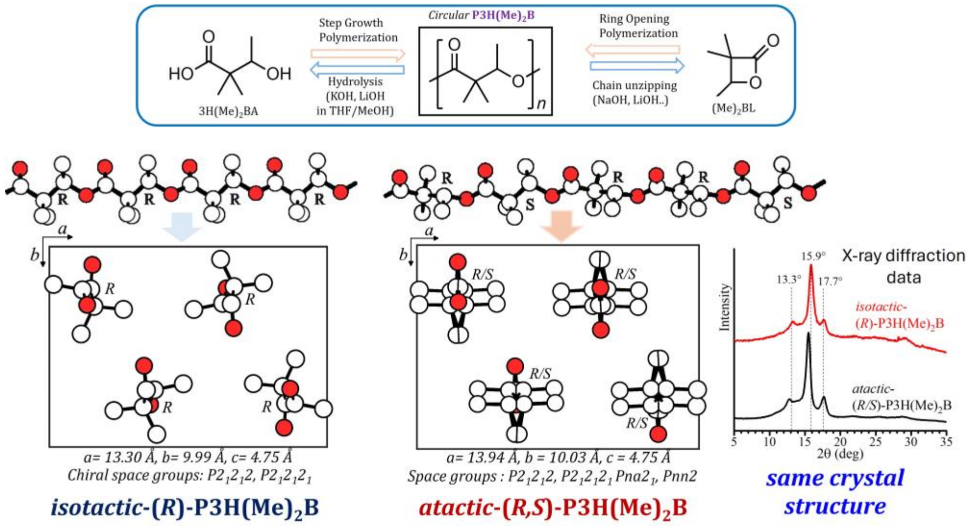

Figure 5

Main collaborations:
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Dr. Giuseppe Leone, CNR-SCITEC (Milano).

Ongoing projects:

- Project PRIN funded by The National Recovery and Resilience Plan (PNRR) 2022 entitled "Polymers of tunable molecular structure and properties from biorenewable sources designed for a complete chemical recycling to monomers (Re-Tune)". PI: Dr. Miriam Scoti.

- Project PRIN 2022 funded by MUR entitled “Dynamically Cross-Linked Polyolefin Thermoplastic Elastomers from Renewable Terpene (Co)monomers (DYNAMITE)”. PI: Prof. Rocco Di Girolamo.

- Project PRIN 2022 funded by MUR entitled “Exploiting block copolymers self-assembly to fabricate ordered protein nanoarrays for the construction of functional nanomaterials (E_BLOCKSY)”. PI: Prof. Anna Malafronte

- Project PRIN 2022 funded by MUR entitled “Speed up the transition from conventional plastic to biodegradable materials (SpeedToBio)”. PI: Prof. Giovanni Talarico

- Project MICS funded by The National Recovery and Resilience (PNRR) PE11 Plan 2022 entitled “COmpatibilization of post-consumer polyolefin wastes for REutilization in leading made-in-Italy sectors, such as furniture components and advanced packaging (CORE)” Prof. Claudio De Rosa and Prof. Rocco Di Girolamo.

- Project SPACE IT UP! (ref. ASI n.2024-5-E.0.) funded by The National Recovery and Resilience (PNRR) PE15 Plan 2022. Prof. Claudio De Rosa

Other collaborations:
ADAPA Italy- FLEXIBLE Packaging
Basell Polyolefins, Italia