

Structural–Mechanical Phase Diagram of Isotactic Polypropylene

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Isotactic polypropylene (iPP) is one of the most used thermoplastic materials and has bigger growth inside commodity polymers because of a combination of outstanding properties, such as good rigidity, high thermal resistance with limited impact resistance at low temperature, low density, good environmental resistance, ease of processability, and recycling at a moderate cost. The wide application range of iPP results from its versatility and the variety of possible modifications of the basic material, which already starts in the polymerization reactor. The main structural factors affecting the physical properties are stereoregularity, molecular mass, and polydispersity, mostly through their influence on crystallinity. Tailoring polymer properties in the polymerization stage requires a profound insight into the relationships between catalyst, chain microstructure, crystallization properties, and final product properties.

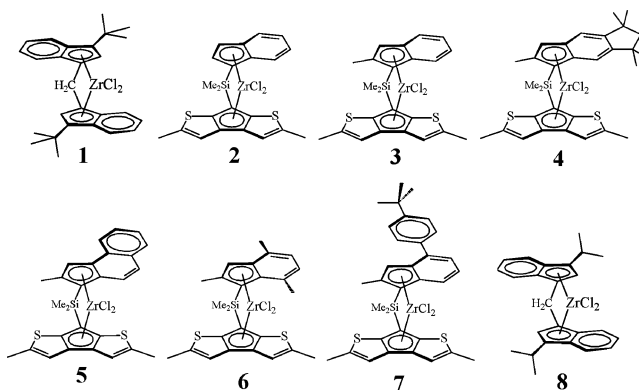
The discovery and development of metallocene catalysts have allowed an increase in our control over the chain microstructure, with relevant impact on the final material properties.^{1,2} A major evolution has been achieved in the field of poly(propylene) that can now be produced with any type and degree of stereoregularity² and physical properties that range between those of stiff materials and elastomers.³

The mechanical properties of iPP are largely related to the crystal structure and morphology, which in turn depend on the chain microstructure generated by the specific used catalyst.³ Moreover, the possible occurrence of polymorphic transformations during plastic deformation induced by application of uniaxial stretching, plays a fundamental role. In particular, it has been reported that the possible formation of the disordered mesomorphic form during solid-state drawing of iPP yields to a different mechanical behavior,⁴ because the mesophase facilitates the subsequent deformation of the sample, so that the material behaves as a highly flexible elastomer.³

In this communication we show that the use of metallocene catalysts allows for a full understanding of the structure–properties relationships of iPP through the precise control of stereoregularity and deformation behavior, which in turn affords a unique opportunity for a construction of a phase diagram of iPP, where the conditions of formation of the mesophase during deformation and of development of high flexibility and elastomeric properties can be extracted.³

We have studied the polymorphic transitions occurring during tensile deformation of iPP samples of different stereoregularity prepared with the metallocene catalysts of Chart 1. These catalytic systems are able to produce iPP samples characterized by chains containing largely one type of stereoirregularity (*rr* triad defects),^{3,5} whose amount depends on the catalyst structure. Samples with a concentration of *rr* defects varying between 0.5 and 17% and melting temperatures in the range 160–45 °C have been analyzed. Melting temperatures and stereoregularity of the samples are reported in the Supporting Information.

Chart 1. Structure of Zirconocene Catalysts



The stress–strain curves of compression-molded films of some iPP samples are reported in Figure 1. Depending on the concentration of *rr* defects, iPPs behave as stiff or highly flexible or elastomeric material.³ Poorly stereoregular samples show remarkable strain hardening due to low plastic resistance of crystals and by straightening of the entangled network.

The different mechanical behavior is also related to the structural transformations that occur during stretching. The polymorphic transitions associated with the plastic deformation have been studied as a function of stereoregularity by recording the X-ray diffraction patterns during stretching (Figure 2).

Compression-molded unstretched films are crystallized as mixtures of α and γ forms of iPP, the amount of γ form increases and the crystallinity decreases with decreasing stereoregularity.³ For the more isotactic samples, the α form partially transforms by stretching into the mesomorphic form already at low deformation (Figure 2A). The formation of the mesomorphic form is indicated by the presence of a broad halo in the range of $2\theta = 14\text{--}18^\circ$ (Figure 2A). A fraction of crystals of α form is still present even at the maximum possible deformation (Figure 2B). These crystals have high plastic resistance and do not allow further deformation. These samples behave as stiff materials, but they can be easily stretched up to 200–300%

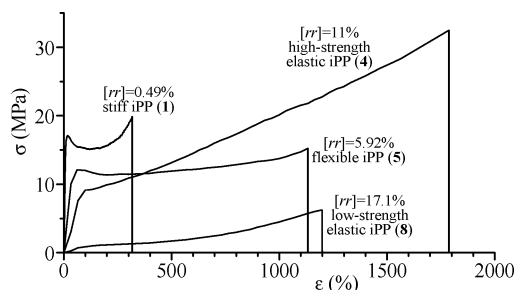


Figure 1. Stress–strain curves of iPP samples of different stereoregularity prepared with the catalysts of Chart 1. The numbers in parentheses indicate the catalyst.

