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Effect of chain length of comonomeric diols on competition and miscibility of isodimorphism: A comparative study of poly(butylene glutarate-co-butylene azelate) and poly(octylene glutarate-co-octylene azelate)

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ABSTRACT

Two series of biobased even-odd aliphatic copolyesters, poly(butylene glutarate-co-butylene azelate) (PBGA) and poly(octylene glutarate-co-octylene azelate) (POGA), were prepared from even diol of 1,4-butanediol or 1,8-octanediol with odd diacids of glutaric acid and azelaic acid, respectively. These even-odd copolyesters can cocrystallize within the entire composition range despite being random, displaying a pseudo-eutectic point when their melting points are plotted as a function of composition. DSC and WAXD studies confirmed the isodimorphic behavior for PBGA and POGA. Then, the competition and miscibility in isodimorphism between PBGA and POGA were comparatively investigated. It demonstrated that the chain length of comonomeric diols can exert a considerable influence on the isodimorphic behavior of copolyesters. The comonomeric diol with longer chain shows greater ability in bridging the gap of competition between comonomer units. This insight contributes to predicting the composition of crystal transition point for isodimorphic copolyesters based on the molecular structure. For miscibility, the mutual insertion of comonomer units in the copolyester containing longer comonomeric diol is easier than in the copolyester with shorter comonomeric diol. Furthermore, a close dependence between the mechanical properties with competition and miscibility in such even-odd copolyesters was observed and discussed. The composition dependence of yield stress presents a similar pseudo-eutectic behavior that matches those exhibited by T_m versus composition, and that of the elongation at break shows an opposite tendency. In conclusion, our work here not only clarifies the effect of chain length of comonomeric diols on competition and miscibility of isodimorphism in the even-odd copolyesters, but also provides guidance in the selection of comonomeric diol for preparation of aliphatic copolyesters with desirable performances.

1. Introduction

Driven by the increasing demand to address environmental concerns and to replace traditional fossil-based polymers, the availability of novel biodegradable materials has attracted much attention both in academia and industry [1–4]. Aliphatic polyester poly(alkylene dicarboxylate)s are known to be one of the most significant degradable materials due to their notable advantageous properties including excellent biodegradability, biocompatibility, and nontoxicity [5]. Among these, even-even poly(alkylene dicarboxylate)s synthesized from even diacids with even diols have been extensively studied in view of its good mechanical strength, representative poly(ethylene succinate), poly(butylene succinate) and poly(hexamethylene adipate) [6–11]. However, even–even poly(alkylene dicarboxylate)s are characterized by slow biodegradation rate and poor toughness due to their high crystallinity, which limit their applications in many fields [12]. In order to obtain materials with tailorable and tunable properties, many efforts are currently focused on designing novel even–odd random copolymers [13–15]. In this way, the hydrophobicity, crystallinity and degradation rate of degradable materials can be controlled by substituting the monomers or adjusting feed ratios of comonomers.

Compared with even diacids, odd diacids used as monomers could enhance degradation rate of polyester [16], since odd carbon atoms make packing of polymer chains difficult and thereby lead to reduced crystallinity and increased degradability. In recent years, some emerging odd diacids have been explored for the synthesis of polyesters [17,18]. Azelaic acid, one of the naturally occurring dicarboxylic acids, has been industrially produced by ozonolysis cleavage of the alkene double bond of oleic acid through an adequate biocatalysis-based process [19,20]. Azelaic acid-based Nylon-6,9 has been characterized by

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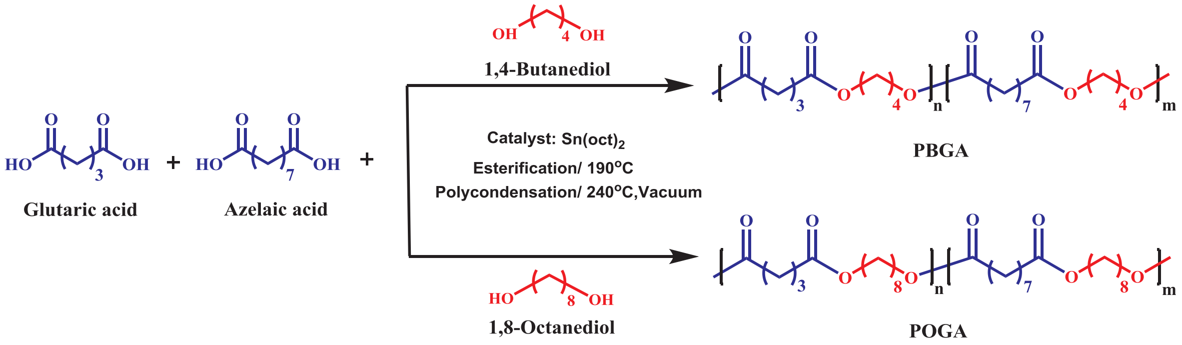

Scheme 1. Synthesis of poly(butylene glutarate-co-butylene azelate) (PBGA) and poly(octylene glutarate-co-octylene azelate) (POGA) copolyesters following the two-step melt esterification and polycondensation process.

high stability and low water absorption, and polyesteramide elastomers were found to have reinforced moduli [21,22]. Apart from azelaic acid, glutaric acid is also a potential odd comonomer derived from renewable resources, which has a similar chemical structure with only difference in the chain length [23]. Therefore, it seems interesting to prepare new aliphatic copolyesters based on azelaic and glutaric acids for increasing the range of biodegradable materials and generating a set of products with easily tunable properties. In addition, compared to even diacids, odd analogues can induce a significant difference in thermal and mechanical properties as well as crystalline behavior for the copolyesters [24]. Up to date, however, the molecular conformation and polymer chain packing arrangement of even-odd copolyesters are still poorly understood. It is well known that some structural and thermodynamic properties are sensitive to the parity, even or odd, of the number of atoms contained in the molecular skeleton [15,16,25].

