



Structure and thermal properties of ethylene/4-methyl-1-pentene copolymers: Effect of comonomer and monomer sequence distribution



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ABSTRACT

A series of ethylene/4-methyl-1-pentene (E/4M1P) copolymers is synthesized, using the Ti (IV) diisopropoxy complex bearing a dianionic $[O^-,S,O^-]$ bis(phenolato) ligand, in combination with methylalumoxane, as catalyst system. The semicrystalline copolymers are characterized by NMR, DSC, WAXD and SAXS. The structure and the thermal behavior of the copolymers are strongly influenced by composition and monomer sequence distribution. The copolymer crystallinity decreases as a function of 4M1P content, while an increase of the periodicity due to the enhancement of the amorphous interlamellar thickness is registered. The non-homogeneous distribution of the 4M1P units along the polymer chains is evidenced by the multimodal crystallization and melting behavior. The chain heterogeneity of the copolymers is investigated by successive self-nucleation and annealing thermal fractionation evaluating the methylene sequence length, the short chain branching and the lamellar thickness. In order to get more information on the comonomer distribution in the copolymers, solvent extraction is performed and all the fractions are characterized by thermal and X-ray techniques.

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1. Introduction

Random copolymers are long chain macromolecules containing two or more chemically distinct monomers. Unlike copolymers with perfectly ordered monomer sequence distributions, that is, alternating or block, the arrangement of the different monomers units inside random copolymers does not possess a long-range order. Due the stochastic nature of the insertion/coordinative (co)polymerization mechanism, random copolymers may exhibit basically two types of heterogeneities: polydispersity in chemical composition and polydispersity in monomer sequence distribution. In addition, just like in any synthetic (co)polymer, there may be a distribution of the polymer chain lengths. These items make the characterization of random copolymers very challenging because the contributions of all the mentioned heterogeneities are connected to each other [1,2].

Random copolymers of ethylene (E) with α -olefins display attractive chemical and physical characteristics that make them usable for applications in many manufacturing sectors. The physical properties of the copolymers mainly depend on the crystallization behavior, which in turn is strongly related to the chemical structure of the single macromolecules, i.e., the sequence distribution of (co)monomeric units, the stereoregularity and regioregularity of the chains, the types

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and concentration of defects in the regular constitutional and the configurational enchainment of monomeric units (*stereo*- and *regio*-defects). The Successive Self-nucleation and Annealing (SSA) is a well-established thermal fractionation technique based on the molecular segregation capacity shown by semicrystalline polymeric systems when isothermally crystallized or annealed [3,4]. The SSA procedure was successfully applied to provide valuable information on the amount and distribution of short chain branches interrupting the crystallizable ethylene sequences in ethylene/ α -olefin copolymers [5–11].

Among the α -olefins, 4-methyl-1-pentene (4M1P) is a promising branched olefin, industrially available at a low price. Ethylene/4-methyl-1-pentene copolymers (E/4M1P) are considered an interesting family of polyolefins since the bulky comonomer is expected to lower polyethylene density more effectively than linear α -olefins, e.g., 1-butene, 1-hexene and 1-octene [12]. Several papers on the E/4M1P copolymerization catalyzed by group IV metallocene and half-metallocene single-site catalysts [13–15], and Ni(II) α -diimine complexes were published in the last years [16,17]. Recently, we investigated the copolymerization of E with 4M1P catalyzed by a post-metallocene complex, i.e., Ti(IV) diisopropoxy bearing a thio-bis(phenolate) ligand [2,2'-S(4-Me,6-tBuC₆H₂O)₂]Ti(OiPr)₂. The catalyst exhibited high activities (up to 10⁶ g mol⁻¹ h⁻¹) and semicrystalline copolymers with a certain tendency for comonomer alternation were obtained with a good 4M1P incorporation [18].

In the present work, we synthesized new copolymers and performed a detailed evaluation of their microstructure and molecular mass distribution. A series of copolymers containing from 2% to 20% mol of 4M1P was subjected to in-depth characterization. The thermal properties and the crystalline structure of the E/4M1P copolymers, assessed by means of differential scanning calorimetry, successive self-nucleation and annealing thermal fractionation, wide angle X-ray diffraction and small angle X-ray scattering, were correlated with the heterogeneity in chemical composition and comonomer sequence distribution.

2. Experimental

2.1. Materials

All manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and the standard Schlenk-line techniques. Toluene (Fluka, >99.5% pure) was refluxed over Na for ca. 8 h and then distilled and stored over molecular sieves under nitrogen. Solid MAO (d-MAO) was prepared by removing toluene and unreacted free-trimethylaluminum (Al(CH₃)₃) under vacuum from the commercially available MAO solution (Aldrich, 10 wt.% solution in toluene). The resulting white powder was heated further to 60 °C under vacuum to a constant weight. A stock solution was then prepared by dissolving 500 mg of d-MAO in 5.4 mL of toluene (92 mg mL⁻¹). Ti(O_iPr)₄ (Aldrich, 97%) and Irganox 1081 (Ciba-Geigy) were used as received. The Ti(IV) thiobis(phenolate) complex [2,2'-S(4-Me,6-tBuC₆H₂O)₂]Ti(OiPr)₂ was synthesized according to the procedure elsewhere reported [19]. 4M1P (Aldrich, ≥99% pure) were refluxed over CaH₂ for about 2 h, then distilled trap-to-trap. Ethylene was purified flowing through BTS catalysts, molecular sieves, and CaCl₂.

2.2. Polymerization procedure

The experiments were carried out in a 50 mL round-bottomed Schlenk flask containing a stirring bar. The reactor vessel was charged with toluene and 4M1P and brought to 50 °C. MAO was added, the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a solution of the titanium compound under continuous flow of ethylene. Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were collected by filtration, repeatedly washed with fresh methanol and finally dried in vacuum at room temperature to constant weight.

2.3. Polymer characterization

Molecular weight (M_w) and polydispersity index (M_w/M_n) were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-dichlorobenzene as the mobile phase, 0.8 mL min⁻¹ flow rate, and 145 °C temperature. Calibration of the SEC system was carried out using eighteen narrow M_w/M_n poly(styrene) standards with molar weights ranging from 162 to 5.6 × 10⁶ g mol⁻¹. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-dichlorobenzene with 0.05% of BHT as an antioxidant.

For ¹³C NMR, about 100 mg of copolymer was dissolved in C₂D₂Cl₄ in a 10 mm tube. Hexamethyldisiloxane was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 spectrometer equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 100.58 MHz (¹³C) in the PFT mode working at 103 °C. The applied conditions were the following: 14.30 μs as 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3–4 K transient. Proton broad-band decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling. The overall branching was determined by ¹H NMR [20].

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