

Study on the crystallization of poly(butylene azelate-co-butylene succinate) copolymers



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ABSTRACT

Poly(butylene azelate-co-butylene succinate) samples with different azelate/succinate ratios were synthesized and characterized. Calorimetric data indicate a semicrystalline character for all copolyesters studied and a melting point depression that could be interpreted on the basis of complete exclusion of comonomers from well organized lamellae. Crystallization first occurred through the succinate rich segments, which resulted in a peculiar behavior of copolymers having an intermediate composition. In this case, crystallization of azelate segments was paradoxically enhanced when samples were quenched. Equilibrium melting temperatures significantly decreased with increasing comonomer content compared to those of the corresponding homopolymers. Incorporation of comonomers had a distinct effect on the secondary nucleation constant depending on the composition as deduced from Lauritzen and Hoffman analysis. Thus, azelate units clearly increased the nucleation constant of copolymers rich on succinate units, whereas the incorporation of succinate units had a lower influence on the constant of copolyesters having high azelate content.

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1. Introduction

Poly(alkylene dicarboxylate)s are polyesters of great interest due to their easy synthesis and potential applications derived from their biodegradability [1,2]. In general, these polymers are highly crystalline, a feature that may improve some properties but also hinder the degradation process. In order to obtain materials with tuneable properties, efforts are currently focused on forming random copolymers that can be easily synthesized by using mixtures of diols and/or dicarboxylic acids. In this way, hydrophobicity, crystallinity and degradation rate can be controlled [3–6]. Polybutylene succinate (PBS), a polymer supplied by Showa High Polymers as Bionolle™, is currently the most widely employed poly(alkylene dicarboxylate) due to its relatively low production cost, good thermal and mechanical properties and easy processability [7,8]. Different types of copolymers and blends of PBS have recently been developed to increase biodegradability, decrease costs, increase commercial offer or even modify final properties [9–14].

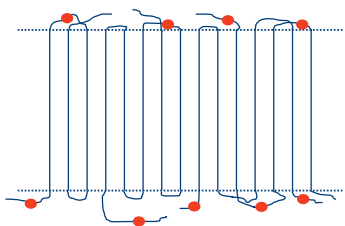
Random copolymers constituted by two crystallizable units may show a different crystallization behavior depending on the compatibility of the two components in crystal lattices. Comonomer units

can generally be excluded in the organized lamellae and remain only in the amorphous phase or are compatible in such a way that they are able to share a crystalline lattice (Fig. 1). Isomorphic co-crystallization is characterized by the formation of only one crystalline phase containing both crystalline units. In this case, these units must meet strict molecular requirements such as having a similar chemical structure and even molecular conformation to allow their incorporation into the resulting crystalline structure with minimum distortion. In contrast, two crystalline phases and pseudo-eutectic behavior are observed when isodimorphism occurs. Increase of minor comonomer concentration in each crystalline phase lowers the melting temperature and crystallinity of copolymers. Obviously, requirements are in this case less strict, and consequently isodimorphism is more frequently observed in random copolymer crystallization than isomorphism. Note, however, that isodimorphism implies that at least one of the two crystalline phases incorporates the corresponding minor component in its crystalline lattice.

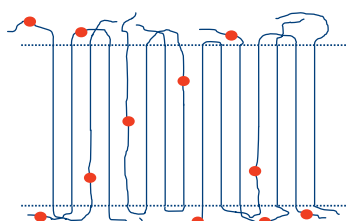
It now seems interesting to get insight into the crystallization behavior of copolyesters constituted by highly differentiated units and evaluate the capability to control thermal properties of new copolyesters since other characteristics like biodegradability are strongly influenced by the amorphous phase content. Azelaic acid has nine carbon atoms while succinic acid has only four, thus appearing as an ideal comonomer for the present study. Furthermore, it can be obtained by ozonolysis cleavage of the alkene double

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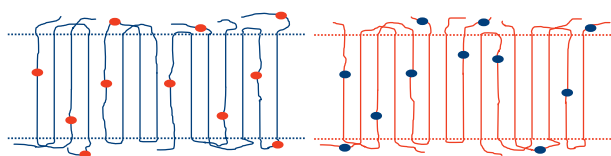
a) Comonomer exclusion



b) Comonomer inclusion



Isomorphism: Single crystalline phase over all compositions



Isodimorphism: Two crystalline phases depending on composition.
Comonomer inclusion is on one or both crystalline phases.

Fig. 1. Scheme of the comonomer unit arrangement in lamellae for full exclusion and inclusion models. In the latter case, isomorphic and isodimorphic structures are considered. In the last case, the two crystalline phases are represented with blue and red colors and the comonomer inclusion has been drawn for both phases. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

bond of oleic acid and subsequent oxidation and reduction [15]. Hence, all new synthesized copolymers can be derived from renewable sources, just like Bionolle™.

