

**STUDY ON CRYSTALLIZATION OF ISOTACTIC
POLYPROPYLENE:
EFFECT OF STEREOTACTICITY DEFECTS AND NANOFILLERS**

by
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ABSTRACT

Although the crystallization of polymers has been a topic of continuing interest for close to fifty years, some fundamental questions, such as the mechanism of crystallization from the melt at early stage, are not still fully understood. In addition, recent developments in catalysts and nanoparticles make it possible to finely adjust the material properties by controlling the microstructure of polymer matrix. However, the understandings of how these microstructures affect the crystallization behavior of polymer and finally determine its properties are very limited. Therefore, the main objectives of this work are to understand the molecular mechanism of polymer crystallization and explore the influence of microstructure, i.e. chain defects and nanofillers, on the crystallization behavior of polymers, which eventually determine the physical properties of materials.

Experimentally, various polypropylene blends were prepared to study the role of each component in the crystallization process and its relationship to final properties. Pure isotactic polypropylene (iPP) exhibits higher melting temperature and degree of crystallinity than iPPs having stereo defects (stereoirregular iPP). Physical ageing significantly promotes the development of crystallization in stereoirregular iPPs, whereas it does not have any effect on pure iPP. Hence, stereoirregular iPP crystals play a dominant role in determining the final mechanical properties of the polymer blend. However, the iPP crystals act as nucleating agents for the crystallization of stereoirregular iPP.

The molecular mechanism of polymer crystallization was investigated in detail by using on lattice Monte Carlo simulations. Stepwise cooling on a melt of relatively short iPP chains indicate that the equilibrium melting temperature of this model is around 385 K, under which the helical structure is long enough to order into a smectic phase and then develop into a crystal phase.

Simulations on iPP chains having stereo defects at various concentrations and distribution suggest that the defected repeat units could exist within helical structures, and they only affect two nearest neighbors' probability of existing within helical structures on each side (total of four nearest neighbors). Multiple stereo defects have a

complicated effect on repeat units' ability to exist in helical structures but the effect of multiple stereo defects could simply be described by summation of the effect of each individual defect. The inclusion of stereo defects results in extended local chain segments, and thus, depresses the melting temperature.

The influence of fillers on polymer crystallization was studied by inserting flat surfaces and nanoparticles into neat iPP simulations. Polymer-particle interaction, confinement, and the shape and size of particles were investigated. The attractive interaction between polymer and particle plays a dominant role in the formation of helices, while the repulsive interaction mainly shows a strong volume exclusion effect. The surface itself only has a weak volume exclusion effect on polymer chains. However, no matter what energy potential was used, the surface always has an orientation effect on the ordering of helices. The confinement by flat surfaces could significantly prohibit the growth of helices, especially long helices, but has no effect on the overall helicity. Similar to flat surface, isodimensional particles also show a strong orientation effect on the ordering of helices. Polymer nanocomposites can be treated as dilute polymer solutions if the size of the nanofiller is smaller than the size of the polymer chain, i.e., R_g .

