

Isothermal Crystallization Kinetics and Crystalline Morphologies of Poly(butylene adipate-*co*-butylene 1,4-cyclohexanedicarboxylate) Copolymers

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Abstract In this study, the isothermal crystallization kinetics and crystalline morphology of poly(butylene adipate-*co*-butylene 1,4-cyclohexanedicarboxylate) (PBAC), which refers to a copolyester containing a non-planar ring structure, were investigated by differential scanning calorimetry and polarized optical microscopy, and compared with those of neat poly(butylene 1,4-cyclohexanedicarboxylate) (PBC). The results indicate that the introduction of butylene adipate (BA) unit into PBAC did not change the intrinsic crystallization mechanism. But, the crystallization rate and ability, and equilibrium melting temperature of PBAC copolymers were reduced. All PBC and PBAC copolymers could only form high density of nucleation from melt at given supercooling, while no Maltese cross or ring-banded spherulites could be observed. PBAC copolymers with a high amount of BA unit became amorphous after quenching with liquid nitrogen from melt, while PBC and PBAC copolymers with a low amount of BA unit could still form a large amount of nuclei under the same treatment.

Keywords Poly(butylene adipate-*co*-butylene 1,4-cyclohexanedicarboxylate); Isothermal crystallization kinetics; Crystalline morphology

Citation: Liu, F.; Chi, D. Q.; Na, H. N.; Zhu, J. Isothermal Crystallization Kinetics and Crystalline Morphologies of Poly(butylene adipate-*co*-butylene 1,4-cyclohexanedicarboxylate) Copolymers. Chinese J. Polym. Sci. 2018, 36(6), 756–764.

INTRODUCTION

Aliphatic polyesters such as poly(butylene adipate) (PBA)^[1, 2] and poly(butylene succinate) (PBS)^[3, 4] have drawn considerable amounts of attention in the scientific community since last decade, mainly because they are renewable, degradable, and sustainable. Meanwhile, their aromatic counterparts, such as poly(ethylene terephthalate) (PET)^[5] and poly(butylene terephthalate) (PBT)^[6], have been practically used as engineering plastics for over 50 years due to their extraordinary thermal and mechanical properties. By combining the advantages of both polyesters, the aliphatic/aromatic copolyesters have been developed so that the growing demand on not only environment friendly issues, but also excellent properties for practical use, can be met simultaneously. Among others, poly(butylene adipate-*co*-butylene terephthalate) (PBAT)^[7] is one of the most attractive and successful aliphatic/aromatic copolyesters that have been developed. On that account, the chemical structure, various properties, and the structure-property relationships of these polyesters^[2, 4, 6, 8–16] and copolyesters^[1, 7, 17–28] have been

studied extensively in great detail, particularly the thermal and mechanical properties, crystallization kinetics, and crystalline morphologies.

Recently, 1,4-cyclohexanedicarboxylic acid (CHDA), a unique component with aliphatic ring other than aliphatic chain or aromatic ring, has been introduced for the synthesis of polyesters, such as poly(butylene 1,4-cyclohexanedicarboxylate) (PBC), as well as copolyesters^[29–33]. These polymers possess interesting properties, such as lower melting temperatures and better thermal stability compared with their counterparts with aromatic ring^[31], excellent gas barrier properties^[33], and potential biodegradability^[34]. More importantly, CHDA has non-planar ring structure which results in conformational transition between *trans* and *cis* isomers^[35–37]. A simple change in the *trans/cis* ratio of CHDA gives rise to a conversion of PBC from a thermoplastic to an elastomer^[29]. Therefore, by substituting the aromatic ring with CHDA, poly(butylene adipate-*co*-butylene 1,4-cyclohexanedicarboxylate) (PBAC), a copolyester similar to PBAT, can be obtained with tunable properties^[38] to be used as a novel elastomer with high performances. Furthermore, this kind of copolyester also has rather good potential to be applied as a highly efficient toughening agent for the modification of poly(lactic acid)^[39].

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Received September 1, 2017; Accepted September 25, 2017; Published online February 8, 2018

Apparently, previous studies have explored the influence of CHDA on the thermal, mechanical as well as gas barrier properties of different polymers. And the potential application of polymers containing CHDA as structural materials or additives has been evaluated. Recently, the influence of *trans/cis* ratio of CHDA on the crystallization behavior of PBC has been studied by Celli *et al.*^[40]. It was found that the *cis* isomer is fully excluded from the crystalline phase. On that account, the impact of butylene adipate unit (BA) on the crystallization kinetics, melting behavior, and crystalline morphologies of PBC is very meaningful. Deep understanding of the crystallization behavior of PBAC is of significance to guide the material processing for expected properties, particularly taking PBAC copolymer as an additive of PLA, with the aim to initiate high thermal performances of PLA/PBAC blend. In other words, a systematic detection of crystallization behavior of PBAC will realize the adaptability towards the processing conditions.

Therefore, in the current study, we focus on the effects of BA unit on the isothermal crystallization kinetics, equilibrium melting temperature as well as crystalline morphology of PBAC copolymers and compare them with those of neat PBC. To the best of our knowledge, this is the first systematic investigation on the crystallization behavior of a copolymer containing CHDA unit.