PBS shows polymorphism but a monoclinic structure known as α -crystal modification is attained under the most common crystallization conditions. Molecular conformation is defined by the torsional angle sequence ($T_7\bar{G}TG$) where the gauche and minus gauche angles belong to the succinate unit [16–18]. To the best of our knowledge of polybutylene azelate, the crystal lattice parameters have so far not been reported. However, an orthorhombic unit cell (instead of a monoclinic one) should be expected when aliphatic polyesters have an odd number of methylene groups in the diol and/or in the dicarboxylic units [19,20].

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Sigma–Aldrich and used without further purification. Copolymers were synthesized by two-stage melt polycondensation of the appropriate mixture of dicarboxylic acids with an excess of 1,4-butanediol (1.2:1 molar ratio) (Fig. 2). The composition of the reaction medium is defined by the molar ratio of azelate units (x), which is also used in the abbreviated copolymer name (e.g. PE4,9/4 0.85 means the polyester (PE) derived from 1,4-butanediol (4) and having 85 and 15 mol% of azelate (9) and succinate (4) units, respectively).

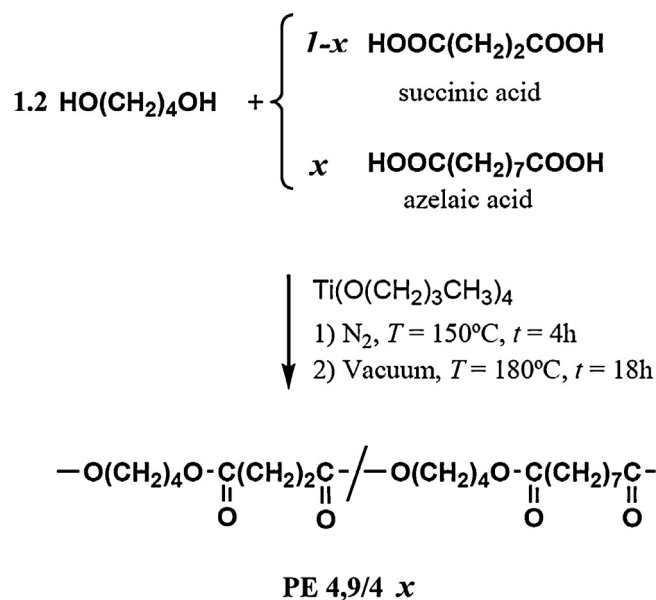


Fig. 2. Synthesis scheme of all poly(butylene azelate-*co*-butylene succinate) copolymers.

Homopolymers will be named PE44 and PE49. Titanium tetrabutoxide was used as a catalyst and the reaction was first performed in a nitrogen atmosphere at 150 °C for 6 h and then in vacuum (5 Pa) at 180 °C for 18 h. Polymers were purified by precipitation with ethanol of chloroform solutions (10 wt%).

2.2. Measurements

Molecular weights were estimated by GPC using a liquid chromatograph (Shimadzu, model LC-8A) equipped with an Empower computer program (Waters) and a refractive index detector. A PL HFIP gel guard precolumn and PL HFIP gel column (Agilent Technologies Deutschland GmbH) were employed. The polymer was dissolved and eluted in 1,1,1,3,3,3-hexafluoroisopropanol at a flow rate of 0.5 mL/min (injected volume 100 μ L, sample concentration 1.5 mg/mL). The number and weight average molecular weights were calculated using polymethyl methacrylate standards.

¹H NMR spectra were acquired with a Bruker AMX-300 spectrometer operating at 300.1 MHz. Chemical shifts were calibrated using tetramethylsilane as an internal standard. Deuterated chloroform was used as the solvent.

Calorimetric data were obtained by differential scanning calorimetry with a TA Instruments Q100 series equipped with a refrigerated cooling system (RCS) operating from –90 °C to 550 °C. Experiments were conducted under a flow of dry nitrogen with a sample weight of approximately 5 mg while calibration was performed with indium. Thermal characterization was performed following a four run protocol consisting on a heating run (20 °C/min) of the as-synthesized sample, a cooling run (10 °C/min) after keeping the sample in the melt state for three minutes, a subsequent heating run (20 °C/min) of the non-isothermally crystallized sample and finally a heating run (20 °C/min) of a sample previously cooled from the melt state at the maximum rate allowed by the equipment.

3. Results and discussion

3.1. Synthesis of PE4,9/4 x samples

Results in Table 1 indicate that samples could be synthesized with a polydispersity index (PDI) and a molecular weight typical of

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