



# Tailoring the rigid amorphous fraction of isotactic polybutene-1 by ethylene chain defects

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## ABSTRACT

The effect of different amounts of ethylene co-units in the butene-1 chain, on the fold-surface structure of crystals of isotactic polybutene-1, has been probed by analysis of the rigid amorphous fraction (RAF). The exclusion of ethylene co-units from crystallization in random butene-1/ethylene copolymers and their accumulation at the crystal basal planes leads to a distinct increase of the RAF with increasing concentration of co-units. A specific RAF was determined by normalization of the RAF to the crystal fraction. While in the butene-1 homopolymer a specific RAF of 20–30% is detected, it increases to more than 100% in copolymers with 5–10 mol% of ethylene co-units, being in accordance with the previously observed increase of the free energy of the crystal fold-surface due to copolymerization. It has also been shown that the specific RAF increases with decreasing temperature of crystallization, due to formation of a fold-surface of lower perfection, containing an increased number of chain segments traversing the crystalline–amorphous interface.

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## 1. Introduction

Semicrystalline polymers consist of crystalline and amorphous phases. The latter can be subdivided into a rigid amorphous fraction (RAF) and a mobile amorphous fraction (MAF), based on the degree of coupling with the crystal phase, affecting the chain mobility [1]. The MAF is made of chain segments which are decoupled from the crystals and mobilize at their glass transition temperature ( $T_{g,MAF}$ ). The RAF has a glass transition temperature ( $T_{g,RAF}$ ) higher than  $T_{g,MAF}$ , and is covalently coupled to the crystals, as it arises from the continuation of the partially crystallized macromolecules across the phase boundaries. For several polymers, including poly (L-lactic acid) (PLLA), poly [(R)-3-hydroxybutyrate] (PHB), and poly (ethylene terephthalate) (PET) it has been proven that vitrification of the RAF on cooling, and devitrification on heating, is indispensably connected with the formation and melting of crystals, respectively [2–4].

The importance to quantify the RAF in semicrystalline polymers derives from the fact that the RAF is glassy at temperatures higher than  $T_{g,MAF}$ , which influences thermo-mechanical properties

[5–10], and that it is of lower density than the MAF, which affects the barrier properties [11–13]. Recent analyses even suggested that vitrification of the RAF may be the cause for early termination of crystallization [14]. Ordering of macromolecules drastically slows down as soon as the vitrified RAF hinders the diffusion of chain segments towards the growing crystals. The hindering effect of RAF vitrification on crystallization was proven for poly ( $\epsilon$ -caprolactone) (PCL), isotactic polypropylene (iPP) and PHB [15–17].

Analysis of the effect of the crystal habit on the RAF of iPP, which can be crystallized to contain either nodular or lamellar crystals of largely different ratio of the areas of lateral and fold surfaces, allowed identification of the structure at the basal planes of crystals as a major source of the immobilization of the amorphous phase [9]. Furthermore, specific annealing experiments performed on PET revealed that the local RAF at the crystal basal planes is reduced with increasing perfection/regularity of the fold-surface [18]. Besides the crystallization history, the structure of the crystal basal planes, and with that of the RAF, may be controlled by the chemical composition of macromolecules. With the present study it is attempted to demonstrate that the presence of a small amount of foreign co-units in a crystallizable macromolecule, which disrupt the lateral growth of crystals due to their exclusion from the crystallization process and accumulate then at the crystal basal planes, is a tool to tailor the RAF and, with that, the ultimate properties.

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We selected a series of random copolymers of butene-1 with low amount of ethylene co-units (up to 10 mol%) in order to test the hypothesis of tailoring the RAF by modification of the structure of crystal basal planes. It has been shown that ethylene co-units in random butene-1/ethylene copolymers are excluded from crystallization, as was proven by analysis of the composition-dependence of the lattice parameter  $a_0$ , measured by wide-angle X-ray diffraction [19–22]. In the case of butene-1/propylene random copolymers, the presence of propylene co-units in the butene-1 chains causes a significant reduction of the unit cell dimension in cross-chain direction, whereas in the case of ethylene co-units a negligible effect is observed. It is assumed that the propylene chain defects are incorporated into the crystals, with the decrease of the average distance between neighbored chain segments related to the smaller size of the  $-\text{CH}_3$  group of the propylene co-unit, in comparison to that of the  $-\text{CH}_2-\text{CH}_3$  side group of butene-1 co-units. Conversely, ethylene co-units are excluded from poly(butene-1) crystals due to their small size [23]. As a consequence, in random butene-1/ethylene copolymers the maximum crystallinity decreases and the kinetics of the transformation of the supercooled melt into tetragonal Form II crystals decreases with increasing molar percentage of ethylene co-units [21,22]. Such a decrease is not detected in butene-1/propylene copolymers, where the kinetics of melt–Form II transition is independent of composition, at least for a content of propylene co-units up to 11 mol % [24]. The exclusion of ethylene co-units from crystallization of butene-1 chain segments, and their enrichment at the crystal fold-surface has been confirmed by quantitative analysis of fold-surface free energies which, in copolymers containing up to 5 mol% ethylene is 50–100% higher than in the butene-1 homopolymer [23]. In contrast, incorporation of either ethylene or propylene co-units into the butene-1 chains leads to an acceleration of the rate of the polymorphic transformation of the unstable Form II phase into stable trigonal Form I crystals [19,24,25].