EXPERIMENTAL

Materials

PBC polymer and PBAC copolymers with different compositions were obtained through a two-step melt polycondensation reaction process as described in our previous study^[38]. Four PBAC copolymers with molar ratios of BC to BA of 50:50, 60:40, 80:20 and 90:10 were prepared and marked as PBAC-50, PBAC-60, PBAC-80, and PBAC-90, respectively. Their compositions and general thermal properties reported in our previous study^[38], were collected and are shown in Table 1.

Table 1 Compositions and basic thermal properties of the PBC and PBAC samples^[38]

Sample	BA (mol%)	BC (mol%)	<i>trans</i> -CHDA (mol%)	T_m (°C)	T_c (°C)
PBAC-50	51	49	84	63	21
PBAC-60	36	64	81	85	39
PBAC-80	20	80	88	123	99
PBAC-90	7	93	91	145	123
PBC	0	100	88	147	125

Isothermal Crystallization Kinetics

The isothermal crystallization kinetic was investigated under a N₂ atmosphere using a differential scanning calorimeter (METTLER-TPLEDO DSC I). The sample was heated from room temperature to 50 °C higher than its T_m and held there for 3 min to eliminate its thermal history. Subsequently, the sample was heated to the selected T_c at a rate of 100 °C·min⁻¹ and held for the completion of isothermal crystallization. The sample was then quenched to room temperature at a rate of 100 °C·min⁻¹ and then heated to 50 °C higher than its T_m again at a rate of 10 °C·min⁻¹. The heat of fusion (ΔH_m) was

obtained from the second heating scan. The degree of crystallinity was calculated according to the following equation:

$$\chi_c (\%) = \frac{\Delta H_m}{f(\text{PBA}) \times \Delta H_m^\theta(\text{PBA}) + f(\text{trans-PBC}) \times \Delta H_m^\theta(\text{trans-PBC})} \times 100\% \quad (1)$$

where χ_c is the degree of crystallinity, f is the weight fraction, ΔH_m is the experimental melting heat of fusion, and ΔH_m^θ is the heat of fusion of 100% crystalline (135 J·g⁻¹ for PBA^[1] and 141 J·g⁻¹ for *trans*-PBC calculated according to the group contribution theory)^[2,3].

Crystalline Morphology

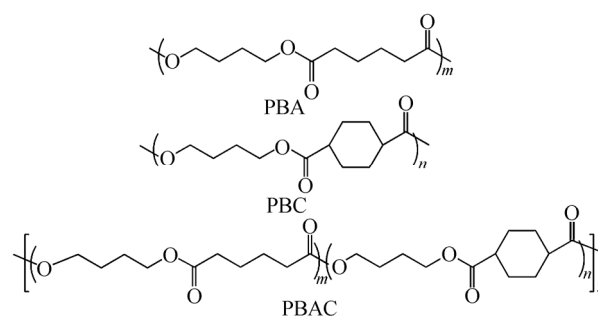
The crystalline morphology was observed with a polarized optical microscope (POM, Olympus BX51). The temperature control of these samples was performed using a hotstage (Linkam, LTA420). Sample films were pressed between two microscopic cover slips at 50 °C higher than their corresponding melting temperatures and held for 3 min to eliminate their thermal history. The sample films were then quenched to a given temperature to observe the crystalline morphology.

RESULTS AND DISCUSSION

Isothermal Crystallization Kinetics

The compositions and basic thermal properties of PBC and the four PBAC copolymers studied in this work (Scheme 1), adopted from our previous study^[38], are listed in Table 1. The compositions are calculated according to ¹H-NMR. The T_m and T_c were obtained from the second heating and cooling scans, respectively, from regular DSC analysis. Detailed information can be found in our previous work^[38]. Generally, with the increase of BA unit molar percentage in the PBAC copolymers from 7% to 51%, both T_m and T_c decrease gradually. The pure PBC polymer has both higher T_m and T_c than PBAC copolymers. In addition, all samples have similar amounts of *trans*-CHDA molar percent ranging from 80% to 90%.

The overall isothermal crystallization kinetics of PBC and PBAC copolymers were studied with DSC at five different temperatures. These temperatures were selected according to their T_m listed in Table 1. We began with a temperature at 2 °C below the T_m and the corresponding DSC isothermal crystallization kinetics curve was recorded. The highest T_c



Scheme 1 Chemical structures of PBA, PBC and PBAC samples

was then determined once a clear and complete crystallization peak was recorded at the designated temperature. Subsequently, the rest of four temperatures were selected accordingly with an interval of 2 °C starting from the highest T_c . Figure 1 shows the development of relative crystallinity with crystallization time for PBC and PBAC-80 copolymer (for other PBAC copolymers, see Fig. S1 in electronic supplementary information, ESI) at different T_c . With the decrease of T_c , it takes less time for all samples to complete crystallization. This observation suggests that the crystallization is inhibited under higher T_c . This is because high temperature is not favorable for nucleation, which is the first step of crystallization. More importantly, although it takes more than an hour to finish the isothermal crystallization process, PBC is able to crystallize at merely 2 °C below its T_m , indicating strong nucleation and crystallization ability. PBAC-90 has similar behavior and it can crystallize at a temperature of only 4 °C below its T_m . On the other hand, for the other three PBAC copolymers with more amounts of BA unit, the temperatures have to go all the way down to the temperatures more than 10 °C below their T_m to initiate crystallization. However, these three PBAC copolymers can complete the isothermal crystallization process in less than 15 min even at the highest T_c . These findings show that the incorporation of BA unit has significant influence on the crystallization behavior of PBAC copolymers, which will be discussed in great detail as following.

