

Appearance of γ -phase of polypropylene terpolymer

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Introduction

It has been well known that different types of crystallites may develop during the crystallization of isotactic polypropylene containing terpolymer, being a polymorphic material with α -, β -, and γ -modification.^[1-3] Types and structural features of crystallites formed are markedly influenced by the thermal condition of the melt, the mechanical load applied to the crystallizing melt (pressure, shear or tensile structures) and by the presence of extraneous materials.^[4-7] Isotactic polypropylene (iPP) forms in the crystalline state exclusively a 3_1 -helix caused by the energy minimum at this conformation. The most common form of iPP is the α -modification which has been well characterized by many researchers.^[1-5] The β -modification occurs in a certain interval of crystallization temperatures and usually induced by nucleating agents.^[6] The γ -modification is commonly observed as a minor constituent in bulk crystallized iPP.^[1] Intriguing fact is that those three modifications have different crystal structures; α phase is monoclinic, β phase is hexagonal while γ phase is orthorhombic.^[4] All of the chains are parallel in the α phase and the adjacent bi-layers contact each other through layers of helices of opposite chirality.^[3] The γ phase is known to grow epitaxially on α crystals. Lotz and coworkers has established the crystallographic relationship between the two phase.^[7] Since the occurrence of γ phase is a representation of a high molecular alignment and high mechanical properties, its presence is quite important in final product performance.^[1,2,7] The content of the γ modification in iPP can be increased by several process such as 1) the presence of very short isotactic sequences due to the random distribution of stereo defects and/or regio defects in iPP samples synthesized by metallocene catalysts, 2) application of high pressure during the crystallization process, 3) using random copolymers of propene with other 1-olefins (Addition of other 1-olefins induces constitutional defects in the polymer chains. The content of the γ -form depends on the amount and on the kind of comonomers.), 4) crystallization in shear fields.^[1,2]

Recently, it was reported that polymer crystallization can be accelerated by increasing orientation as well as stretching of the polymer chains.^[8,9] This means extensional components and shear components in a mixed flow can significantly affect the crystallization kinetics. According to Grizzuti et al's calculation, the presence of even a small amount of extensional component determines an abrupt upturn in flow induced crystallization.^[8] The nucleation rate increases very rapidly under extensional flow condition especially when the flow elasticity becomes appreciable.^[9] As the nucleation rate goes up, more nuclei are formed. Hence, there can be a plenty of chance that the concentration of crystallizable sequences of polymer molecules may exceed required length for a nucleus of critical size. Then, defects can be induced in the growing crystallites due to less available space for ordering of long chains in the melt state. Inspired by the foaming process which includes both flow components, we have examined how different flow conditions can influence the crystallization kinetics of a polypropylene-containing

terpolymer and the appearance of γ modification. We would like to suggest an easy route to prepare γ phase of polypropylene.

Our approach was to apply the foaming process to a terpolymer of poly(propylene-co-ethylene-co-1-butane) composed of 94.5 wt% of polypropylene unit, 3wt% of ethylene unit, and 2.5 wt% of 1-butene unit. By using random copolymers of propene with other 1-olefins, γ -modification in iPP is known to be increased.^[7,9] This copolymer is frequently used to improve the drawbacks of polypropylene. Practically this expanded terpolymer (foam of the terpolymer) has been developed in lieu of expanded polystyrene and polyurethane foam. Because the foaming process has both shear and elongational flow components,^[10] it is expected to get flow-induced crystallization (FIC) during the cooling process.^[9,11] Crystallization of polymers means the transition from the thermodynamically unstable state to more ordered state via the nucleation and growth process. Entangled polymer chains are put into the ordered lattice and the polymer morphology is decided by the crystallization condition in the stage of processing. The flow enhanced crystallization rate is generally attributed to a significant acceleration of the first step, i.e., the nucleation rate.^[9]

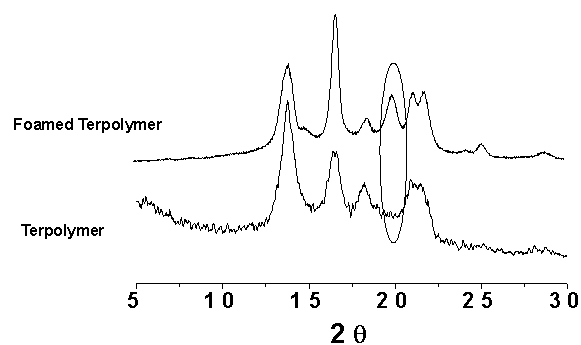


Figure 1 WAXS traces of samples as prepared : (a) virgin terpolymer , (b) foamed terpolymer

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