The formation of an RAF was proven for isotactic polybutene-1 (iPB-1) [7,26]. It amounts to 15–25%, depending on crystallization temperature ( $T_c$ ), and on the Form II/Form I crystal polymorphism [27–30]. It has been shown that the RAF in semicrystalline iPB-1 decreases with  $T_c$ , and increases after Form II – Form I transformation. Note that the density of Form I crystals is about 4% higher than that of Form II crystals, which may cause an increase of the local stress at the crystal surfaces due to the phase transition, and an increase of the RAF.

In summary, the goal of this contribution is the establishment of a link between the chemical structure of macromolecules, the morphology/fold-surface structure of crystals, and the RAF. An additional aim is to complete prior work on the crystallization kinetics and the semicrystalline morphology of random butene-1/ethylene copolymers, and to explore in particular the influence of ethylene content not only on the crystal fraction, but on the overall three-phase structure as function of copolymer composition and crystallization conditions. This study we consider being of

importance not only to advance the current knowledge on the three-phase structure of semicrystalline polymers, but also as an effort to permit further tailoring of structure-property relations of random butene-1/ethylene copolymers, which have a large economic importance, being used e.g. as component in the seal layer of easy-opening packaging films [31–33].

## 2. Experimental

Random isotactic butene-1/ethylene copolymers were obtained from Lyondell Basell (Germany). Table 1 is a list of the homo- and copolymers used in this work, including information about the concentration of ethylene co-units and the mass-average molar mass [25,34]. The as-received sample chips were processed to films of 500  $\mu\text{m}$  thickness by compression-molding using a Perkin–Elmer FTIR press in combination with a Lot-Oriel/Specac film maker die and heating accessory.

Thermal analysis was conducted with a Perkin–Elmer Pyris Diamond DSC, equipped with an Intracooler II as cooling system. The instrument was calibrated regarding temperature with high purity standards (indium and cyclohexane) and regarding energy by the heat of fusion of indium. Dry nitrogen was used as purge gas at a rate of 48  $\text{ml min}^{-1}$ .

To analyze the effect of crystallization conditions on RAF formation, isothermal crystallization experiments were performed. The compression-molded samples were heated to 180  $^{\circ}\text{C}$  at a rate of 20  $\text{K min}^{-1}$ , maintained at this temperature for a period of 2 min in order to destroy all traces of previous crystalline order, and then rapidly cooled to the desired crystallization temperature at a rate of 100  $\text{K min}^{-1}$ , to allow crystallization. The isothermally crystallized samples were then rapidly cooled to  $-68^{\circ}\text{C}$ , and heated to 180  $^{\circ}\text{C}$  at a rate of 20  $\text{K min}^{-1}$ .

In order to obtain precise heat-capacity values, the experimentally measured heat-flow-rate raw data were corrected for instrumental asymmetry by subtraction of a baseline, measured under identical conditions as the samples, including close match of the masses of the aluminum pans. The heat-flow rate data were then converted to specific apparent heat capacities by point-by-point calibration with sapphire [35]. All measurements were repeated three times to improve accuracy.

The RAF of the polymers listed in Table 1 was determined as a function of the conditions of melt-crystallization by analysis of crystalline fraction  $X_{\text{cry}}$  and of the MAF, according to Equation (1):

$$\text{RAF} = 1 - \text{MAF} - X_{\text{cry}} \quad (1)$$

The MAF was obtained by the heat-capacity increment  $\Delta c_{p,\text{meas}}$  at  $T_{g,\text{MAF}}$  on heating of the semicrystalline sample, and its normalization to the expected heat-capacity step  $\Delta c_{p,100}$  for a fully amorphous sample, according to Equation (2):

$$\text{MAF} = \Delta c_{p,\text{meas}} / \Delta c_{p,100} \quad (2)$$

The heat-capacity step  $\Delta c_{p,100}$  of a fully amorphous sample is the difference between the heat capacities of the glassy and liquid phases of the sample under consideration,  $c_{p,\text{solid}}$  and  $c_{p,\text{liquid}}$ , respectively. Both,  $c_{p,\text{solid}}$  and  $c_{p,\text{liquid}}$  depend on the copolymer composition and were calculated for the iPB–Eth copolymers by averaging of the heat capacities of polybutene-1 (iPB-1) and polyethylene (PE), taking into account their molar fraction  $n$  in the copolymers, as shown by Equation (3a) and (3b) [36–39]:

$$c_{p,\text{solid, iPB-Eth}} = c_{p,\text{solid, iPB-1}} \times n_{\text{butene}} + c_{p,\text{solid, PE}} \times n_{\text{ethylene}} \quad (3a)$$

**Table 1**

List of isotactic random butene-1/ethylene copolymers used in this work, including information about the content of ethylene co-units and the mass-average molar mass.

Trade name [33]	Sample code	Ethylene content mol% m% [25]		Molar mass $\text{kg mol}^{-1}$ [25,34]
PB 0300M	iPB-Eth 0–347	0	0	347
PB 0110M	iPB-Eth 0–711	0	0	711
PB 8340M	iPB-Eth 1.5–293	1.5	0.75	293
PB 8640M	iPB-Eth 1.5–470	1.5	0.75	470
PB 8220M	iPB-Eth 4.3–400	4.3	2.2	400
DP 8310M	iPB-Eth 10.5–305	10.5	5.5	305

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