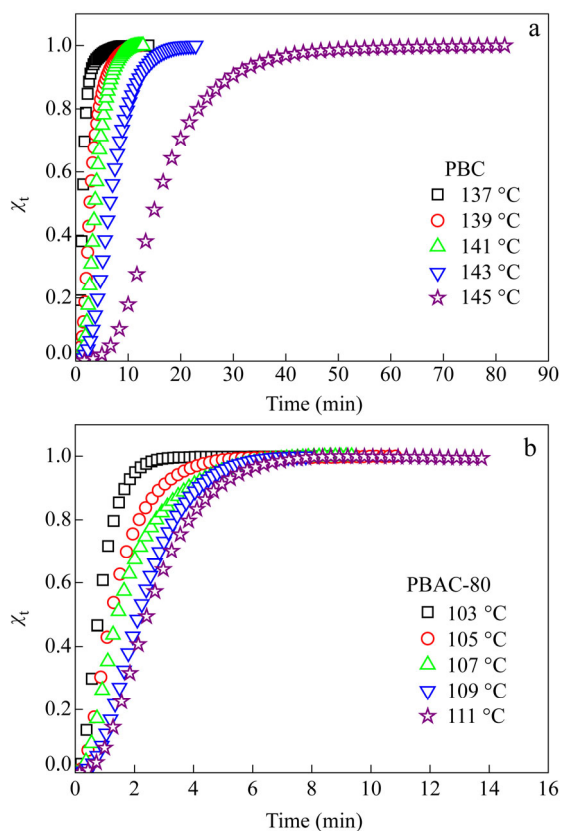


Fig. 1 Relative crystallinity (χ_t) versus crystallization time at different T_c s in isothermal crystallization process for (a) PBC and (b) PBAC-80

First of all, the development of relative crystallinity with crystallization time can be quantitatively described using Avrami equation (Eq. 2). The isothermal crystallization kinetics can be analyzed accordingly.

$$1 - \chi_t = \exp[-k(t - t_0)^n] \quad (2)$$

In the Avrami equation, χ_t is the relative crystallinity at time t , k is the crystallization rate constant related to both nucleation and growth rate parameters, and n is the Avrami exponent depending on the nature of nucleation, and growth geometry of the crystals. For the calculation of χ_t from the DSC results, χ_t at t is defined as the ratio of the area under the exothermic curve between the crystallization onset time t_0 and t to the whole area under the exothermic curve from t_0 to the crystallization offset time. Logarithmic arithmetic operation can be carried out for Eq. (2) to give Eq. (3):

$$\ln[-\ln(1 - \chi_t)] = \ln k - n \ln(t - t_0) \quad (3)$$

Thus a plot of $\ln[-\ln(1 - \chi_t)]$ versus $\ln(t - t_0)$ would give a straight line. As a result, the rate constant k and the Avrami exponent n can be calculated from the intercept and slope of the straight line, respectively.

Figure 2 gives the Avrami plots for PBC and PBAC-80 copolymer (for other PBAC copolymers, see Fig. S2, in ESI). A series of almost parallel straight lines are obtained for PBAC copolymers and PBC at different T_c s, suggesting that the Avrami equation is suitable for the description of the isothermal crystallization kinetics of PBAC copolymers and PBC. Subsequently, the Avrami parameters n and k are calculated and collected in Table 2. From Table 2, it is clear that the values of n are varied slightly between 2.0 to 3.0 for PBAC copolymers with different compositions within the range of T_c studied in this work, while the values of n for PBC are around 3.0 at different T_c s. These results indicate that the crystallization kinetics of both PBAC copolymers and PBC could correspond to the three-dimensional truncated spherulitic growth with athermal nucleation. That is to say, the incorporation of BA unit will not change the intrinsic crystallization mechanism of PBAC.

Although the values of k for PBC and PBAC copolymers show a decreasing trend with the increase of T_c , which suggests that the crystallization becomes slower under higher T_c , it is generally considered to be inappropriate to compare the overall crystallization rates directly from the values of k . This is due to the fact that the unit of k is min^{-n} while n varies at different T_c s. Therefore, the crystallization half-time ($t_{1/2}$), the time needed to achieve χ_t of 50%, is introduced for the study of isothermal crystallization kinetics. $t_{1/2}$ can be calculated from n and k according to Eq. (4)

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (4)$$

The reciprocal of $t_{1/2}$, *i.e.*, $\tau_{1/2}$, is usually employed to represent the overall crystallization rates of polymers. Values of $t_{1/2}$ and $\tau_{1/2}$ for PBAC copolymers and PBC are listed in Table 2. In addition, the observed crystallization half-time ($t_{0.5}$), obtained directly from curves in Fig. 1 and Fig. S1 (in ESI), is also presented in Table 2 for comparison. On one

