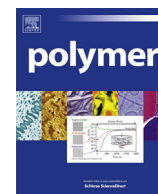




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Aliphatic copolyester with isomorphism in limited composition range

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ABSTRACT

A series of random poly(hexamethylene succinate-co-hexamethylene fumarate) (PHSF) samples was synthesized through a two-step reaction process, and their properties were systematically studied using wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR). The crystal modification of polyester changes from monoclinic to orthorhombic after substituting hexamethylene succinate (HS) units by hexamethylene fumarate (HF) units, and the chain conformation changes from all-trans to gauche. The copolyesters were found to be in a particular case as strict isomorphism in a limited composition range, adopting the same crystal modification when HF content ranged from 19 to 100 mol%. The melting point of the copolyester increases almost linearly with increasing molar content of HF, and the melting enthalpy hardly changes. Interestingly, FTIR results suggest that a special hydrogen-bonding interaction, in “C=C–H···O=C–C=C” form, forms in the crystalline phase of PHSF and poly(hexamethylene fumarate) (PHF). The strong hydrogen-bonding interaction might be responsible for the transformation of conformation from all-trans to gauche in hexamethylene segments, and triggers the variation of crystal modification.

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1. Introduction

Isomorphism represents two or more different substances with similar structure can co-crystallize into a single crystal unit cell. This phenomenon has been commonly observed in both small molecular and macromolecular system, which provides a unique view for studying the crystallization theory and fabricating functional structure [1–5]. The concept of isomorphism in polymer field was first arisen by Natta et al. [6,7]. Later, Allegra and Bassi [8] stated two fundamental requirements for the formation of isomorphism in crystalline polymer system: first, different types of monomers must approximately have the same shape, occupy the similar volume; second, the conformation of the two types of monomers must be compatible with each other. Random copolymerization is an easy and convenient way to randomly place different monomers on polymer chains, which benefits for the formation of isomorphism. Therefore, until now lots of random copolymer serials exhibiting isomorphism phenomena have been

observed, such as styrene/*p*-fluorostyrene copolymer [7], ethylene/ α -olefin copolymers [9], polyhydroxyalkanoates [10,11], etc.

Linear polyesters have attracted great attention in recent decades due to their excellent mechanical properties and easy biodegradability. Meanwhile, it is convenient to achieve chain structure with required composition for various applications just through changing the feeding monomers during synthesis. Hence a great amount of random copolyesters have been prepared, studied and used. Among them, isomorphism phenomena have been reported in poly(ethylene terephthalate-co-ethylene 2,6-naphthalate) [12], poly(butylene succinate-co-ethylene succinate) [13], poly(hexamethylene adipate-co-butylene adipate) [14], poly(hexamethylene sebacate-co-hexamethylene suberate) [15], etc. Nevertheless, isomorphic system in strict sense demands: only a unique crystal modification exhibits for the whole composition; different monomeric units are equally distributed in both the amorphous and crystalline regions. When more than one crystalline phase containing two types of units are detected, depending on the composition and/or thermal or mechanical treatment, it should be exactly named as isodimorphism or isopolymorphism. Often, for a copolyester system consisted of two types of monomeric units, the homopolymer of each type of monomeric unit respectively occupies its particular crystal structure. Randomly introducing another monomeric unit (comonomeric unit) into the

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homopolymer, the melting point and crystallinity decrease with increasing comonomeric content when the copolymer adopts the same crystal modification as its original homopolymer. While the melting point and crystallinity turn to increase with more comonomeric content once the copolymer adopts the crystal modification as homopolymer of the comonomeric units. The copolymer could even display a total amorphous state in a certain composition range. The distribution of comonomeric units in amorphous and crystalline regions is not the same. Thus, most of the reported copolyesters are not exact isomorphism systems in the whole composition range but either quasi-isomorphism in part composition range, or isodimorphism, or isopolymorphism.

Up to our knowledge, it could be summarized that only three possible isomorphous linear polyester systems in the whole composition range have been reported until now, ϵ -caprolactone and 2-oxepane-1,5-dione random copolyesters [16], ω -pentadecalactone and ϵ -caprolactone random copolyesters [17], and poly(-butylene succinate-co-butylene fumarate) (PBSF) random copolymers [18]. The two former ones exhibit decreasing melting point and enthalpy value with increasing ϵ -caprolactone content, which was due to the quite different molecular structure between comonomeric units. The latter one, PBSF, was reported by our group recently through substituting the succinyl units by fumaryl units in poly(butylene succinate) (PBS). Succinyl unit and fumaryl unit possess almost the same spatial volume; the succinyl units in crystalline region of PBS have been reported to adopt the trans conformation, which is just the same conformation as fumaryl unit. Experimental results confirmed the formation of isomorphism in strict sense in the whole composition range [18]. Besides, the chain conformation in melt state takes more probability to adopt trans conformation at dicarboxyl position on polymer chains with more fumaryl units, closing to that in crystal state, and results in the decreased entropic barrier during crystallization, which accelerates the crystallization rate and provides a method to explore polymeric nucleating agents based on epitaxial crystallization theory. Beyond that, after substituting of succinyl units by fumaryl units in poly(-alkylene succinate), the conformation of alkylene segments in the crystalline region might be affected and changes accordingly, then the copolyesters would deviate from the isomorphism in strict sense in whole composition range. So the study on the crystallization behavior of poly(alkylene succinate-co-alkylene fumarate) specimens besides PBSF should be attractive and will uncover more details on polyester crystallization.

