

Metallocene iPP-1-Hexene Copolymers: Effect of Irradiation at Medium 1-Hexene Content

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Isotactic polypropylene, iPP, exhibits a remarkable polymorphism, depending on microstructural features, crystallization conditions and other factors like the use of specific nucleants. Thus, three different polymorphic modifications, α , β and γ , all sharing a three-fold conformation, have been reported. Moreover, a fast quenching of iPP leads to a phase of intermediate or mesomorphic order. In addition to those four modifications, a new trigonal form has been recently described in the case of copolymers of iPP with high contents of 1-hexene or 1-pentene as comonomers. The use of metallocene catalysts makes possible the synthesis of such copolymers with a homogeneous distribution of comonomer. It has been described for iPP-1-hexene copolymers that the new trigonal modification is the only one obtained for comonomer contents above around 14 mol%, while variable proportions of it with the α modification were found in the comonomer range from around 8 to 13 mol% 1-hexene. However, a further study reported in the literature has established that the monoclinic α crystallites are not the only competitors of the new trigonal phase that these propylene-1-hexene copolymers develop, but the mesomorphic form [1] is also playing a primary role in this composition range.

On the other hand, the irradiation of polymers can induce different alterations on the molecular structure of these polymeric materials, such as chain scission, chain branching and crosslinking. Usually all these processes coexist. The predominant effect is dependent on several factors, such as chemical structure and morphology of the polymer as well as the irradiation conditions and the type of post-irradiation treatment. Therefore, the aim of this investigation is to learn preliminarily how irradiation affects the polymorphic behavior of an isotactic copolymer based on propylene and 1-hexene at an intermediate 9.2 mol % content, CiPH9.2. Gamma irradiation at room temperature was carried out at the Ezeiza Atomic Center (Argentina) on CiPH9.2 films using a ⁶⁰Co source under vacuum. The dose analyzed was 100 kGy and a dose rate of 10 kGy/h was applied. It has been described in the literature that irradiation has two main effects on the molecular structure of polypropylene: changes on the molar mass and formation of chain branching. Table 1 shows the characteristics found in the metallocene CiPH9.2 copolymer before and after gamma irradiation. It can be seen an increase in either M_w molecular weight or polydispersity, PD. In addition, macromolecular crosslinking has occurred probably because of the presence of the comonomeric lateral chains.

Table 1. Characteristics found in the metallocene CiPH9.2 copolymer before and after gamma irradiation.

specimen	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	PD	Gel content (%)
CiPH	52.8	110.8	2.10	-
CiPH-100kGy	47.4	132.6	2.80	19.1

The left plot in Figure 1 shows the effect of treatment on the polymorphic behavior exhibited by this CiPH9.2 copolymer. The thin film (around 150 μ m) obtained from the original powder by compression molding applying a slow cooling (approximately 1.5 °C/min) from the molten state, **CiPH9.2-S specimen**, primarily displays the α polymorph although a small amount of δ trigonal crystallites with a characteristic diffraction at 10° is also observed. A very different behavior is achieved if a fast cooling (about 65 °C/min) is imposed during film preparation also using the powder attained during synthesis as initial material, **CiPH9.2-Q sample**. The coexistence of three types of crystallites can be deduced. The majority mesomorphic form and the other two minority polymorphs: the trigonal δ one and the monoclinic α

modification. The irradiated film was thicker than those aforementioned ones (around 1mm thick) and it was prepared also by compression molding for 2 minutes at 180 °C. Once 2 minutes elapsed, the plates were placed out of the press allowing them coming down to room temperature by themselves. Then, this thick film was irradiated with a dose of 100 kGy. As observed, no evidence of the δ polymorph is seen, as deduced from the **CiPH9.2-100kGy** profile. The absence of this modification, on the contrary of that observed for the other two thermal treatments, could be associated with the fact that temperature within sample slightly increases –reaching around 60 to 70 °C- during irradiation. This moderate raise is high enough to melt the trigonal crystallites, their melting temperature being reported around 50-60 °C [1]. Its further development after irradiation seems to be hindered since it is not detected.