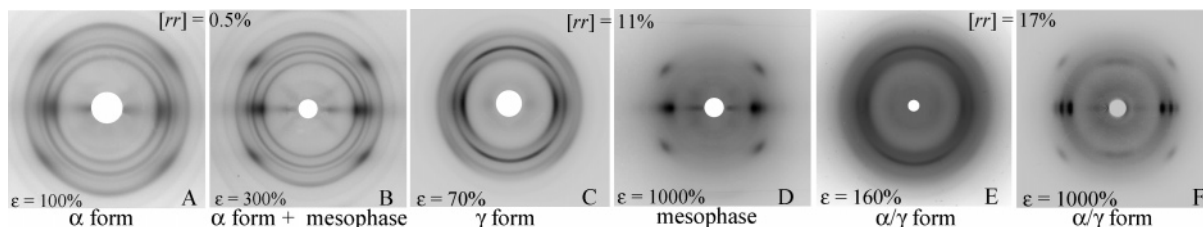


Figure 2. X-ray fiber diffraction patterns of fibers of iPP samples of different stereoregularity stretched at the indicated values of deformation ϵ .

strain, because the fraction of crystals that undergoes plastic deformation without sample breaking transforms into the mesomorphic form that, in turn, facilitates successive deformation (Figure 1).

For more flexible samples with rr contents in the range 4–11% (Figure 1), the γ form present in compression-molded films gradually transforms into the mesomorphic form by stretching. For high rr concentration, in the range 7–11%, the γ form first transforms into the α form, which, in turn, transforms into the mesomorphic form at very high deformations (Figure 2C,D). In these samples, the low crystallinity and the presence of high degrees of structural disorder³ reduce the stress level necessary for inducing plastic deformation of crystals. The formation of the mesomorphic form after yielding, which is consequent to the easy plastic deformation (Figure 2D), facilitates successive further deformation up to very high strains (Figure 1). The presence of rr stereodefects included in crystals of γ form and the formation of the mesophase produce the development of outstanding properties of high flexibility and elasticity, which are unusual for polypropylene.³

For a very high concentration of rr defects (17 mol %), the sample is basically amorphous but still presents high flexibility and elastomeric behavior (Figure 1).⁶ This nearly atactic sample slowly crystallizes upon aging at room temperature or by stretching in a disordered modification intermediate between α and γ forms, with a maximum degree of crystallinity of only 16%.⁶ The stretching of this sample, even at high deformation, does not produce formation of the mesomorphic form, probably due to the breaking of the sample prior to the transition, but only α/γ disordered modifications, more similar to the α form, are obtained (Figure 2E,F).

These data have allowed building the phase diagram of iPP at room temperature (Figure 3), where the regions of stability of the different polymorphic forms of iPP in oriented fibers are defined as a function of stereoregularity and degree of deformation ϵ . The boundary lines in the phase diagram have been determined by the emergence during deformation of X-ray reflections typical of the various polymorphic forms (see Supporting Information). The values of the critical strain at which the polymorphic transitions start, and at which the transformation is complete, depend on the stereoregularity.

Inspection of Figure 3 suggests that large values of ductility may be achieved thanks to the occurrence of phase transitions. During stretching, the mechanical energy is, indeed, converted into a latent heat of fusion that induces local melting of crystals, followed by recrystallization into a new form and, at high deformation, into the mesophase.

The transformation of α or γ forms into the mesomorphic form plays the most important role in defining the mechanical behavior.

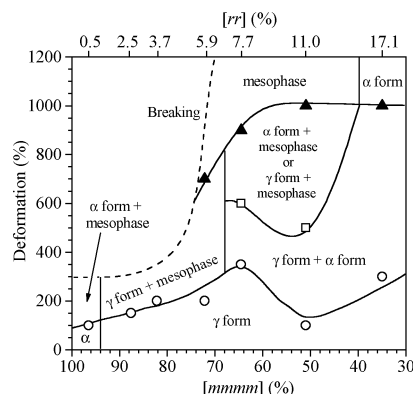


Figure 3. Phase diagram of iPP showing the region of stability of the different polymorphic forms as a function of strain and stereoregularity.

The phase diagram of Figure 3 provides for the first time an easy picture of the conditions of formation of the mesomorphic form, in term of microstructure and processing, which is the basis for the development of the unusual mechanical properties of metallocene-made iPP.

In conclusion, we have demonstrated the novel utility of single-center metallocene catalysts in that a phase diagram of iPP can be constructed through the integration of catalyst design, stereo-selective polymerization, structural characterization, and analysis of mechanical properties.

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Supporting Information Available: Experimental details of X-ray diffraction and mechanical analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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