Unique isodimorphism and isomorphism behaviors of even-odd poly(hexamethylene dicarboxylate) aliphatic copolyesters

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Abstract

Three series of even-odd aliphatic copolyesters, poly(hexamethylene gluarate-co-hexamethylene pimelate) (PHGP), poly(hexamethylene pimelate-co-hexamethylene azelate) (PHPA), and poly(hexamethylene gluarate-co-hexamethylene azelate) (PHGA), were firstly synthesized derived from even diol of 1,6-hexanediol with odd diacids of glutaric acid, pimelic acid or azelaic acid, respectively. Then, their cocrystallization behaviors were systematically investigated by DSC, WAXD, and POM techniques. It is found that both PHGP and PHPA showed isodimorphism with a characteristic eutectic behavior observed from the plot of melting point versus composition, however, PHGA exhibited strict isomorphism in the whole composition range without a eutectic point. WAXD studies also confirmed the unique isodimorphism and isomorphism behaviors for even-odd copolyesters. The only slight change of the methylene number in alkyl unit of comonomers could generate so large difference in crystallization behavior, which exhibits unique physicochemical properties and structure-properties correlations in such even-odd copolyesters. Furthermore, the difference in cocrystallization miscibility effect of comonomers was analyzed by thermodynamics based on the defect Gibbs energy calculated from Wendling-Suter model. For PHGP and PHPA, the comonomer units have better miscibility in the case of the incorporation of shorter unit into the longer unit crystal than the opposite case. By contrast, in the case of PHGA, the HG and HA units are perfectly miscible in a same crystal lattice with only a little difference in crystal cell dimensions due to the identity of chain conformation of HG and HA units during packing into the crystal lattice. Finally, a model of crystal lattice structure of copolyesters was proposed to better understand the difference in cocrystallization miscibility effect of comonomers between isodimorphism and isomorphism.

Keywords: Even-odd copolyester; Isomorphism and isodimorphism; Cocrystallization miscibility

1. Introduction

The fossil resource depletion and environmental pollution have become the two primary challenges. Biodegradable polymers are materials with the required ecological advantages to offer alternative solutions for such challenges.¹⁻³ Among these, aliphatic polyesters undoubtedly are considered to be the most preferable classes, as they can be prepared from renewable resources and can be biodegraded into feedstocks with a low environmental impact.^{4,5} As one of the most promising polymers, poly(alkylene dicarboxylate)s have attracted more and more attention due to their favorable features of biodegradability and biocompatibility.⁶⁻¹¹ In order to obtain such materials with tunable properties, copolymerization has been a convenient way of controlling their crystallinity, hydrophobicity and degradation rate. As is well known, the characteristics of random copolymers can be modified to fit specific needs simply by introducing appropriate comonomeric units into the polymeric chains, varying their relative amounts, arrangement, and so forth.¹² 1,6-Hexanediol-based aliphatic copolyesters that are synthesized by polycondensation of 1,6-hexanediol and dicarboxylic acids have received increasing attention in virtue of their interesting properties, including biodegradability, melt processability and compostability.¹³⁻¹⁶ Recently, 1,6-hexanediol has been successfully produced from biomass-derived raw materials,¹⁷⁻¹⁹ which would further stimulate the growth of those polyesters. Furthermore, the even-even copolyesters which are synthesized by 1,6-hexanediol and even diacids have been extensively studied, and specifically poly(hexamethylene succinate-co-butylene succinate),²⁰ poly(hexamethylene sebacate-co-hexamethylene adipate),^{21,22} poly(hexamethylene succinate-co-hexamethylene adipate),²³ poly(hexamethylene sebacate-co-hexamethylene suberate),²⁴ poly(hexamethylene suberate-co-hexamethylene adipate),²⁴ poly(hexamethylene adipate-co-butylene adipate)²⁵, poly(hexamethylene succinate-co-ethylene succinate)²⁶ and poly(hexamethylene succinate-co-hexamethylene fumarate)²⁷ are representative examples. 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.²⁸⁻³²

In recent years, some emerging odd diacid and/or diol monomers are explored for the synthesis of polyesters.^{33,34} Azelaic acid, one of the naturally occurring dicarboxylic acids, has been industrially produced by ozonolysis cleavage of the alkene double bond of oleic acid³⁵ and can be directly extracted in barley, rye, sorghum, or wheat through an adequate biocatalysis-based process.³⁶ Azelaic acid-based Nylon-6,9 was characterized by high stability and low water absorption,³⁷ and polyesteramide elastomers were found to have reinforced moduli.³⁸ Therefore, it

seems interesting to prepare new aliphatic copolyesters based on azelaic acid for increasing the range of biodegradable materials and even generating a set of products with easily tunable properties. Apart from azelaic acid, pimelic acid and glutaric acid are also potential comonomers with odd number of methylene units in the molecule, which have similar chemical structure with only difference in the chain length.