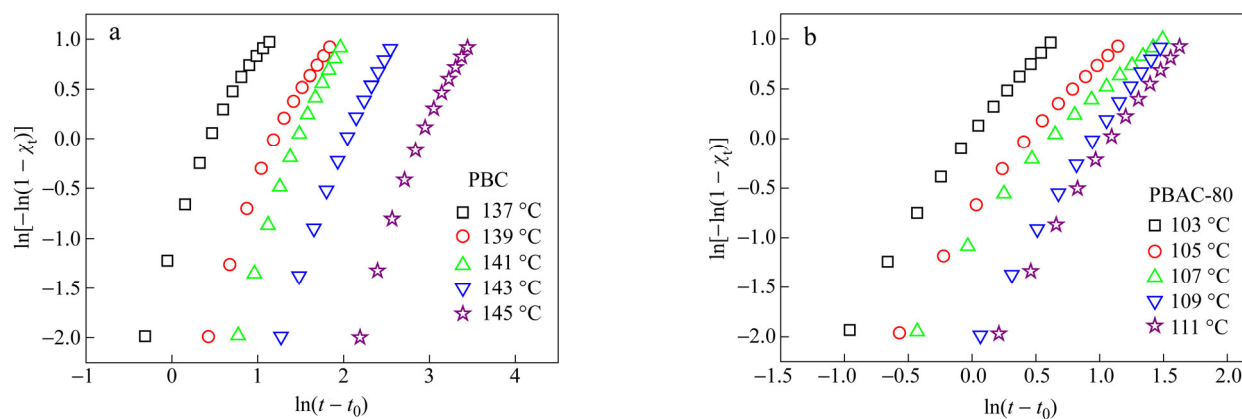


Fig. 2 Plots of $\ln[-\ln(1 - \chi_t)]$ versus $\ln(t - t_0)$ for isothermal crystallization kinetics at different T_c s for (a) PBC and (b) PBAC-80

Table 2 Isothermal crystallization kinetic parameters of PBC and PBAC samples at different T_c ^a

Sample	T_c (°C)	n	k (min ⁻ⁿ)	$t_{0.5}$ (min)	$t_{1/2}$ (min)	$\tau_{1/2}$ (min ⁻¹)	ΔE (kJ·mol ⁻¹)
PBAC-50	45	2.4	1.8×10^{-1}	1.77	1.76	0.569	-84.1
	47	2.3	1.4×10^{-1}	1.98	1.97	0.508	
	49	2.5	7.0×10^{-2}	2.55	2.51	0.398	
	51	2.4	6.8×10^{-2}	2.67	2.63	0.380	
	53	1.9	5.4×10^{-2}	3.90	3.89	0.257	
PBAC-60	61	2.9	1.3×10^{-1}	1.80	1.79	0.560	-133.5
	63	2.8	1.0×10^{-1}	1.97	1.96	0.510	
	65	2.6	7.5×10^{-2}	2.37	2.36	0.424	
	67	2.7	2.2×10^{-2}	3.62	3.61	0.277	
	69	2.0	2.9×10^{-2}	4.58	4.77	0.210	
PBAC-80	103	2.2	1.2×10^0	0.79	0.77	1.294	-163.8
	105	2.1	4.8×10^{-1}	1.22	1.19	0.843	
	107	2.1	3.6×10^{-1}	1.44	1.37	0.732	
	109	2.3	1.2×10^{-1}	2.15	2.11	0.474	
	111	2.4	8.7×10^{-2}	2.44	2.39	0.418	
PBAC-90	133	2.6	3.6×10^{-1}	1.29	1.28	0.782	-463.7
	135	2.6	1.3×10^{-1}	1.94	1.88	0.531	
	137	2.7	2.6×10^{-2}	3.44	3.34	0.300	
	139	3.0	2.2×10^{-3}	6.59	6.60	0.151	
	141	3.1	1.5×10^{-4}	16.33	15.62	0.064	
PBC	137	2.9	3.4×10^{-1}	1.31	1.27	0.787	-431.5
	139	2.9	3.9×10^{-2}	2.76	2.67	0.375	
	141	3.3	1.1×10^{-2}	3.69	3.54	0.282	
	143	2.9	3.6×10^{-3}	6.49	6.26	0.160	
	145	3.2	1.1×10^{-4}	15.36	14.74	0.068	

^a n is Avrami exponent, k is crystallization rate constant, $t_{0.5}$ and $t_{1/2}$ are respectively observed and calculated crystallization time when the χ_t is 50%, $\tau_{1/2}$ is the reciprocal of $t_{1/2}$ and ΔE is the crystallization activation energy.

hand, values of $t_{1/2}$ are in good agreement with those of $t_{0.5}$, indicating that Eq. (4) is reasonably good for the calculation of $t_{1/2}$. On the other hand, as shown in Fig. 3, $\tau_{1/2}$ values decrease with increasing T_c for all samples, suggesting that the overall isothermal crystallization rate decreases with increasing T_c . This trend is very common for the isothermal crystallization of polymers, because it is a nucleation control process and the nucleation becomes more difficult under higher T_c .

