European Polymer Journal 64 (2015) 52–61

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthesis, molecular characterization, evaluation of polymorphic behavior and indentation response in isotactic poly(propylene-*co*-1-heptene) copolymers

Alberto García-Peñas [a], José M. Gómez-Elvira [a], Vicente Lorenzo [b], Ernesto Pérez [a], María L. Cerrada [a,*]

[a] *Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain*

[b] *Grupo de Investigación "POLímeros: Caracterización y Aplicaciones" (U.A. del ICTP-CSIC), E.T.S.I. Industriales, Universidad Politécnica de Madrid, José Gutiérrez Abascal 2, 28006 Madrid, Spain*

ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 23 December 2014
Accepted 24 December 2014
Available online 31 December 2014

Keywords:
Indentation hardness
Mesomorphic entities
Monoclinic and orthorhombic crystallites
Isotactic polypropylene
1-heptene copolymers

ABSTRACT

Different polymorphs are developed in isotactic poly(propylene-*co*-1-heptene) copolymers depending on 1-heptene molar content and thermal history: monoclinic and orthorhombic crystallites as well as mesomorphic entities. Indentation hardness values and deformability are found to be related to those variables as well as to crystallinity degree. Consequently, mechanical behavior can be tailored mainly by varying all of these parameters and a range from rigid to soft and more easily deformable materials is attained by synthesis of copolymers based on isotactic propylene with 1-heptene as comonomeric unit. Evaluation of the influence of molecular weight, intrinsic viscosity and microstructural details is also performed.

1. Introduction

Isotactic polypropylene, iPP, is one of most versatile polymers currently produced at industrial level primarily because of its relatively low manufacturing cost and its rather interesting properties, both as a plastic and as a fiber. Therefore, iPP is used in a variety of applications, including packaging, textiles, plastic parts and reusable containers of various types, laboratory equipment, automotive components, and polymer banknotes, among others. The good inherent properties and the fact that iPP is reasonably economical, make it competitive to other more expensive engineering plastics. Incorporation of specific fillers or other polymers can allow spreading out even more its application fields. This addition can be performed either by direct blending of the different components, filled polypropylenes [1–6] or blends [7,8], or by polymerization in the presence of fillers [9–11].

Another approach to vary structure and, then, the ultimate performance of iPP is by incorporation of comonomers during its synthetic stage. Metallocene catalysts have constituted a great tool from mid 90s to synthesize polypropylenes with low amounts of oligomers and different tacticities [12] (atactic, isotactic, isoblock, stereoblock, syndiotactic), and also copolymers with ethylene, 1-butene and longer chain α-olefins [13–16] with high comonomeric proportions. Consequently, properties could be tunable depending on the ultimate practical requirements.

The interest on those copolymers allowed finding a new polymorphic form [17] in 2005 for metallocene isotactic copolymers of propylene with high contents of 1-hexene (cPHe) or 1-pentene (cPPe) as comonomers [18–23]. This structure shows a trigonal cell and indicates that the packing of polymer molecules is mainly driven by density

---

* Corresponding author.
E-mail address: mlcerrada@ictp.csic.es (M.L. Cerrada).

http://dx.doi.org/10.1016/j.eurpolymj.2014.12.035
0014-3057/© 2015 Elsevier Ltd. All rights reserved.

(principle of entropy-density driven phase formation in polymers) [24]. At contents lower than 14 mol%, this polymorph competes with the other ones that can be developed (α and γ forms as well as the mesomorphic phase), depending on rate applied during the crystallization process and/or on supercooling from the isotropic melt before ordering.

The mesomorphic form is already well-known in iPP [25–29] for decades, obtained by very fast cooling from the melt. In the copolymers, however, these mesomorphic entities can be attained under much milder conditions than those necessary ones for their achievement in the iPP homopolymer. Consequently, there exists a reduction in the rate of mesophase formation that depends upon comonomer content at a given counit and upon length of the chain branches at a specific content. Mesomorphic entities formation is, then, easier as the comonomer content increases and as the length within branches is enlarged [16,30,31].

On the other hand, it is important to remark that the trigonal δ polymorph has been exclusively attained using 1-hexene or 1-pentene as comonomers in propene based copolymers and, very recently, in propylene terpolymers containing both 1-pentene and 1-hexene as comonomeric units [32,33]. Furthermore, the new trigonal polymorph is the only one able to crystallize at compositions higher than 14 mol% (up to a limit for 1-hexene copolymers of around 30% of hexene units [17b]), although there are kinetic differences between using 1-hexene or 1-pentene as comonomers [20,30].

