Polymer Testing 68 (2018) 379–387

Contents lists available at ScienceDirect

Polymer Testing

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

Material Behaviour

Crystallization of isomorphic poly(butylene succinate-co butylene fumarate) biopolyester: Single crystals and ring-banded spherulites

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ARTICLE INFO

Keywords:
PBSF
Single crystal
Selected area electron diffraction
Isomorphism
Ring-banded spherulite

ABSTRACT

Poly(butylene succinate-*co*-butylene fumarate) (PBSF) copolymers with butylene fumarate (BF) molar ratio varies from 1% to 40% were synthesized and their single crystals were prepared using a self-seeding method. For PBSFs with low content of BF units, the single crystals are regular hexagonal shape. With the increase of BF molar ratio, the single crystal boundary turns rounded and the aspect ratio decreases. PBSF single crystals with different BF content were prepared at the same temperature, the supercooling degree of the PBSF increases with the increase of BF content, resulting the crystalline density increases and the single crystal size decreases. Selected area electron diffraction (SAED) was used to investigate the crystalline structures of the PBSF single crystals, and the results approve strict isomorphism between butylene succinate (BS) and BF in PBSF, verifying that preparing the single crystal and characterizing the crystalline structure by SAED is a direct method to check for isomorphic polymers. PBSFs can form ring-band spherulites at suitable crystallization temperatures. The band spacing of PBSF increases with the increase of isothermal crystallization temperature. At the same isothermal crystallization temperature, the band spacing PBSF decreases with the increase of BF molar ratios. The crystallization temperature range of forming ring-banded spherulites broadens with the increase of BF molar ratios.

1. Introduction

Isomorphism, a property that originates from inorganic compounds, means that two or more distinct substances can crystallize together into one crystal unit cell. The isomorphic substances usually have an analogous size and chemical structure. So far, isomorphic crystallization has been extensively observed in inorganic and organic small molecules [1–5]. The concept of isomorphism in the polymer field was first brought up by Natta et al., in 1959 [6]. They divided isomorphism into two cases: (1) isomorphism of chains, where chemically or structurally different polymer chains are present in the same crystal lattice, including cocrystallization of different homopolymers, blends of copolymers or homopolymer/copolymers such as poly(4-methyl-1-pentene)/poly(4-methyl-1-hexene) [7], poly(ethyleneterephthalate)/poly(ethylene 2,6-naphthalate) [8], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/poly(3-hydroxybutyrate-*co*-3-hydropropionate) [9], poly(3-hydroxybutyrate)/poly(3- hydroxybutyrate-*co*-3-hydroxyvalerate) [10], polyethylene/poly(ethylene-*co*-butene) [11], etc. and (2) isomorphism of different monomer units, which occurs in semicrystalline copolymers containing a more or less random distribution of comonomer units, such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [12], poly(hexamethyleneadipate-*co*- butylene adipate) [13], poly(hexamethylenesebacate-co-hexamethylenesuberate) [14], etc. Based on the crystallization of such isomorphic systems, Allegra and Bassi summarized two requirements for the formation of macromolecular isomorphism: first, the different types of monomer units must have approximately the same shape and occupy a similar volume; second, the chain conformation of the parent homopolymers must be compatible with either crystal lattice [15]. Isomorphism is a general term for the cocrystallization of different polymeric units or segments. In a strict sense, isomorphism means that only one crystalline phase is observed, and the crystal structure is essentially the same throughout the range of compositions [5,16]. In isodimorphism or isopolymorphism, there are two or more crystal structures, respectively, depending on the composition of the polymeric units [17,18]. Therefore, most examples mentioned above do not ideally represent strict isomorphism in the whole composition range but isomorphism in a limited composition range or isodimorphism (isopolymorphism). In this work, the general term "isomorphism" is used for "strict isomorphism" and does not include isodimorphism or isopolymorphism.

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https://doi.org/10.1016/j.polymertesting.2018.04.035
Received 26 March 2018; Received in revised form 24 April 2018; Accepted 24 April 2018
Available online 25 April 2018
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Macromolecular isomorphism is a special crystallization behavior for semicrystalline polymers. Suitable characterization methods are needed to determine isomorphism in the blends or copolymer systems. Wide angle X-ray diffraction (WAXD) is a common method to investigate isomorphism: a single crystalline phase is possible only in isomorphism, and the crystal lattice parameters vary with composition [19–21]. Solid-state nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy are very sensitive to the conformation and packing modes of molecular chains in the crystalline phase, and they can be used to analyze the structure of polymer crystals to judge whether they are isomorphic or not [22–25]. NMR, in particular, can confirm the incorporation of different units in the crystal lattice, as well as quantitatively determine the compositions of different units in the crystalline and amorphous phases. Differential scanning calorimetry (DSC) is another conventional method used to study the phenomenon of isomorphism: the plot for the melting temperature versus the copolymer composition is a perfectly linear curve, and the melting enthalpy barely changes [26,27]. Frequently, DSC is employed in combination with the structure-sensitive techniques mentioned above. Up to now, isomorphism has only been demonstrated for polymers with spherulite crystals, therefore, the characterization methods utilized are those suitable for spherulites.