Secondly, comparing PBAC-90 with PBC, it is worth noting that the crystallization rates of PBAC-90 are

significantly lower than those of PBC at the same given T_c (e.g. 137, 139 and 141 °C). This observation strongly suggests that the incorporation of BA unit hinders the process of crystallization of PBC. Our previous study demonstrated that only *trans*-PBC part is crystallizable in PBAC copolymer^[38], while the presence of both BA and *cis*-BC units could bring obstacles to the crystallization, resulting in decreased T_m for PBAC copolymer^[38]. By the detailed research of isothermal crystallization kinetics in current work, it further clearly exhibits that the increase of BA unit in PBAC results in the decrease of crystallization rate. This phenomenon can be

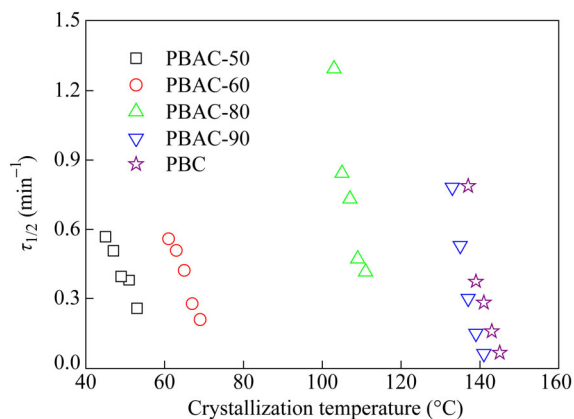


Fig. 3 Values of $\tau_{1/2}$ of PBC and PBAC samples at various T_c s

ascribed to the following two reasons. In the first place, the incorporation of amorphous BA unit would dilute the content of the crystallizable *trans*-PBC component and slow down the crystallization rate. In the second place, it would significantly reduce the equilibrium melting temperature (T_m^0) of the PBAC copolymers compared with PBC. Thus the supercooling ($T_m^0 - T_c$), known as the driven force for the isothermal crystallization, would decrease largely with the increase of BA unit at the same given T_c . Consequently, the crystallization rate would inevitably decrease as well.

The dilution effect described above can be quantitatively compared with the crystallization activation energy ΔE calculated according to the Arrhenius equation (Eq. 5), while the supercooling effect will be discussed in detail in the next section.

$$k^{1/n} = k_0 \exp\left(-\frac{\Delta E}{RT_c}\right) \quad (5)$$

$$\frac{\ln k}{n} = \ln k_0 - \frac{\Delta E}{RT_c} \quad (6)$$

Equation (5) can be rewritten to Eq. (6) after carrying out logarithmic arithmetic operation. In these two equations, n is the Avrami exponent, k is the crystallization rate, k_0 is the temperature independent pre-exponential factor, R is the gas constant, ΔE is the crystallization activation energy and T_c is

the crystallization temperature. After plotting $(\ln k)/n$ versus $1/(RT_c)$, ΔE can be obtained through the slope. As shown in Table 2, the value of ΔE is negative because it has to release energy when transforming the molten fluid into the crystalline state. Therefore, the larger the absolute value of ΔE is, the more energy it will release during the crystallization process, indicating stronger inclination of crystallization. As a result, PBAC copolymers have decreased absolute value of ΔE with increasing amounts of BA unit, which further confirms that BA unit hinders the crystallization of *trans*-PBC. Thus a more amount of BA unit has greater dilution effect on the process of crystallization of PBAC copolymers.

Melting Behavior of Isothermally Crystallized Samples

It has been mentioned in the previous section that the supercooling is a crucial parameter for the evaluation of crystallization ability including nucleation ability and crystal growth rate. The supercooling is calculated based on T_m^0 and T_c . The T_m^0 is usually determined according to the Hoffman-Weeks method (Eq. 7)

$$T_m = T_m^0 \left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma} \quad (7)$$

where T_m is the observed melting temperature of a crystal formed at crystallization temperature (T_c), γ is the ratio of final to initial lamellar thickness. Therefore, plotting T_m as function of T_c gives a straight line and the T_m^0 can be obtained from the point of intersection of the line with the $T_m = T_c$ line.

Figure 4 shows the second heating scans of DSC analysis after isothermal crystallization at different T_c s for PBC and PBAC-80 copolymer (for other PBAC copolymers, see Fig. S3, in ESI). Obviously, all samples show double melting peaks and all peaks shift to higher temperature under higher T_c . The values of these peaks are summarized in Table 3. The double melting behaviors are quite common for semicrystalline polymers. The lower endothermic peak (T_{m1}) is generally associated with the melting of poor crystals which grow at T_c between large crystals, while the higher endothermic peak (T_{m2}) can be ascribed to the fusion of crystals actually formed at T_c during the primary crystallization. This result is a little similar to the report by Celli *et al.*^[40]. However, a third peak that usually results from