In this work, we studied a series of aliphatic random copolyesters of hexamethylene succinate (HS) and hexamethylene fumarate (HF). The incorporation of HF into poly(hexamethylene succinate) (PHS) chains induces the copolyester to form the same crystal modification as poly(hexamethylene fumarate) (PHF) at even 19 mol% HF content. Furthermore, the poly(hexamethylene succinate-co-hexamethylene fumarate) (PHSF) exhibited isomorphism in a limited composition range where HF content ranged from 19 to 100 mol%.

2. Experimental section

2.1. Materials

Hexamethylene glycol (purity > 98%) and fumaric acid (purity > 99.5%) were purchased from Aladdin Reagent Company (Shanghai, China). Succinic acid (purity > 99.5%) was kindly supplied by Hexing Chemical Corporation Limited (Anqing, China). Tetra-*n*-butyl titanate (TBT), chloroform and methanol were analytical reagent and purchased from Beijing Chemical Reagent Factory. All reagents were used as received.

2.2. Synthesis and purification of polyester

PHSF with different HS/HF molar ratios and homopolyesters were synthesized via a two-stage reaction of esterification and polycondensation in molten state. Similar process can be found in literature [18,19]. Tetra-*n*-butyl-titanate and *p*-hydroxyanisole (each was 0.5 wt % relative to the total reactants) were used as catalyst and free radical inhibitor during the reaction, respectively. The final products were dissolved in chloroform and centrifuged to remove impurities, then precipitated in excess amount of cold methanol. The precipitates were collected and dried in vacuum at 50 °C for two days before use.

2.3. Measurements

The molecular weights (M_n and M_w) of synthesized polyesters were determined by Viscotek-M302 TDA Multiple testing gel chromatography system, the measurements were carried out at 40 °C with a Shimadzu GPC-804C column at a flow rate of 1.0 mL/min, chloroform was used as the eluent. Fluka polystyrene standards were used to obtain the calibration curve. The compositions of polyesters were determined by ^1H NMR spectrometer (JEOL, ECA-300M) with chloroform-*d* as solvent and tetramethylsilane as reference. Highly-oriented fiber samples of the polyesters were prepared through the melt spinning and cold stretching method. Initial fiber was prepared using a Rosand 2000 capillary rheometer at a shear rate of 60 s $^{-1}$ at 140 °C, the diameter of capillary was 1 mm. Then the initial fiber was stretched to six times length using a home-made drawing mill at room temperatures. Single crystals of PHF were grown from methanol/chloroform (1/1, v/v) solution with a concentration of 0.02 wt% at 50 °C for 48 h from homogenous solution.

Both nonisothermal and isothermal crystallization behaviors of the samples were performed on a differential scanning calorimeter (DSC, NETZSCH 204 F1) equipped with intercooler as cooling system under an argon atmosphere. Atomic force microscopy (AFM, Veeco Multimode-IIIa) and transmission electron microscopy (TEM, FEI Tecnai G 2 F20) were utilized to characterize the morphologies and electron diffraction patterns of single crystals of PHF, respectively. The wide angle X-ray diffraction (WAXD) (including temperature-dependent WAXD) analyses were performed on a PGENERAL XD-3 instrument with a graphite-filtered Cu radiation. The supplied power was 1.4 kW. The scanning was carried out with 2 θ from 10° to 40° with a step interval of 0.01° at a scanning rate of 2°/min. Two-dimensional WAXD patterns of oriented polyester fibers were measured on a Rigaku R-Axis Spider instrument with a Mo radiation at 25 °C. FTIR spectra were recorded on a Nicolet-560 IR spectrometer by signal averaging over 32 scans at a resolution of 4 cm $^{-1}$ in the wavenumber range of 4000–400 cm $^{-1}$. The experimental density was measured by a solid densimeter (ED-300A).

3. Results and discussion

3.1. Characterization of polyesters

The comonomer compositions of synthesized copolyesters were calculated from ^1H NMR spectra using the relative intensities of proton peaks arising from HS and HF repeating units. Fig. 1 shows the ^1H NMR spectrum of PHSF57, in which succinate and fumarate show characteristic peaks at 2.616 and 6.844 ppm, respectively. The content of HF units in PHSF57 was calculated from the integrated area of ^1H peak at the two corresponding positions. The compositions of the synthesized polymers are summarized in Table 1. The actual composition deviates slightly from the succinic acid/fumaric acid feeding ratio. Herein, the samples are referenced using the

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