Several works have recently been addressed to study the aliphatic copolyesters based on these odd diacids,^{31,32,39-42} however, there has been no attempt to create new even-odd copolyesters derived from 1,6-hexanediol and azelaic acid, pimelic acid or glutaric acid. The odd-chain segments of polyesters make packing of polymer chains difficult as compared to the even segments, and consequently lead to reduced crystallinity and increased biodegradability as it depends to a large extent on polymer crystallinity.⁴³

Cocrystallization is an ideal crystalline state for random copolymers whose thermal and mechanical properties can be controlled without significant loss of crystalline properties through the variation of the copolymer composition. Cocrystallization behavior includes two kinds of situations: isodimorphism and isomorphism,^{44,45} which depends on the miscibility extent between comonomer units.⁴² In isodimorphism, the comonomer units need have similar chemical structures and occupy approximately the same volume, therefore the comonomer units crystallizes into the crystalline structure of one comonomer and changes over to the crystalline structure of the other comonomer at an intermediate composition. Fortunately, isodimorphism phenomenon is easily observed for many copolymers. However, for isomorphism, except the formation conditions for isodimorphism, some more rigorous requirements must be met: the crystalline phase of parent homopolymers should be analogous in the chain conformation, as well as in lattice symmetry and dimensions; the excess free energy for cocrystallization of the comonomer units into the resulting crystalline structure is very low.⁴⁶ In a strict sense, isomorphism means that the copolymer system forms only one crystalline phase whose lattice parameters gradually change with composition from the crystal lattice of one homopolymer to that of the other. So actually, strict isomorphism is a very rare phenomenon which deserves investigating in depth. Up to now, to the best of our knowledge, there are only three isomorphism copolyester systems, that is, ϵ -caprolactone and 2-oxepane-1,5-dione copolyesters (PCL-OPD),⁴⁷ ϵ -caprolactone and ω -pentadecalactone copolyesters (PCL-DL),⁴⁸ and poly(butylene succinate-co-butylene fumarate) (PBSF) copolymers⁴⁹, have been reported in the whole composition range. Nevertheless, all the three reported examples only elucidated a single copolymer system showing isomorphism. A deep comparative study between the isodimorphism and isomorphism behaviors from the point of view of the miscibility extent in different comonomers

are needed to be carried out in order to comprehensively understand the mechanism of how does the chemical structures of comonomers regulate the cocrystallization behavior of aliphatic copolyesters. Furthermore, the cocrystallization behavior of even-even poly(alkylene dicarboxylate)s have been extensively studied in past,^{21-25,27} however, the exploration for the cocrystallization behavior of even-odd poly(alkylene dicarboxylate)s is not nearly enough. As a critical influencing factor, the even-odd effect can exert remarkable influence on the crystal structure and thermal behavior of aliphatic copolyesters. Therefore, some special properties and structure-properties correlations are expected to be possessed by even-odd copolyesters.

In this study, we firstly synthesized three series of even-odd copolyesters with progressive variation in composition derived from even 1,6-hexanediol and odd diacids (i.e. glutaric acid, pimelic acid or azelaic acid), that is, poly(hexamethylene gluarate-co-hexamethylene pimelate) (PHGP), poly(hexamethylene pimelate-co-hexamethylene azelate) (PHPA) and poly(hexamethylene gluarate-co-hexamethylene azelate) (PHGA). As we known, the physical properties and biodegradability of polyesters are greatly dependent on the spherulite morphology, crystal structure and degree of crystallinity.¹⁰ Therefore, apart from the synthesis and characterization of these even-odd copolyesters and their parent homopolyesters, the cocrystallization behavior and morphology are systematically investigated. The main motivation of this contribution is to reveal a new system of strict isomorphism which is a very rare crystallization phenomena for copolymer based on PHGA and further introduce the isodimorphic copolyesters of PHPA and PHGP with the aim to comparatively investigate the isodimorphism and isomorphism behaviors from the perspective of the miscibility extent of comonomers based on the thermodynamics analysis. It is expected that the results presented herein will shed some insight on the relationships between the chemical structure and physical properties for the even-odd aliphatic copolyesters.

2. Experimental

2.1 Materials

1,6-Hexanediol (99.0 %), glutaric acid(99.0 %), pimelic acid (98.0 %), azelaic acid (99.0%) and stannous octoate ($\text{Sn}(\text{Oct})_2$, >96.0 %), were purchased from J&K Chemical. All the materials were used as received without further purification.

2.2 Synthesis of homopolyesters and copolyesters

Synthesis of random even-odd copolyesters and the parent homopolyesters, followed by the two-step melt polycondensation method containing esterification and polycondensation, as depicted in Scheme 1 (detailed polymerization condition was described in Supporting Information).

Scheme 1. Synthesis of poly(hexamethylene gluarate-co-hexamethylene pimelate) (PHGP), poly(hexamethylene pimelate-co-hexamethylene azelate) (PHPA) and poly(hexamethylene gluarate-co-hexamethylene azelate) (PHGA) copolyesters following the two-step melt esterification and polycondensation process

2.3 Characterization

Number- (M_n) and weight-average (M_w) molecular weights and dispersities ($D = M_w/M_n$) were determined by gel permeation chromatography (GPC) relative to linear polystyrene (GPC_{PSI}) from calibration curves of $\log M_n$ vs elution volume at 25 °C using tetrahydrofuran (THF) as solvent (1.0 mL/min), the Ultrastaygel® columns, a differential refractometer detector, and Waters 1515 HPLC system.

^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at a 400 MHz resonance frequency with 32 scans, a 4.0 s acquisition time and a 6.5 ms pulse width. ^{13}C NMR spectra were recorded at a resonance frequency of 100 MHz with 17 000 scans, a 1.4 s acquisition time and a 6.5 ms pulse width. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Deuterated chloroform (CDCl_3) was used as the solvent.