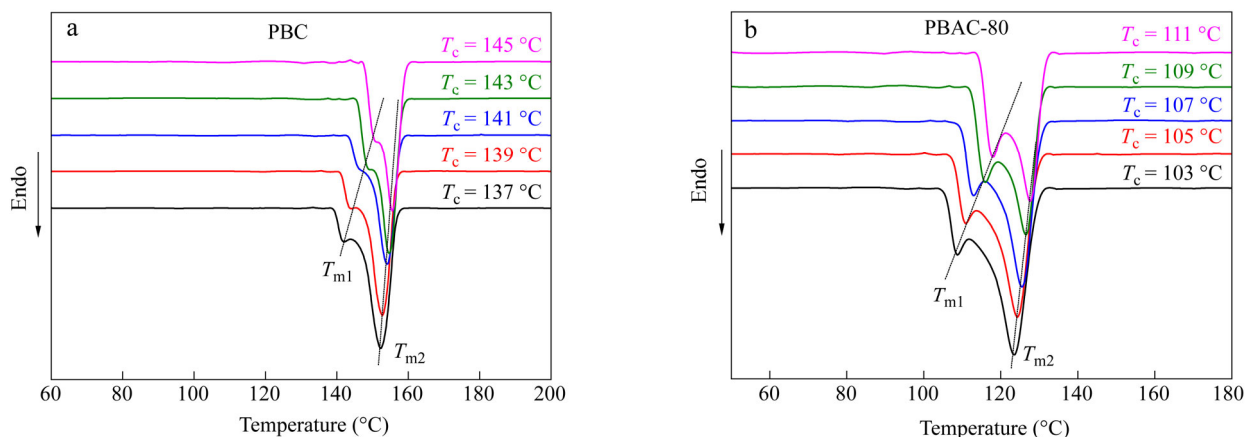


Fig. 4 Melting endotherms obtained by DSC for (a) PBC and (b) PBAC-80 after isothermal crystallization at various T_c s

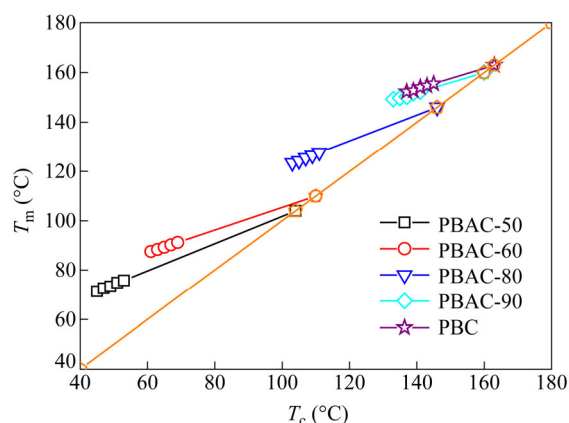
Table 3 Melting temperatures (T_m), melting enthalpy (ΔH_m), degree of crystallinity (χ_c), calculated equilibrium melting temperatures (T_m^0) and supercooling ($T_m^0 - T_c$) of PBC and PBAC samples after isothermal crystallization at various T_c s

Sample	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J·g ⁻¹)	χ_c (%)	T_m^0 (°C)	$T_m^0 - T_c$ (°C)
PBAC-50	45	51.5	71.3	10.4	8.2	104	59
	47	53.7	72.5	9.3	7.3		57
	49	55.7	73.3	9.2	7.3		55
	51	58.3	74.8	9.6	7.6		56
	53	60.0	75.7	7.7	6.1		51
PBAC-60	61	67.0	87.5	18.3	15.1	110	49
	63	69.0	88.3	18.0	14.8		47
	65	71.0	89.2	16.5	13.6		45
	67	73.0	90.2	14.4	11.8		43
	69	74.8	91.2	12.4	10.2		41
PBAC-80	103	108.8	123.5	17.2	13.6	146	43
	105	111.0	124.3	15.8	12.5		41
	107	113.0	125.5	15.3	12.1		39
	109	116.0	126.5	14.0	11.1		37
	111	118.0	127.7	13.5	10.7		35
PBAC-90	133	138.0	149.3	24.0	18.6	160	27
	135	140.2	149.8	24.4	18.9		25
	137	142.3	150.3	21.2	16.4		23
	139	144.3	151.7	20.4	15.8		21
	141	147.2	152.3	19.3	15.0		19
PBC	137	141.9	152.3	27.2	21.9	163	26
	139	143.9	152.7	25.2	20.3		24
	141	146.3	154.0	21.4	17.2		22
	143	148.8	154.7	25.7	20.7		20
	145	150.6	155.5	23.6	19.0		18

melting, recrystallization and remelting mechanism is not observed for all samples in the current study. The T_{m1} of PBAC copolymers tends to separate from T_{m2} with more amount of BA unit at lower T_c , indicating that the presence of BA unit would result in more amount of imperfect crystals under low T_c . It is worth noting that all T_{m1} is approximately 7 °C higher than the corresponding T_c . Subsequently, T_{m2} is used for the Hoffman-Weeks equation to estimate the T_m^0 values for PBC and PBAC copolymers.

Figure 5 displays the Hoffman-Weeks plots for PBC and PBAC copolymers. T_m^0 values are determined accordingly and are listed in Table 3. PBC has the highest T_m^0 of 163 °C, while PBAC-90 is 3 °C lower. What is more important, with the increasing amount of BA unit from 20% to 50%, the T_m^0 of the PBAC copolymers decreases straight from 146 °C to 104 °C. These results confirm that incorporation of BA unit results in depression of T_m^0 for PBAC copolymers, and as a result, their crystallization rates decrease. Afterwards, the corresponding supercooling can be calculated accordingly and are given in Table 3.