The irradiated **CiPH9.2-100kGy** specimen was molten and further crystallized at very different rates (1.5 °C/min and 64 °C/min) in order to simulate the effect of two thermal S and Q treatments applied to the original synthetic powder. In this way, the effect on the crystalline structure of those crosslinked chains developed because of gamma irradiation could be analyzed. Therefore, the **CiPH9.2-100kGy_c1.5** only shows at room temperature the monoclinic polymorph. The increase of temperature does not change the crystalline structure, which melt at around 90 °C. A lower crystallinity is obtained in this **CiPH9.2-100kGy_c1.5** than in its homologous non-irradiated **CiPH9.2-S** sample. The same feature, i.e., a lower ordering, is also reached after imposing to the irradiated molten state a fast cooling, **CiPH9.2-100kGy_c64** sample. This specimen is amorphous at room temperature, instead of presenting majority mesomorphic entities. By increasing temperature, very defective and small monoclinic α crystallites seem to be formed as depicted in the right plot of Figure 1.

Summing up, the irradiation of an isotactic propylene-1-hexene copolymer with intermediate 1-hexene content has a deep effect on the crystalline structure, probably because of the formation of crosslinkings.

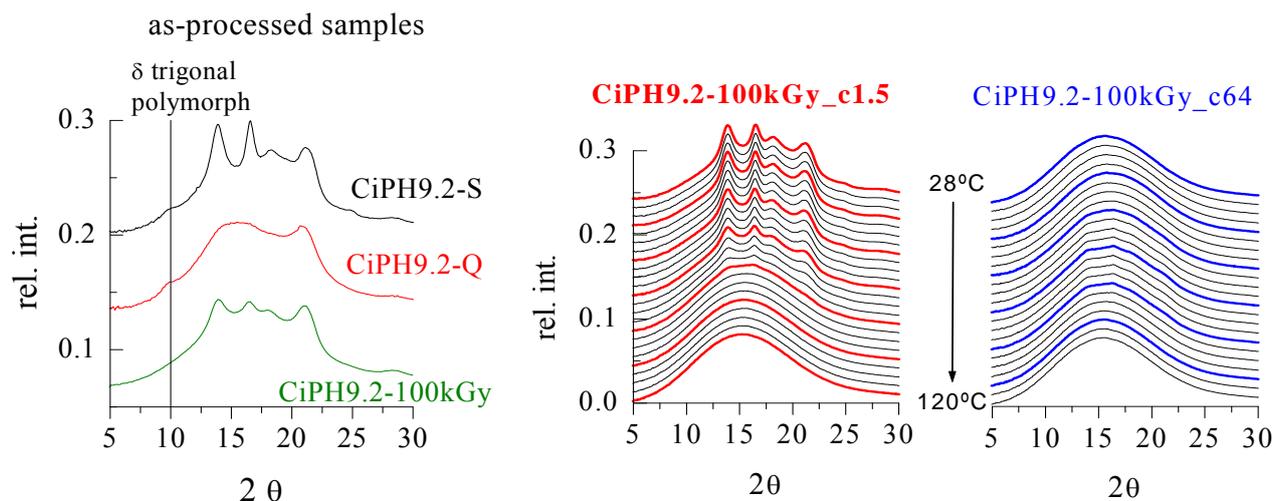


Figure 1: Left plot: WAXS profiles at room temperature for CiPH9.2 slowly cooled, quenched and irradiated with 100 kGy; middle plot: melting process for an irradiated specimen crystallized at 1.5 °C/min from the melt; and right plot: melting process for an irradiated specimen cooled at 64 °C/min from the melt.

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References

- [1] M. L. Cerrada, M. J. Polo-Corpa, R. Benavente, E. Pérez, T. Velilla, R. Quijada. *Macromolecules* **42**, 702-708 (2009).