Calorimetric measurements were carried out by means of a DSC1 (Mettler-Toledo, Switzerland) instrument under a nitrogen atmosphere. The instrument was calibrated using high purity indium and zinc standards. Samples of approximately 5 mg sealed in aluminium pans were used to test the thermal behavior. The samples were heated for the first run from 25 to 100 °C for 5 min to erase the thermal history, then cooled to -60 °C at a rate of 10°C/min, and heated again for the second run from -60 to 100 °C at a rate of 10°C/min. The crystallization peak temperature (T_c) and its enthalpy (ΔH_c) were obtained from the DSC cooling run. The melting temperature (T_m) and

enthalpy of fusion (ΔH_m) were measured on the second heat scanning. In the isothermal melt-crystallization experiment, the samples were quenched to the desired crystallization temperature under a cooling rate of 60°C/min after being melted at 100 °C for 3 min. After the isothermal crystallization was fully completed, the samples were heated to the melt again at a rate of 10°C/min to study the subsequent melting behavior for the estimation of equilibrium melting point temperatures.

The crystalline structure of prepared homopolyesters and copolyesters were performed on a D max-Ultima + X-ray diffractometer with Ni-filtered Cu/K α radiation ($\lambda = 0.154$ nm). The operating target voltage was 40 kV and the tube current was 100 mA. The scanning speed was 2°/min in the angle 2θ range from 5° to 40°. The films (ca. 1 mm thickness) for WAXD measurements were hot-pressed followed by cooling to room temperature. Each sample before measurement was annealed for 24 h at 25°C.

The spherulitic morphologies of the homopolyesters and copolyesters were investigated using a Leica DM4500P polarized optical microscope that was connected with the Linkam THMS600 hot stage. The samples were placed between two cover glasses, melted and pressed at 110 °C for 2 min, then quenched to predetermined temperature for isothermal crystallization, and the representative spherulitic morphologies were recorded.

3. Results and discussion

3.1 Synthesis and characterization of even-odd copolyesters

Even-odd copolyesters poly(hexamethylene gluarate-co-hexamethylene pimelate) (PHGP), poly (hexamethylene pimelate-co-hexamethylene azelate) (PHPA) and poly(hexamethylene gluarate-co-hexamethylene azelate) (PHGA) with various compositions were synthesized, as shown in Table 1. The molecular weight values and the dispersities of the prepared copolyesters were estimated by GPC, which were also summarized in Table 1. The number average molecular weight (M_n) ranged from 20.2 to 41.3 k g /mol and the average molecular weight (M_w) ranged from 35.2 to 74.8k g /mol were obtained with dispersity index ($\mathcal{D}$) values from 1.62 to 2.39. In any case, final molecular weights were rather high to ensure film- and fiber-forming properties.

^1H NMR spectra were used to determine the exact compositions of PHGP and PHGA. Figure 1 displayed the ^1H NMR spectra of PHGP as an example (^1H NMR spectra of PHPA and PHGA were presented in Figure S1). The spectra were consistent with the expected structures. The relative areas of the peaks of H1 from gluarate moiety and H6 from pimelate moiety were used to determine the molar composition of the PHGP. However, the ^1H NMR spectra of PHPA were observed as overlapping peaks at $\delta = 2.27$ ppm. To further confirm the structure of the PHPA

and the correct peak assignments, ^{13}C NMR spectra was used since the vicinal carbons of the dicarboxylate units appeared well differentiated (i.e. 34.30 and 34.10 ppm for azelate and pimelate units, respectively). The areas of these two signals were employed to determine the molar composition of PHPA as shown in Figure S2. The obtained results were summarized in Table 1. It could be concluded that the composition of the copolyesters was in good agreement with those expected from the composition of the feed. This result indicated that the comonomer unit composition in these three series of copolymers can be easily controlled by adjusting the feeding molar ratio of dicarboxylic acids. Unfortunately, both ^1H and ^{13}C NMR spectra were insensitive to triad effects, and consequently the information of sequence distribution could not be obtained. However, random copolyesters were expected to be obtained in this study, not only due to the random polycondensation and transesterification reactions during preparation process, but also due to the similar reactivity of those reactants at high temperature.^{24,41}

Figure 1. ^1H NMR spectra for PHGP copolyesters.

Table 1. Copolymer composition, molecular weight, thermal parameters and degree of crystallinity of three series of copolyesters