Random copolymers, with two different crystallizable units joined together at random, exhibit diverse phase behaviors in crystallization. Specially, cocrystallization behavior is an ideal crystalline state for random copolymers whose thermal and mechanical properties can be controlled without a significant loss of crystalline properties through the variation of the copolymer composition [26,27]. Cocrystallization includes two kinds of situations: isomorphism and isodimorphism, which depends on the miscibility of two components in crystal lattice [28]. In isodimorphism, two crystalline phases were observed in copolymers, each of which contained comonomer units as a minor component [29]. In this case, an increase in the content of the minor component in each crystalline phase is accompanied by a lowering of the melting and crystallization temperatures. Accordingly, complex structural and thermodynamic behaviors were presented in isodimorphism, which remained numerous issues to be clarified [30].

Regarding isomorphism, comonomers possess perfect miscibility, and thereby the copolymer system forms only one crystalline phase for the whole composition. The melting and crystallization temperatures of the copolymer increase or decrease linearly with increasing molar ratio of comonomer units. So actually, strict isomorphism is a very rare phenomenon. To the best of our knowledge, there are only four isomorphic copolyester systems, ε-caprolactone and 2-oxepane-1,5-dione copolyesters (PCL-OPD) [31], ε-caprolactone and ω-pentadecalactone copolyesters (PCL-DL) [32], poly(butylene succinate-co-butylene fumarate) (PBSF) copolymers [27], and our recently reported poly(hexamethylene glutarate-co-hexamethylene azelate) (PHGA) copolymers [33]. Our isomorphic system demonstrated that both comonomer units were perfectly miscible in a same crystal undergoing isomorphous substitution. In the report, two other even-odd copolyesters of poly(hexamethylene glutarate-co-hexamethylene pimelate) (PHGP) and poly(hexamethylene pimelate-co-hexamethylene azelate) (PHPA) based on even 1,6-hexanediol and other odd alkyl diacids with different chain length were also prepared for comparative study. However, both PHGP and PHPA copolyesters present isodimorphic behaviors. It is the first time to uncover that the chain length of comonomeric diacids can exert a decisive influence on the formation of isodimorphism and isomorphism behavior. The only slight change of chain length of comonomeric diacids generates so large difference in cocrystallization behavior, which exhibits unique structure–properties correlations in such even-odd copolyesters. Consequently, the detailed cocrystallization behavior of poly(alkylene glutarate-co-alkylene azelate) matrices with varied chain length of even comonomeric diols is desired to be investigated.

In these contexts, two series of biobased even-odd poly(butylene glutarate-co-butylene azelate) (PBGA) and poly(octylene glutarate-co-octylene azelate) (POGA) copolyesters with progressive variation in composition were designed to be synthesized for the first time. And the isodimorphic behaviors of these two series of even-odd copolyesters were comparatively investigated. The main motivations of this article are to clarify the effect of chain length of comonomeric diols on the competition and miscibility of isodimorphism, and to give an insight into the mechanism of how the comonomeric diol through the competition and miscibility of isodimorphism regulates the physical properties.

2. Experimental

2.1. Materials

1,4-butanediol (99.0%), 1,8-octanediol (99.0%), glutaric acid (99.0%), and azelaic acid (99.0%) were purchased from J&K Chemical. Stannous octoate (Sn(Oct)$_2$, > 96.0%), was purchased from Sigma-Aldrich. Chloroform (99.0%) and ethanol (99.0%) were purchased from Sinopharm Chemical Reagent Co.,Ltd. All the materials were used as received without further purification.

2.2. Synthesis of copolyesters

Even-odd copolyesters poly(butylene glutarate-co-butylene azelate) (PBGA) and poly(octylene glutarate-co-octylene azelate) (POGA) were synthesized by the two-step melt polycondensation method containing esterification and polycondensation, as depicted in Scheme 1. (detailed polymerization condition was described in Supporting Information).

2.3. Characterization

Gel permeation chromatography (GPC): Number- (M_n) and weight-average (M_w) molecular weights and dispersities ($Đ = M_w/M_n$) were determined by gel permeation chromatography (GPC) relative to linear polystyrene (GPC$_{PSt}$) from calibration curves of log M_n vs elution volume at 25 °C using tetrahydrofuran (THF) as solvent (1.0 mL/min), the Ultrastyragel® columns, a differential refractometer detector, and Waters 1515 HPLC system. The concentration of polymer solution was 2.0 mg/mL.

Nuclear magnetic resonance: ^{1}H NMR and ^{13}C NMR spectra were