



Structure and characterization of random aliphatic–aromatic copolyester

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ABSTRACT

New aliphatic–aromatic copolyester containing three different aliphatic comonomers: butylene adipate, butylene succinate and butylene glutarate, and one aromatic butylene terephthalate comonomer, all of petrochemical origin, has been synthesized (PBASGT) and its molecular characteristic, crystallization aptitude and morphology were examined by various techniques. Using the assignment of ¹H NMR resonances due to homogeneous and heterogeneous dyads, the average block lengths were determined and it was found that PBASGT is a nearly random copolymer. During solidification only butylene terephthalate blocks are able to crystallize. However, some of the reflections from crystal planes are shifted towards lower diffraction angles as compared to butylene terephthalate homopolymer. Nonisothermal crystallization revealed the peak of crystallization at 37 °C while melting of those crystals occurred at 108 °C, in contrast to a homopolymer of butylene terephthalate (228 °C). PBASGT crystallizes in the form of thin fibrous crystals, few nanometers thick, which is the main factor influencing the depression of its melting temperature. Although the crystallinity degree is low (around 20%) the crystals form spherulitic aggregates filling the entire volume of the material. The chemical structure, morphology and crystallization behavior of PBASGT were compared with commercial aliphatic–aromatic copolyester of butylene terephthalate and butylene adipate (PBAT), Ecoflex. It appeared that, in contrast to aliphatic part of PBAT, aliphatic part of PBASGT is unable to crystallize, when annealed below room temperature. It appeared also that, similarly as PBAT, PBASGT is biodegradable.

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1. Introduction

Due to increasing awareness about the global environment a range of new polymeric materials is being developed, especially biodegradable polyesters. Contrary to conventional polymers, biodegradable polyesters can be converted into biomass or into carbon dioxide and water by microorganisms in their environment [1,2]. The commercially available example is poly(lactic acid) (PLA). Even though it is not the only one available on the market, there are drawbacks, which do not allow polyesters to be used in

many applications (e.g. [3]). To improve the physical properties without sacrificing the biodegradability, introducing aromatic units into main chains of aliphatic polyesters has been explored and aliphatic–aromatic copolyesters (ACC) have been developed [4,5]. The effort was made to obtain materials with varied composition by changing types of aliphatic and aromatic comonomers or even introducing few types of aliphatic comonomers into macromolecules [6–8].

Aliphatic–aromatic copolyesters are products that are based on components from petrochemical origin. Most of them are biodegradable under rigorous condition of sufficiently short aromatic sequences. In the literature several aliphatic–aromatic copolyesters are described such as: random poly(butylene adipate-co-terephthalate) (PBAT)

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[3,9–12], random poly(butylene succinate-co-terephthalate) (PBST) [13], random poly(butylene adipate-co-succinate-co-terephthalate) (PBAST) [6,7], and copolymer of random poly(butylene adipate-co-succinate-co-glutarate)-with blocks of poly(butylene terephthalate) (PBASG-b-PBT) [8]. It is worth to underline that all above mentioned publications concern random copolymers except the last one [8]. Owing to the presence of PBT blocks the PBASG-b-PBT copolymer exhibits strong crystallization ability but its susceptibility to biodegradation is strongly reduced [14]. It can be noticed that in most of the compositions adipate units are present. Thus, the knowledge about copolyesters with adipate units led to the development of commercial PBAT-Ecoflex® (BASF AG).

The exploitation of those materials depends on their solidification mode either by vitrification or by crystallization. Often two glass transition temperatures can be noticed: one for aliphatic component at -40 to -30 °C and the second for aromatic component at $+50$ to $+65$ °C. Solidification can also occur by crystallization. The distribution of comonomer units plays a crucial role in crystallization. It is rather obvious that shortening of sequences that are able to crystallize decreases the ability of AAC to crystallize. The amorphous AACs with the main glass transition temperature much below room temperature become useless for many applications. On the other hand too long crystallizing sequences may create problems with biodegradability of AACs.