Generally polymer single crystals were used to investigate the crystalline structure by SAED. Yan's group confirmed that syndiotactic poly(propene-*co*-butene) (sPPBU) is a successful example for preparing a copolymer single crystal [28,29]. SAED investigations show the comonomeric units, propene or 1-butene, are included in the unit cells of both homopolymers, but the SAED patterns have streaks around the (*h*20) reflection, which are important for confirming that sPPBU crystallizes into different structures depending on its composition. sPPBUs, with a small content of 1-butene, crystallized in a structure similar to that of form I of syndiotactic polypropylene (sPP), although a disorder in the alternation of right and left-handed helical chains is present. With an increasing content of 1-butene, the amount of the b/4 shift disorder increases, and disordered modifications with intermediate structures between the form I of sPP and the form I of syndiotactic poly(1-butene) (sPB) are obtained. Samples with a 1-butene content higher than 70–80% crystallize in a structure similar to that of the form I of sPB. The SAED results demonstrate that sPPBU copolymers crystallize in an isopolymorphic manner, which is not strict isomorphism. Based on Yan's work, we speculate that SAED may be used as a tool to determine isomorphism in the blends or copolymer systems.

Biodegradable polyesters are important biocompatible materials [30–33]. Some copolyesters can crystallize in isopolymorphism, such as poly(hexamethylene adipate-*co*-butylene adipate) [13,34], poly(hexamethylene sebacate-*co*- hexamethylene suberate) [14] and poly(butylene succinate-*ran*-butylene azelate) [35] etc. Recently, Guo's group synthesized a series of poly(butylene succinate-*co*-butylene fumarate) (PBSF) copolyesters and detailed investigated the crystallization of PBSFs by using DSC and WAXD [16]. They found that PBSF crystallized in strict isomorphism in a whole range of comonomer composition, verified that PBSF copolyester is scarce isomorphic macromolecules. Until now, the crystal morphologies of PBSFs with different BF molar ratios have rarely been reported [36]. The morphological analyses are of great importance for investigating the influence of BF units on the crystallization behavior of BS units in PBSF. Electron diffraction of single crystals could give a more precise indexing of the reflections and more information about the crystalline structure of PBSFs as a function of the BF content. To the best of our knowledge, no one reported isomorphic polymer single crystal. In this work, we synthesized PBSF with a wide range of compositions and successfully prepared PBSF single crystals by the self-seeding method. The similar single crystal structures of a series of PBSF samples with different compositions verify the strict isomorphism between the BS units and the BF units in PBSF. The result implies that preparing the polymer single crystal and characterizing the crystalline structure by SAED is a direct method of confirming isomorphism. Moreover, the effects of BF composition on the morphology, formation temperature and band spacing of the PBSF ring-banded spherulites were investigated in this work.

2. Experimental section

2.1. Materials and synthetic methods

Butylene succinate, fumaric acid, tetra-*n*-butyl-titanate and *p*-hydroxyanisole were purchased from Aladdin (Shanghai, China). Succinate acid and 1,4-butanediol were obtained from Xilong Chemical Corp (China) and Tianjin jinke chemical research institute (China), respectively. Chloroform and methanol (analytical grade) were purchased from Beijing Chemical Reagents Corp. (China). All materials were used as received. Tetra-*n*-butyl-titanate and *p*-hydroxyanisole (each with a 1.0 wt% relative to the total reactants) were used as the catalyst and free radical inhibitor during the reaction. PBS, poly(butylene fumarate) (PBF), and their copolymers PBSF were synthesized from 1,4-butanediol, succinic acid and fumaric acid with desired feeding molar ratios by a two-step reaction of esterification and polycondensation in melt, as reported in previous literature [16]. The products were dissolved in chloroform to remove the impurities, precipitated in the methanol and finally dried under vacuum at 40 °C for 24 h.

2.2. Single crystal preparation

PBS and PBSF single crystals were prepared by the self-seeding method from a 0.01 wt% *o*-dichlorobenzene (ODCB) solution. First, the solution was heated to 120 °C and held for 30 min to completely dissolve the polymer in a methylsilicone oil bath; then, the solution was quenched to 40 °C in a water bath and held for 2 h to crystallize completely. Subsequently, the solution was slowly heated to 80 °C (a suitable self-seeding temperature) with a heating rate of 0.2 °C/min. Finally, the solution was quenched to 60 °C for isothermal crystallization by moving the solution into another water bath.

2.3. Film preparation

PBS or PBSF with different BF molar ratio was dissolved in chloroform with a polymer mass composition of ca. 1.0 wt% and stirred at 50 °C for 48 h. The polymer films were prepared by dropping 100 μL solution onto clean glass slides and evaporating the solvent in air at room temperature. The polymer films were dried in a vacuum oven at room temperature for a week to remove the solvent remnants. The thickness of the polymer films was between 1.0 and 1.1 μm, which was measured by a Dektak 6 M surface profilometer.

2.4. Nuclear magnetic resonance (NMR)

The chemical structures of the synthesized PBS, PBF and PBSFs were investigated by a 400 MHz NMR spectrometer (Bruker 400M) using deuteriochloroform as the solvent at room temperature.

2.5. Gel permeation chromatograph (GPC)

The number- and weight-average molecular weights (M_n, M_w), and the polydispersity index (PDI) were measured by GPC (PLGPC50). The solvent used was chloroform, and the flow rate was 1 mL/min; the measurement temperature was 40 °C. Narrow linear polystyrene (PS) is used as the standard sample.

2.6. Differential scanning calorimetry (DSC)

DSC experiments were performed by using a Perkin-Elmer diamond 8000 differential scanning calorimeter for observing the crystallization

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