The following question can be, then, addressed: what does it occur in random isotactic copolymers if chain-branching length within counit is slightly enlarged, i.e., if 1-heptene, Hp, is incorporated as comonomer)? It should be said that these propene-*co*-1-heptene copolymers (cPHp) have been barely referred in open literature. There are few investigations [34,35] that compare some aspects of their copolymerization kinetics and microstructure with those exhibited by others olefinic counits, but to the best of our knowledge there are not other investigations concerning either structural studies or properties evaluation in these cPHp copolymers. Although there was not yet experimental support, Lotz et al. [17b] established as hypothesis from the analysis of the relative intensity of 110 and 300 reflections of the 1-hexene based copolymers that "folded" conformations of the hexene side chains were favored instead of those stretched ones. Their reasoning also suggested that copolymers of propene with olefins different from hexene may possibly crystallize in a similar form-I-type poly(1-butene) crystal structure when the average side-chain material approaches that of poly(1-butene). Additionally, de Rosa et al. [18] proposed, from the crystal structures obtained for 1-hexene based copolymers and the principle of density (entropy)-driven phase formation, that copolymers of propylene with olefins different from hexene might crystallize in a similar trigonal form, the form I-type poly(1-butene) crystal structure, when the crystal density and the average composition of the copolymer approach those of poly(1-butene), if distribution of the comonomer was random. The crystallization of the trigonal form would be probably dependent on comonomer type, in such a way that in the case of smaller comonomer as, for instance, pentene, it could be developed at higher comonomer concentrations and in the case of bigger comonomers, as heptene at lower comonomer contents.

All of these preliminary investigations point out the importance of evaluating propene-*co*-1-heptene copolymers to fill out the existing gap. Therefore, the aim of this article is, firstly, to describe the synthesis (using a metallocene catalyst) of these propylene-*co*-1-heptene copolymers at different comonomer contents in a broad composition interval as well as to perform their complete molecular characterization. Secondly, to evaluate the crystalline structure generated as function of both composition and crystallization conditions (type of polymorph, competition between lattices, and crystallinity) and correlate these structural features with their mechanical response examined by indentation measurements.

2. Experimental

2.1. Materials

Toluene (Merck) and the comonomer 1-heptene (TCI Tokyo Kasei) have been previously refluxed over sodium, distilled and kept under N_2 to avoid the presence of traces of water and oxygen. Both propylene (Praxair 2.5) and nitrogen (Praxair 3X) were passed through oxygen-trap columns and molecular sieves before their use. The catalyst *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride (Strem) and the cocatalyst methylaluminoxane (MAO) (10 wt.% solution in toluene, from Aldrich) were used as received. The activated catalyst was prepared by dissolving 15 mg of the metallocene in 3 mL of MAO solution. A volume of 0.125 mL containing $1.39 \cdot 10^{-6}$ moles of the active complex was used in each polymerization. Ethanol (Aroca, 96%) and HCl (VWR, 37%) were used for the precipitation of the polymers.

2.2. Synthesis of poly(propylene-co-1-heptene) copolymers

The copolymerization of propylene with 1-heptene was carried out in a 500 mL Büchi glass ecoclave at −5 °C in toluene (250 mL) for 30 min by using *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride/MAO as the catalyst/cocatalyst system ([Al]/[Zr] = 3648). The initial propylene pressure was 0.40 bar, the catalyst amount was $1.39 \cdot 10^{-6}$ mol and the starting comonomer/propylene molar ratio ranging from 0 to 0.893. The copolymerization reaction was stopped after 30 min of reaction time by adding 5 mL of ethanol and enabling the unreacted propylene out from the reactor. The polymer was obtained as a powder by pouring the reaction batch on a mixture of ethanol/HCl (30:1). The precipitated solid was stirred thoroughly overnight, filtrated, washed again with ethanol and, afterwards, dried under vacuum at room temperature. Table 1 shows the different copolymers attained, which are referred as cPHp followed by the closest integer value of the 1-heptene mol% content in the copolymer.

Film samples of the different copolymers were obtained by compression molding in a Collin press between hot