Sample	Composition ^a (mol %)				DSC ^c							
	feed		product		Molecular weight ^b			cooling		2nd heating		
	HG	HP	HG	HP	M_n (kg/mol)	M_w (kg/mol)	$\bar{D}$	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c^d (%)
PHG	100	0	100	0	36.5	60.7	1.66	3.9	51.7	30.3	51.7	51.8
PHGP91	90	10	89.3	10.7	25.1	42.3	1.68	2.9	57.7	29.2	50.8	50.8
PHGP82	80	20	82.6	17.4	31.4	74.9	2.39	-1.1	63.0	29.0	50.4	50.2
PHGP73	70	30	70.9	29.1	22.5	38.5	1.71	5.3	55.5	32.4	51.8	52.2
PHGP64	60	40	62.1	37.9	20.2	35.2	1.74	11.1	56.0	34.2	53.6	53.7
PHGP46	40	60	42.2	57.8	37.8	66.0	1.75	18.2	57.3	40.4	54.7	54.5
PHGP28	20	80	21.8	78.2	35.1	63.8	1.82	21.4	59.2	44.4	57.0	56.1
PHP	0	100	0	100	27.2	48.1	1.77	23.8	63.4	49.9	60.8	59.2
	HP	HA	HP	HA	M_n	M_w	$\bar{D}$	T_c	ΔH_c	T_m	ΔH_m	X_c
PHP	0	100	0	100	27.2	48.1	1.77	23.8	63.4	49.9	60.8	59.2
PHPA91	90	10	89.0	11.0	26.5	47.8	1.52	21.5	67.2	45.4	59.3	58.6
PHPA82	80	20	77.4	22.6	24.3	48.5	2.00	18.3	77.9	40.5	58.1	57.1
PHPA73	70	30	68.7	31.3	22.1	38.5	1.74	19.8	73.8	41.7	58.9	58.9
PHPA64	60	40	58.2	41.8	26.1	51.4	1.97	20.9	77.3	42.3	59.2	61.4
PHPA46	40	60	38.3	61.7	31.3	53.6	1.71	28.0	67.0	46.8	64.8	63.9
PHPA28	20	80	21.3	78.7	35.6	64.1	1.80	29.1	65.0	47.8	68.8	64.2
PHA	0	100	0	100	40.5	74.8	1.85	33.7	77.3	53.3	87.2	68.0
	HG	HA	HG	HA	M_n	M_w	$\bar{D}$	T_c	ΔH_c	T_m	ΔH_m	X_c
PHG	100	0	100	0	36.5	60.7	1.66	3.9	51.7	30.3	51.7	51.8
PHGA91	90	10	89.3	10.7	21.2	35.4	1.67	4.3	55.1	32.8	58.0	52.9
PHGA82	80	20	79.2	20.8	33.6	64.6	1.92	6.2	65.9	34.1	64.0	55.4
PHGA73	70	30	69.4	30.6	21.2	41.6	1.96	10.8	69.7	37.2	67.2	55.7
PHGA64	60	40	62.1	37.9	27.2	44.0	1.62	14.5	72.8	39.0	70.0	55.9
PHGA46	40	60	41.3	58.7	41.3	72.1	1.75	23.0	80.3	43.4	78.8	57.6
PHGA28	20	80	21.9	78.1	28.4	46.9	1.65	29.3	77.6	48.8	82.7	64.2
PHA	0	100	0	100	40.5	74.8	1.84	33.7	77.3	53.3	87.2	68.0

^aMolar composition in the feed and in the product calculated by integration of ¹H NMR spectra or ¹³C NMR spectra. ^bNumber- and weight-average molecular weights and dispersities measured by GPC in THF against PS. ^cMelting (T_m) and crystallization (T_c) temperatures and their respective enthalpies (ΔH_m , ΔH_c) measured by DSC at heating/cooling rates of 10°C/min. ^dThe crystallinity (X_c) was measured by WAXD patterns of samples prepared by melt casting and crystallized during cooling in air.

3.2 Thermal behavior of even-odd copolyesters

Thermal analysis recorded by DSC for PHGP, PHPA, PHGA copolyesters and the parent homopolyesters is shown in Figure 2. The thermal data was summarized in Table 1. For each samples from PHGP, PHPA and PHGA, a single crystallization peak and a single melting peak were observed in non-isothermal crystallization and the subsequent melting process, respectively. It indicated that the resultant crystals formed in the non-isothermal crystallization process did not show obvious fractional crystallization. In the case of PHGP and PHPA, a depression of both melting temperature and enthalpy with increasing comonomer unit content was exhibited as shown in Figure 3 and Figure S3. The eutectic points for the two series of copolyesters were observed for PHGP82 and PHPA82 respectively. Therefore, the thermal analysis suggested that isodimorphism behavior existed in PHGP and PHPA.^{10,50,51}

Figure 2. The non-isothermal crystallization curves and subsequent melting curves: (a) crystallization curves of PHGP, (b) crystallization curves of PHPA, (c) crystallization curves of PHGA, (d) melting curves of PHGP, (e) melting curves of PHPA and (f) melting curves of PHGA.

Unlike the thermal phenomena of PHGP and PHPA, the melting temperature and enthalpy of PHGA increase with the increase of HA content, as plotted in Figure 3(c) and Figure S3(c). Moreover, the melting point versus copolymer composition is a perfect linear curve, with a slope of 0.23 °C/ (mol %). And the melting enthalpy monotonically also changes with composition. Absence of eutectic composition indicates that PHGA shows isomorphism behavior which is a rare phenomenon in random copolymers. As mentioned in the INTRODUCTION, strict isomorphism behavior has only been reported for three random copolyester systems in the whole composition range.

Figure 3. Composition dependences of T_m : (a) PHGP copolyesters, (b) PHPA copolyesters and (c) PHGA copolyesters.

3.3 Cocrystallization behavior of even-odd copolyesters

Further analysis of the crystalline structure of copolyesters at various comonomer compositions and the corresponding homopolyesters were performed with WAXD. To the best of our knowledge of PHG, PHP and PHA homopolyesters, their crystal lattice parameters have so far not been reported. However, an orthorhombic unit cell should be expected when aliphatic polyesters have an odd number of methylene groups in the diol and / or in the dicarboxylic units.^{41,52,53} In addition, chemical structures of these homopolyesters only differ in the number of methylene groups between ester groups, which imply that the copolyesters based on PHG, PHP and PHA satisfy the requirements of cocrystallization in the views of chemical structure and crystalline structure.⁵⁴