Plotting $\tau_{1/2}$ as a function of supercooling gives Fig. 6 which also demonstrates the crystallization rate and ability of PBC and PBAC copolymers. Higher $\tau_{1/2}$ with the same supercooling indicates fast crystallization rate, while smaller supercooling with the same $\tau_{1/2}$ suggests better crystallization ability, especially nucleation ability. Therefore, it is quite clear that PBC has the highest crystallization rate and best

**Fig. 5** Hoffmann-Weeks plots for the calculation of T_m^0 of PBC and PBAC samples

crystallization ability followed by PBAC-90. Their supercoolings are in the range of 20 °C to 30 °C with $\tau_{1/2}$ varying from 0.1 min⁻¹ to 0.8 min⁻¹. However, with the increasing amount of BA unit in the PBAC copolymers from 20% to 50%, the supercoolings increase all the way from 30 °C to almost 60 °C, indicating significant decrease of crystallization rate and ability. These results provide a reasonable explanation for the observation from Fig. 1 and Fig. S1 (in ESI) that PBC and PBAC-90 can initiate crystallization at only 2 and 4 °C below their T_m , respectively,

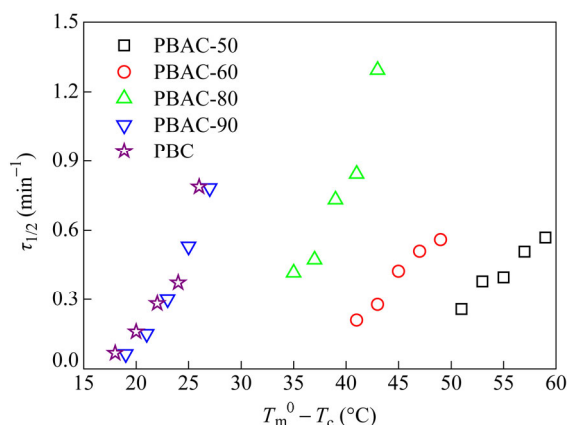


Fig. 6 Values of $\tau_{1/2}$ as a function of the supercooling ($T_m^0 - T_c$) for PBC and PBAC samples

while PBAC-80, PBAC-60, and PBAC-50 cannot crystallize until the temperatures are more than 10 °C below their T_m . Therefore, BA unit decreases the crystallization rate of BC unit in the PBAC copolymer, and more BA units tend to result in lower crystallization rate for the PBAC copolymer.

Crystalline Morphology

The crystalline morphology has significant influence on the physical properties of a polymer. The impact of CHDA on the crystalline morphologies of PBAC copolymers is of great importance to be studied. Therefore, the crystalline morphologies of PBC and PBAC copolymers were investigated by POM from isothermal crystallization at the same supercooling of 50 °C for 5 min. As shown in Fig. 7, all samples form a large number of nuclei, indicating high density of nucleation. It is worth noting that, for all PBC and PBAC copolymers, a large number of nuclei formed immediately after the temperature was cooled down to the isothermal crystallization temperature from melt. Their crystalline morphologies were recorded after 5 min and remained unchanged after kept still for another 30 min. This result shows that PBC and PBAC copolymers have strong

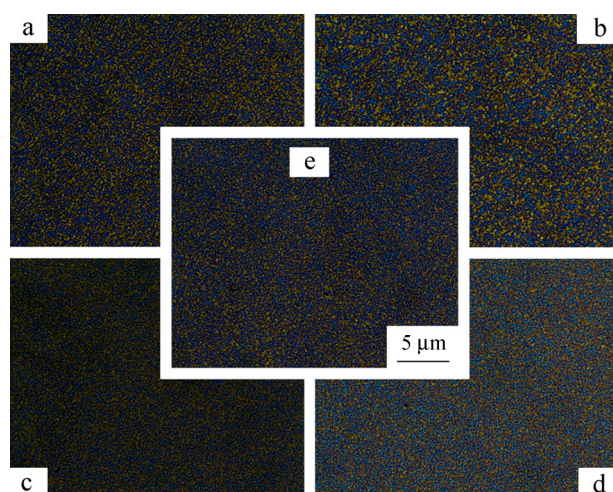


Fig. 7 Crystalline morphologies of PBC and PBAC copolymers formed at supercooling of 50 °C for 5 min: (a) PBAC-50, (b) PBAC-60, (c) PBAC-80, (d) PBAC-90 and (e) PBC (All the images share the same scale.)

ability to form nuclei from melt, while they have poor ability to grow large spherulites. Therefore, neither Maltese cross nor ring-banded spherulites were observed for PBC and PBAC copolymers. This result is quite similar to the crystalline morphology of a PBAT sample reported by Kuwabara *et al.*^[19] in which the spherulitic morphology cannot be detected, while many small particles with a size of about 100 nm were observed. Thus the crystalline regions of both PBC and PBAC copolymers are not well-ordered compared with that of PBT^[15].