In the literature there are no reports on synthesis of a random copolyester consisting of all four butylene units: adipate, succinate, glutarate and terephthalate.

Our study focuses on such a novel copolyester of poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT), with a random distribution of comonomers, synthesized by us. Our synthesis was essentially based on a two-step melt polycondensation method that was described and used originally for the synthesis of poly(tetramethylene succinate) with terephthalic acid [15] and for the synthesis of a block copolymer of poly(butylene terephthalate) with poly(butylene cyclohexenedicarboxylate)-*b*-poly(ethylene glycol) [16]. We intended to synthesize a copolymer that will be able to crystallize yet biodegradable. Further, we planned to characterize the crystallization and the development of supermolecular structures of the copolyester. It has to be emphasized that for applications such as melt-blowing of nonwovens, fiber spinning, film extrusion, film blowing or injection molding fast solidification is required to maintain high yield of melt processing.

The pilot experiments demonstrated that the copolymers were able to crystallize despite their complex chemical structure and the randomness of comonomer distribution although it was unclear whether co-crystallization of different comonomers takes place or not. The particular aims of this study are:

- to determine the distribution of comonomer units along macromolecular chains of PBASGTs and correlate their crystallization ability with sequence distribution;
- to characterize habits of PBASGTs to form crystals;
- to characterize supermolecular structures of PBASGTs.

The structure and some of the properties of the synthesized PBASGT were compared to the structure and properties of a commercial aliphatic–aromatic copolyester PBAT produced by BASF AG.

2. Experimental section

2.1. Raw materials

Dimethyl terephthalate (DMT) was purchased from Mogilev (Belarus); 1,4-butanediol (BD) was obtained from PPH Standard Co., Ltd. (Poland); and Uniestrol was delivered by Pilot Plant “Organika” Co., Ltd. (Poland). The Uniestrol is a mixture of dicarboxylic acid dimethyl esters, which contain 31% of dimethyl adipate (DMA), 14% of dimethyl succinate (DMS), and 55% of dimethyl glutarate (DMG). Tetrabutyl orthotitanate ($\text{Ti}(\text{OBu})_4$) was supplied by Sigma-Aldrich® Co. All chemicals were used without purification.

For comparison, Ecoflex® supplied by BASF AG and poly(butylene terephthalate) (PBT) supplied by Goodfellow in the form of pellets were used.

2.2. Synthesis of copolyesters

The scheme of reactions leading to copolyesters is presented in Fig. 1. Copolymers were prepared by a two-step melt polycondensation method. Exemplary recipe for PBASGT with aromatic comonomer molar content of 40% is as follows: into 30 dm³ acid-proofclave warmed to 140 °C with nitrogen atmosphere were introduced 3500 g of DMT, 5600 g of BD, 4400 g of Uniestrol and 2.5 g of $\text{Ti}(\text{OBu})_4$ as a catalyst. Theclave was then warmed up to the temperature in the range from 165 °C to 225 °C under atmospheric pressure. Simultaneously methanol was distilled out theclave. The transesterification was completed within about 100 min. The excess of 1,4-butanediol ensures a high yield (90%) of the first stage of the process and prevents escaping the volatile components in the second stage, when the pressure is decreased.

Subsequently, 3.5 g $\text{Ti}(\text{OBu})_4$ was added, the pressure was slowly decreased to 0.53 hPa and the reaction temperature was raised to 250 °C. Excess of 1,4-butanediol was distilled in this period. Total time for the polycondensation process was 120 min. The molten polymer was extruded in the form of 2–3 mm thick strings and pelletized.

2.3. ¹H NMR

To investigate the composition of PBASGT and the sequence distribution of comonomers, ¹H NMR measurements were conducted under ambient temperature using a Bruker Avance DRX500 spectrometer operated at a resonance frequency of 500 MHz. Copolyester pellets were dissolved in deuterated chloroform (CDCl_3).

Copolyester molar composition and sequence distribution of comonomers were obtained from the corresponding methylene proton resonance integrals.

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