The WAXD patterns of PHGP, PHPA, PHGA and the corresponding homopolyesters were shown in Figure 4, where both the homopolyesters and copolyesters shown well defined crystalline diffraction peaks. As displayed in Figure 4(a), (b) and (c), the WAXD patterns of copolyesters are found to be quite similar to the corresponding homopolyesters, indicating that the introduction of comonomer unit did not change the crystal structure of parent

homopolyesters. Moreover, these three series of copolyesters had some shifts in all the reflection peaks positions with the increasing of comonomer unit content in the copolyesters. For PHGP and PHPA, an interruption could be observed between the continuous shifts, which represented the existence of two different crystal types in the two copolyesters. A similar variation tendency of WAXD patterns was also discovered in poly(hexamethylene sebacate-co-hexamethylene suberate) and poly(hexamethylene suberate-co-hexamethylene adipate), indicating isodimorphism behavior in nature.²⁴ The PHG crystal type was developed up to 20 mol% of the HP unit content, while the PHP crystal type was formed in PHGP with the HP unit content higher than 20 mol% as shown in Figure 4(a). It is valid that the crystal type of PHGP changes from PHG type to PHP type crystals at the composition of 20 mol % HG unit content which is accordance with the critical points from the thermal analysis discussed previously. Similarity, with increasing content of HA comonomer unit in the PHPA the crystal transition point was confirmed at PHPA20 as shown in Figure 4(b). However, for PHGA, the WAXD patterns change continuously from PHG to PHA with no interruption between the shifts as shown in Figure 4(c). This observation directly provides evidence that PHGA shows isomorphism behavior.

Figure 4. WAXD patterns of the three series of copolyesters (a) PHGP, (b) PHPA and (c) PHGA.

The degree of crystallinity (X_c) of those PHGP, PHPA and PHGA were also estimated from the WAXD patterns and summarized in Table 1. A systematic decrease of crystallinity with increasing comonomer unit content was observed for both PHGP and PHPA as shown in Figure S4 (a) and (b). The changeover point of the crystallinity with comonomer unit content is consistent with the eutectic point. On contrary, the crystallinity of PHGA monotonically increases with the increase of HA composition, as plotted in Figure S4(c). A linear dependence consistent with an isomorphism phenomenon is different compared to PHGP and PHPA.

Figure 5. d-spacing values of characteristic planes of the samples: (a) PHGP, (b) PHPA and (c) PHGA.

The d-spacing values of the crystalline planes of PHGP, PHPA and PHGA were calculated with the Bragg equation based on these WAXD patterns. The extent of cocrystallization can be qualitatively measured by the change of the lattice *d*-spacing in the WAXD pattern.^{55,56} As shown in Figure 5(a), the variation of the d-spacing values for some characteristic planes of PHGP with hexamethylene pimelate comonomer content (molar fraction) was presented. As a consequence of the corresponding comonomer unit incorporation in each of PHG and PHP crystal type lattice, d-spacing values of the crystal lattice change with the corresponding comonomer unit content. Evidently, the d-spacing values of PHG crystal type lattice tend to increase as the HP unit content increased from 0 to 20 mol%, indicating that PHG crystal unit cells have to enlarge crystalline lattice volume to accommodate the inserted HP unit that coexist with the PHG major component. On the other hand, the d-spacing values of PHP crystal type lattice remain unchanged irrespective of comonomer, indicating that PHP type crystal does not have to enlarge its unit cell in order to include the HG unit. Therefore, the HP crystal lattice has better miscibility with the inserted HG unit. For the case of PHPA, the d-spacing values of PHP crystal type lattice obviously decrease as the HA unit content increased from 0 to 20 mol%, while the d-spacing values of PHA crystal type lattice are not significantly varied with increasing the HP comonomer unit content in the bulk copolymer as shown in Figure 5(b). We consider that the lattice of PHP unit tends to contract its unit size to exclude as much HA comonomer unit as possible, whereas the lattice of PHA unit has better miscibility with the inserted HP unit. Based on the analysis of d-spacing values and the melting temperature data of PHGP and PHPA, the crystal type transitions are confirmed for PHGP82 and PHPA82. It indicates that the comonomer unit with longer chain (HP or HA) has stronger competitive ability in controlling the cocrystallization even when they are present in a minor proportion. This could arise due to the higher rigidity of the comonomer unit with longer chain when compared to the shorter comonomer. On the other hand, aliphatic polyesters with more methylene units are similar to polyethylene and the ester groups are analogous to defects for the crystal.⁵⁷ Consequently, the crystal lattice of homopolyester with lower density of ester groups is

more stabilized. However, when the d-spacing values are plotted as a function of HA comonomer content for PHGA, the d-spacings change linearly and continuously with the HA comonomer content, as shown in Figure 5(c). The smooth changeover of PHG lattice into PHA shows that HG and HA unit are perfectly miscible in a same crystal, that is, undergo isomorphous substitution.

3.4 Spherulitic Morphology of even-odd copolyesters

POM offers the opportunity to watch directly the formation of a crystalline phase when the sample is cooled from the melt.⁵⁸ Therefore, the effects of crystallization temperature and copolymer composition on the crystalline morphology of these copolyesters and the corresponding homopolyesters were further investigated because they influence the final physical properties and biodegradation characteristics. Initially, a series of optical micrographs for the homopolyesters during isothermal treatments at various crystallization temperatures were presented in Figure S5. The detailed analyses of spherulitic morphology for them were provided in the Supporting Information. For all these three series of optical micrographs of the homopolymers, ringed spherulites could not be detected in a wide temperature range even at very low degree of supercooling. Ringless spherulites maybe is a peculiarity of even-odd aliphatic homopolyesters.⁴⁰

To further investigate the influence of the comonomer composition on the spherulitic morphology and growth of copolyesters, Figure 6 illustrates a series of POM images for PHGP, PHPA and PHGA with various comonomer composition crystallized isothermally at almost the same degree of supercooling. Therefore, the influence of spherulitic morphology caused by the degree of supercooling could be ruled out. For PHGP, the average diameter of PHGP spherulites was smaller than that of neat PHG and PHP spherulites (Figure S5 (a4), (b4)) as shown in Figure 6 (a1)-(a6). The reduced spherulite size and increased nucleation of PHGP is obvious effect of the introduction of the comonomer unit in the crystal of corresponding homopolyesters. In addition, the depression of equilibrium melting temperature in PHGP drops the thermodynamic driving force required for the growth of spherulites.