Since the crystalline morphologies of PBC and PBAC copolymers are similar after isothermal crystallization from melt, we designed another experiment to further illustrate the

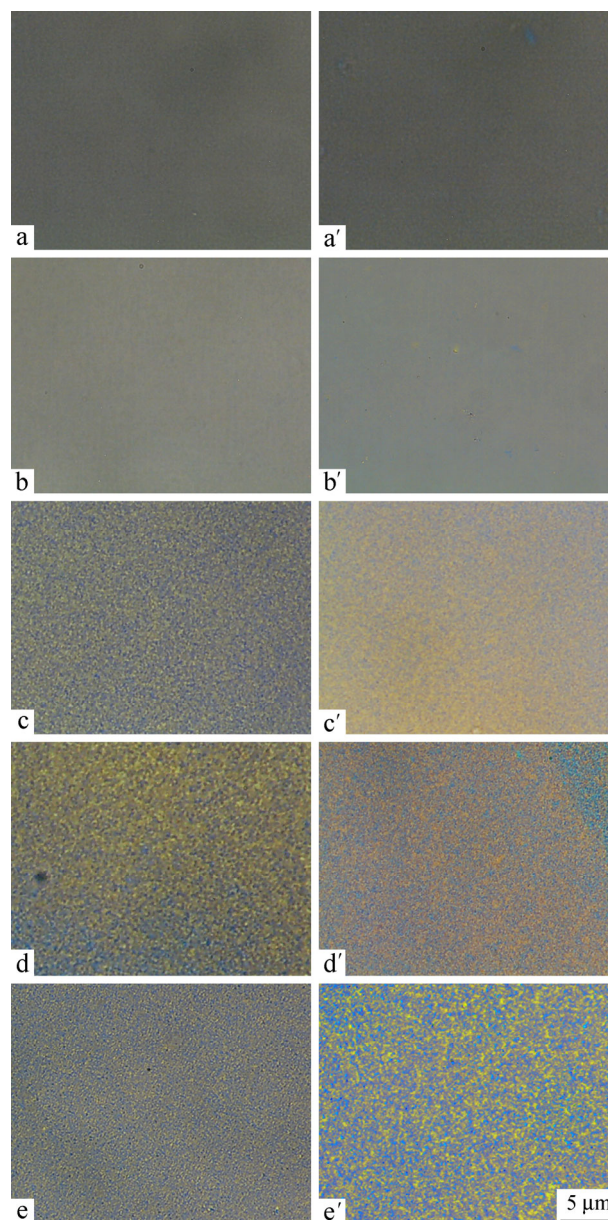


Fig. 8 Crystalline morphologies of PBC and PBAC copolymers formed (a–e) after quenching in liquid nitrogen from melt and (a'–e') subsequently subjected to isothermal crystallization at supercooling of 50 °C for 5 min: (a, a') PBAC-50, (b, b') PBAC-60, (c, c') PBAC-80, (d, d') PBAC-90, and (e, e') PBC (All the images share the same scale.)

impact of BA unit amount on the crystallization ability of PBAC. Instead of performing isothermal crystallization from melt, we observed the crystalline morphologies of PBC and PBAC copolymers immediately after quenching in liquid nitrogen from melt, as shown in Figs. 8(a)–8(e). PBAC-50 and PBAC-60 became totally amorphous (Fig. 8a and 8b), while PBAC-80, PBAC-90 and PBC still showed considerable amount of nuclei (Figs. 8c, 8d and 8e), indicating fairly strong ability of nucleation even under large cooling rate (quenching with liquid nitrogen). Subsequently, the quenched PBC and PBAC samples were subjected to isothermal crystallization at the same supercooling of 50 °C for 5 min. The crystalline morphology was then recorded and is shown in Figs. 8(a')–8(e'). It is quite clear that both PBAC-50 and PBAC-60 remain amorphous, and no nuclei can be observed, while for PBAC-80 and PBAC-90, the density of nucleation and the size of the small particles remain unchanged. On the other hand, for PBC, the size of the particles became larger after the isothermal crystallization. These results indicate that less amount of BA unit would result in better crystallization ability for the PBAC copolymers, which is greatly consistent with our observation in the previous section.

CONCLUSIONS

The isothermal crystallization kinetics and crystalline morphology of PBC and PBAC copolymers were investigated in depth in this study. The isothermal crystallization kinetics behavior of PBC and PBAC copolymers are well investigated by applying Avrami equation. PBC has the highest crystallization rate and ability. The introduction of BA unit in PBAC does not change its intrinsic crystallization mechanism but decreases the crystallization rate and ability of PBAC copolymers. And with the increase of the amount of BA unit from 10% to 50%, the equilibrium melting temperatures gradually decrease from 163 °C to 104 °C. Because of the nearly identical intrinsic crystallization mechanism, PBC and PBAC copolymers show the same crystalline morphologies after isothermal crystallization treatment at supercooling of 50 °C for 5 min. All samples show strong ability of nucleation from melt and thus form high density of nuclei, while their spherulites grow ability is poor. Moreover, PBC and PBAC copolymers with low amount of BA unit (PBAC-80 and PBAC-90) possess significantly strong ability of nucleation under fast cooling rate (quenched with liquid nitrogen), while amorphous morphology is observed for PBAC copolymers with relatively high amount of BA unit (PBAC-50 and PBAC-60) under the same treatment.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2051-9>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51503217), Zhejiang Province

Public Welfare Project (No. 2017C31081), the Open Project Program of MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Zhejiang University (No. 2016MSF001), and Youth Innovation Promotion Association CAS (No. 2017339).

REFERENCES

- 1 Tserki, V.; