



## Relationships among migration properties, molecular structure and catalytic process of isotactic copolymers of propene



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### ABSTRACT

Isotactic polypropylene-based (iPP) materials find large applications for the food packaging. In this article the structure, thermal and mechanical properties of some commercial grades of ethylene/propene copolymers produced by heterogeneous Ziegler-Natta (ZN) catalysis, have been characterized. These grades can be potentially used for manufacturing food containers. However, despite the desired performances in terms of mechanical and optical properties, we found that the samples exceed the overall migration limit set by the EU Directive into isooctane, used as fatty food simulant. The migrating species are highly defective copolymer chains with low molecular mass and high ethylene content. The migration is intrinsically related to the presence of fractions generated by the heterogeneous multisite surface of the ZN catalysts. A simple chemical route to allow the iPP-based materials to fall within the overall migration limit is proposed.

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## 1. Introduction

Over the last years the food industry is increasing the percentage of budget devoted to the food packaging [1]. The main focus is on polymeric materials able to combine their mechanical strength, inexpensive cost and ease of processing with the necessity to extend shelf-life as well as protection from contamination, and degradation that would otherwise occur [2]. The materials used for the food packaging are forced to follow strictly rules listed in the European Union's Synoptic Document for the primary packaging to avoid the substances migration or contaminant and, in a general sense, to give the best protection of the consumer. The UNI EN 1186 and the recent regulations by EU 10/2011 guide the conditions and test methods to determine the overall migration from plastic materials and articles in contact with foodstuffs [3,4]. Migration of chemical substances is highly dependent on the nature of the packaging material, processing conditions and compounds it may contain [5].

Within the large family of polymeric material applied for food packaging, polyolefins like polypropylene (PP), polyethylene (PE), or polystyrene (PS) are the best candidates due to the low cost combined with their good performances like chemical and heat resistance, gas permeability, abrasion resistance and thermal and mechanical behavior [6]. In particular, isotactic polypropylene (iPP) [7] as well as iPP copolymers with ethylene are excellent performers combining the versatility of the industrial production technologies (e.g. solution, fully gas-phase or mixed processes composed of a liquid monomer polymerization step, followed by one or more gas-phase reactor(s)) [8], with the extraordinary development of the catalysts

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(e.g. heterogeneous Ziegler-Natta (ZN) catalysts modified with external donors in combination with aluminium-alkyls [8] or homogeneous single site systems [9]). On the market, within the grades of thermoplastic iPP a large set of materials spanning a broad range of properties are available. Due to the relatively inexpensive prices they have come to be the dominant forms of food plastics [1].

Migration and release of some components of these iPP-based materials may depend on the molecular structure of the polymer, which, in turn, depends on the process used (chemical nature of the precursor catalysts and production technologies). Because of the large set of available materials having different properties, depending on the specific packaging application, analysis of the migration phenomenon at the molecular level is not immediate. In addition, due to the mechanism of polymerization, the iPP promoted by heterogeneous ZN catalysis is a mixture of polymers with different stereoregularity and a “non random” distribution of stereodefects along the polymer chains [10]. This scenario appears to be even more complicated in the presence of iPP copolymers which show further variables like reactivity ratio between propene and comonomer units promoted by the (various) active site on the heterogeneous surface [11–14].

The large number of variables depicted above seems to conflict with the need of standard, stable and low cost materials requested for food packaging applications according the EU directive. Moreover, besides controlled values of migration, materials for food packaging might also require different properties as high melting point, low  $T_g$  or high impact strength combined with tenacity, ductility and clarity.

A full understanding of the relationships between molecular structure of iPP produced with a given catalyst and industrial process, crystallization behavior and physical and mechanical properties may allow for the right choice of a particular polymer grade for a suitable end use. We already analyzed the relationships between the molecular structure, the polymorphic behavior and mechanical properties of iPP [15] and its copolymers [16], for model systems as iPPs produced with metallocene catalysts. In this paper we report a study of the molecular structure, crystallization behavior, mechanical and migration properties of commercial iPP grades synthesized by heterogeneous ZN catalysts, used for manufacturing rigid food containers, aimed at finding a relationship between the migration phenomenon and the microstructure of the iPP grades. The samples resulted suitable for contact with acid and alcoholic foodstuffs. The migration tests into isooctane and ethanol 95% (v/v), as simulants of fatty foods, showed, instead, overall migrations higher or very close to the limit set by the EU Directive. The chemical nature of the migrating species has been identified and a simple chemical approach, allowing the material to fall within the EU limits, is proposed.

## 2. Experimental

The four iPP grades (see Table 1) were supplied in pellets and correspond to commercialized samples with the trade name of BorPure (in the following indicated as Bor), Capilene (Cap), Sabic (Sab) and TIPPLEN (TVK), respectively. The samples were analyzed by  $^{13}\text{C}$  NMR spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction. The  $^{13}\text{C}$  NMR spectra of the samples were recorded on a Varian XL-200 operating at 200 MHz in the Fourier transform mode of 10% w/v polymer solutions in deuterated tetrachloroethane (also used as internal standard) at 125 °C. The calorimetric measurements were performed with a differential scanning calorimeter (DSC) Mettler Toledo DSC-822 in a flowing  $\text{N}_2$  atmosphere. The melting temperatures of the samples were taken as the peak temperature of the DSC curves. X-ray powder diffraction profiles were obtained at room temperature with an automatic Philips diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation. The indices of crystallinity ( $x_c$ ) were evaluated from the diffraction profiles by the ratio between the crystalline diffraction area ( $A_c$ ) and the total area of the diffraction profile ( $A_t$ ),  $x_c = 100 \times (A_c/A_t)$ . The crystalline diffraction area has been determined from the total area of the diffraction profile by subtracting the amorphous halo after scaling. The amorphous halo was obtained from the X-ray diffraction profile of an atactic polypropylene. The relative amount of crystals in the  $\gamma$  form present in the samples was determined from the X-ray diffraction profiles after subtraction of the amorphous contribution, by measuring the ratio between the intensity of the  $(117)_\gamma$  reflection at  $2\theta = 20.1^\circ$ , typical of the  $\gamma$  form, and the sum of the intensities of the  $(117)_\gamma$  reflection at  $2\theta = 20.1^\circ$  and the  $(130)_\alpha$  reflection at  $2\theta = 18.6^\circ$ , typical of the  $\alpha$  form. The samples were fractionated by exhaustive Kumagawa extraction using sequentially boiling diethyl ether (Et), hexane (He) and heptane (H). Fractions soluble and insoluble in diethyl ether (EtS and EtI), insoluble in diethyl ether and soluble in hexane (EtI-HeS), insoluble in hexane and soluble in heptane (HeI-HS) and, finally, insoluble in heptane (HI), were separated and

**Table 1**

Ethylene (E) content (mol%), degree of crystallinity ( $x_c$ ), molecular mass ( $M_n$ ), molecular mass distribution ( $M_w/M_n$ ) and melting temperatures ( $T_m$ ) of the heterogeneous iPP copolymers Bor, Cap, Sab, TVK.

Sample	E content <sup>a</sup> (mol%)	$x_c$ <sup>b</sup> (%)	$M_n$ <sup>c</sup> (KDa)	$M_w/M_n$ <sup>c</sup>	$T_m$ <sup>d</sup> (°C)
Bor	7.0	60	93	3.3	145
Cap	5.3	58	73	3.1	155
Sab	8.2	57	133	4.2	151
TVK	5.9	57	88	2.4	150

<sup>a</sup> From  $^{13}\text{C}$  NMR spectra.

<sup>b</sup> From X-ray diffraction profiles.

<sup>c</sup> From GPC analysis.

<sup>d</sup> From DSC scans at heating rate of 10 °C/min.

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