In the case of PHPA, spherulites of PHPA91 and PHPA82 showed a coarser texture with an irregular edge (not perfectly circular) as shown in Figure 6 (b1) and (b2). It is attributed to that HA unit could not form perfect cocrystals with HP unit. The amorphous units intersperse among the crystalline lamellae, and thus result in the interference to the crystalline lamellae. This result is consistent with the analysis of d-spacing values for PHPA that the lattice of PHP unit is hard to accommodate the inserted HA unit and it tends to contract unit size to exclude as much HA as possible in the amorphous region, whereas the lattice of PHA unit has better miscibility with the

inserted HP unit.

For PHGA, the diameter and morphology of spherulites compared to that of neat PHG and PHA (Figure S5 (a4), (c4)) are similar, which may be attributed to the strict isomorphism behavior of PHGA. The fascinating morphologies of copolyesters in comparison with the parent homopolyesters identify their peculiar characteristics and suggest that further investigation is required to better understand their cocrystalline structure and thermal properties of even-odd aliphatic copolyesters.

Figure 6. The spherulitic morphologies of (a) PHGP copolyesters, (b) PHPA copolyesters and (c) PHGA copolyesters (scale bar = 50 μm).

3.5 Difference in cocrystallization miscibility effect of even-odd copolyesters

It is of great importance to investigate the miscibility extent of the two even-odd components in copolyesters in order to further understand the isomorphism and isodimorphism behavior of even-odd aliphatic copolyesters. As mentioned in Introduction, cocrystallization behavior in random copolymers consisting of two crystallizable components is largely subdivided into two cases, that is, isodimorphism and isomorphism.^{44,45} In the case of isodimorphism, the competitive effect derived from the two crystallizable components divides the cocrystallization into two types of crystal which belong to the two corresponding homopolymers respectively, therefore two crystalline phases are observed. For each crystal, the inserted unit is neither complete exclusion nor uniform inclusion with the host crystal. A problem of cocrystallization miscibility extent exists in the copolyesters. By contrast, in isomorphism, the different types of monomer units have approximately the similar crystalline structure

and occupy the same volume, the excess free energy of cocrystallization would be very small, and therefore the chain conformation of both corresponding homopolymers becomes perfect miscibility with either crystal lattice. On the whole, the miscibility between comonomer units decides whether the cocrystallization behavior is isodimorphism or isomorphism. As revealed by the DSC, WAXD and POM results, it is clear that PHGP and PHPA display an isodimorphism behavior, whereas PHGA exhibits a strict isomorphism phenomenon in the whole composition range.

Through the qualitative analysis of d-spacing values mentioned above, for PHGP and PHPA, we can draw the conclusion that the comonomer with less methylene units (shorter unit) is easily incorporated into the crystal lattice of longer unit, whereas the longer unit is hard to squeeze into the crystal lattice of shorter unit. By contrast, for PHGA, HG and HA unit have perfect miscibility with either crystal lattice. Furthermore, the quantitative study of cocrystallization miscibility effect could be carried out by thermodynamic analysis.⁴⁵ Therefore, we have determined the equilibrium melting temperatures of PHGP, PHPA and PHGA, which are important parameters for evaluating thermodynamics of copolymer crystallization. Based on the definition, the equilibrium melting point (T_m^0) is the melting temperature of lamellar crystal with an infinite thickness. Since it is impossible to obtain the final thermodynamically stable lamellar crystal in experiment due to the kinetic barriers, extrapolative method is used to estimate T_m^0 .⁵⁹ Among them, the Hoffman-Weeks procedure has been commonly used and accepted to estimate T_m^0 , particularly for the copolyester systems.^{12,45} Despite criticism, the Hoffman-Weeks method is still in use because of its general applicability, simplicity and straightforward experimental implementation. The Hoffman-Weeks equation is given by⁶⁰:

$$T_m = T_m^0 \left(1 - \frac{1}{r} \right) + \frac{T_c}{r} \quad (1)$$

where γ is the thickening coefficient, which depends on the lamellar thickness during the crystallization. According to this equation, a linear extrapolation of observed T_m as a function of crystallization temperature T_c intersects the equilibrium line $T_m = T_c$ at an intersection point, and this point is T_m^0 . The melting temperatures of tested copolymers and parent homopolymers are well fitted by straight regression lines, as shown in Figure S6.

Several well-known theoretical approaches have been developed to explain copolymer crystallization and can be largely classified into two categories: the comonomer exclusion⁶¹⁻⁶⁴ and the comonomer inclusion model.^{65,66} The attempts to explain crystallization in random copolymers began with the early work of Flory(exclusion theory).^{61,62} He supposed that the melting point depression was a result of the variation of configurational entropy of the system,

but he took no count of any enthalpy of mixing for comonomer units. Baur⁶⁴ improved the exclusion theory on the basis of the concept of “hindered equilibrium” introduced by Kilian⁶³, but its implementation generally underestimated the T_m^0 . Subsequently, the models of comonomer inclusion were proposed by Helfand and Lauritzen⁶⁵ and by Sanchez and Eby⁶⁶. They assumed that the comonomer units were included into the host crystal and acted as defects, however, it is still difficult to find consensus between theoretical prediction and the experimental data.^{59,67} Wendling and Suter⁶⁸⁻⁷⁰ have proposed a new general model combined the Sanchez–Eby model and the Baur model, who introduced a novel method to calculate the defect Gibbs energy of comonomer inclusions via the thermodynamic-integration approach. This theoretical approach has been tested with success on the crystallization behavior for many copolymer systems.^{12,58,71-74}

The theoretical method of Flory^{61,62} was given by:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \ln(1 - X_B) \quad (2)$$

where T_m^0 and ΔH_m^o denote the homopolymer equilibrium melting temperature and heat of fusion, respectively, R is the universal gas constant. X_B is the concentration of the minor comonomer B in the copolymer, and $\ln(1 - X_B)$ equals the collective activities of A sequences in the limit of the upper bound of the melting temperature.

The expression for the equilibrium melting temperature proposed by Sanchez and Eby⁶⁶ method was:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \ln(1 - X_B + X_B e^{-\epsilon/RT}) \quad (3)$$

Here, $X_B e^{-\epsilon/RT}$ equals the equilibrium fraction of B that repeat unit is able to crystallize, and ϵ is the excess free energy of a defect created by the incorporation of one B unit into the crystal.

The equation proposed by Baur⁶⁴ was:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} [\ln(1 - X_B) - \langle \xi \rangle^{-1}] \quad (4)$$

Where $\langle \xi \rangle = [2X_B(1 - X_B)]^{-1}$ is the average sequence index of homopolymer sequences in the melt.

A new general model proposed Wendling-Suter⁶⁸⁻⁷⁰, which was also able to describe the comonomer inclusion as well as the comonomer exclusion. The model was shown as follows:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \left[\frac{\epsilon X_{CB}}{RT} + (1 - X_{CB}) \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln \frac{X_{CB}}{X_B} + \langle \xi \rangle^{-1} \right] \quad (5)$$

Where X_{CB} is the concentration of the B unit in the crystal.

In the equilibrium comonomer inclusion, the concentration of comonomer B unit in the crystal formed by A unit

was given by:

$$X_{CB}^{eq} = \frac{X_B e^{-\epsilon/RT}}{1 - X_B + X_B e^{-\epsilon/RT}} \quad (6)$$

When X_{CB} in Eq. (5) is substituted by Eq.(6), Eq. (5) turns out to be simplified and becomes:

$$\frac{1}{T_m} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \left\{ \ln(1 - X_B + X_B e^{-\epsilon/RT}) - \langle \xi \rangle^{-1} \right\} \quad (7)$$

Where

$$\langle \xi \rangle^{-1} = 2(X_B - X_B e^{-\epsilon/RT})(1 - X_B + X_B e^{-\epsilon/RT}) \quad (8)$$

When $X_{CB} = X_B$ and $X_{CB} = 0 (\epsilon \rightarrow \infty)$, Eq. (7) reduces to the inclusion situation and the exclusion situation, respectively.

Figure 7. Comparison of the experimental equilibrium melting temperatures with the theoretical melting temperatures predicted by the Sanchez-Eby theory (orange curves), the Flory theory (green curves), Baur theory (blue curves) and the Wendling-Suter theory (black curves): (a) PHGP, (b) PHPA and (c) PHGA.

In Figure 7, the equilibrium melting temperatures calculated using the Flory, Baur, Sanchez-Eby and Wendling-Suter equations are shown in comparison to the experimental values acquired from the Hoffman-Weeks extrapolation. When cocrystallization behaviors of the three series of copolymers are analyzed with various models, it indicates that the Wendling-Suter theory predicts the experimental results better than the others. As expected, the Flory and the Sanchez-Eby equations lead to overestimation of the melting points. Meanwhile, Baur's prediction seems to be realistic. However, the predicted values were lower than the experimental. We attribute it to the fact that the second comonomer is neither complete exclusion nor uniform inclusion with the host crystal. Therefore, the Wendling-Suter model is employed to calculate the defect Gibbs free energy (ϵ) by comparing melting temperatures predicted by the model with T_m^0 of PHGP, PHPA and PHGA determined experimentally. The ϵ is calculated from the function ϵ/RT which is an adjustable parameter and is constant, regardless of the comonomer composition.⁶⁸

Easier the inclusion behavior is, lower the defect Gibbs free energy is. In such fitting work, the **equilibrium** melting enthalpies of PHG, PHP and PHA were taken to be 31, 39 and 47 kJ/mol calculated by the Van Krevelen approach based on group contributions.⁷⁵

For PHGP, the best fit to the experimental data was for $\epsilon/RT=1.4$ for PHG. Calculation of ϵ from ϵ/RT for PHG ($X_{HP}=0$), leads to an average defect free energy $\epsilon=3.7$ kJ/mol in the case of incorporation of HP unit into the PHG crystal as shown in Figure 7 (a). On the other hand, the defect Gibbs free energy is found that $\epsilon=2.8$ kJ/mol in the case of incorporation of HG unit into the PHP crystal. These results lead us to conclude that the defect free energies for incorporation of HG unit into PHP crystal are lower than the opposite case, indicating that the comonomer units have better miscibility in the case of the incorporation of shorter unit into the longer unit crystal than the opposite case. As shown in Scheme 2 (a), in the case of longer HP unit squeezes into the crystal of shorter HG unit, a part of longer HP unit is obliged to adopt twist fold or other forms of defects in order to insert into the lattice of HG and others have to be pushed out of the cell.⁷⁶ Nevertheless, when the shorter HG unit inserts into longer PHP crystal, owing to the HG unit randomly distributes in the backbone of the chains of longer HP unit and it has shorter chain length, the incorporation of some HG units into the crystal lattice of HP unit is unavoidable when the crystal of HP unit grasps any type of comonomers around the growth interface front of crystal. This happens as a result of the larger enthalpy penalty caused by the hindrance of chain length and the molecular chain of longer HP unit is stiffer.

For PHPA, the average defect free energy in case of incorporation of HA unit into PHP crystal is 8.3 kJ/mol Figure 7 (b). This high value is due to HA unit is longer than HP unit, and so it is preferably excluded than incorporated in the PHP crystal lattice. However, this does not mean complete rejection. Moreover, some extent of comonomer cocrystallization was verified by the WAXD study. This fact agrees well with the result from the analysis of d-spacing values that the d-spacing values of PHP crystal type lattice obviously decrease as the HA unit incorporated into the PHP crystal. Then the average defect free energy in case of HP inserted into PHA crystal is 2.7 kJ/mol, indicating that the shorter HP unit does not cause significant disturbance of the lattice if incorporated in the PHA crystal. What is more, the experimental data at low HP comonomer concentrations are fitted best, however, the excess free energy decreases with increasing HP comonomer content. It shows that the comonomer inclusion is favored for copolymers with high comonomer content.⁷⁴ This reason is that it is easier to produce the necessary excess volume for a comonomer unit in an already imperfect crystal lattice than to create it in a defect-free crystal lattice.⁷³

(a) Isodimorphism: PHGP and PHPA

(b) Isomorphism: PHGA

Scheme 2. Schematic models of the comonomer unit arrangement in crystal lattice: (a) isodimorphism for PHGP and PHPA copolyesters and (b) isomorphism for PHGA copolyesters. The red fold lines represent shorter comonomer unit in copolyester, while black fold lines represent longer comonomer unit in copolyester.

In the case of PHGA, it showed an almost linear variation in the equilibrium melting point of PHGA with comonomer content as shown in Figure 7 (c). This further confirms that PHGA shows strict isomorphism behavior in the whole composition range. Moreover, it is revealed that the average defect free energy is 1.4 kJ/mol when HA unit and HG unit form cocrystallization in the crystal lattice of the copolyester. This value is so low that it meets the requirements of strict isomorphism in the view of energy barrier of cocrystallization. In combination with the analysis from DSC, WAXD and POM, it demonstrates that HG and HA unit are perfectly miscible in a same crystal only with a slightly change in cell dimensions, that is, undergo isomorphous substitution as shown in Scheme 2 (b). Once a polymer chain crystallizes, the energy barrier comes from both enthalpic and entropic origin.^{77,78} As mentioned above, the melting enthalpy monotonically increases with the increase of HA comonomer composition, which shows a same linear dependence consistent with the melting point versus copolymer composition. Therefore, we consider that the HG and HA unit adopt the identity of chain conformation during packing into the crystal lattice, that is, the entropic barrier which stems from the adjustment of chain conformation during crystallization keeps almost constant. At the same time, the melting enthalpy continuously increases from PHG to PHA, and as a result, the melting temperature increases. The identity of chain conformation induces HG and HA unit to coexist in the common crystalline structure and both units are equally distributed in crystalline regions.

4. Conclusions

In this study, even-odd copolyesters PHGP, PHPA, and PHGA with various compositions were firstly synthesized derived from even diol of 1,6-hexanediol and odd diacids of glutaric acid, pimelic acid or azelaic acid through an adapted two-step melt polycondensation reaction. GPC revealed average molecular weight ranged from 20.2 to 41.3 k g /mol and the average molecular weight ranged from 35.2 to 74.8k g /mol with dispersity index values from 1.62 to 2.39. Good agreement between theoretical and experimental comonomer unit molar ratios was attested by NMR.

For PHGP and PHPA, isodimorphism behavior was verified by DSC and WAXD studies. Moreover, the crystal type transitions were confirmed for PHGP82 and PHPA82. By contrast, in the case of PHGA, the melting temperature, melting enthalpy and crystallinity exhibited linear dependence with composition, without showing a eutectic point. Meanwhile, WAXD patterns of PHGA changed continuously from PHG to PHA with no interruption between the shifts, and the d-spacings also changed linearly and continuously with the composition. Recorded by POM, no significant change was observed in the size and morphology of spherulites of PHGA copolyesters compared to that of neat PHG and PHA at the same degree of supercooling. These facts lead us to conclude that PHGA shows strict isomorphism behavior in the whole composition range. It attributes to that the HG and HA units adopt the identity of chain conformation during packing into the crystal lattice. The only slight change of the methylene number in alkyl unit of comonomers could generate so large difference in crystallization behavior, which exhibits unique physicochemical properties and structure-properties correlations in such even-odd copolyesters.

The difference in cocrystallization miscibility effect of comonomers was analyzed by thermodynamics based on the defect Gibbs energy calculated from Wendling-Suter model. For PHGP and PHPA, it reveals that the comonomer units have better miscibility in the case of the incorporation of shorter unit into the longer unit crystal than the opposite case. By contrast, in the case of PHGA, the HG and HA unit are perfectly miscible in a same crystal lattice with only a little difference in crystal cell dimensions, which meets the requirement of strict isomorphism in the view of energy barrier of cocrystallization. Furthermore, a proposed model of crystal lattice structure gives an insight into the difference in miscibility effect of comonomers between isodimorphism and isomorphism for the even-odd copolyesters.

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Supporting Information Available:

Synthesis and microstructure of homopolymers and copolyesters (^1H NMR, ^{13}C NMR); Thermal data of copolyesters; Spherulitic morphology for homopolyesters.

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Graphical Abstract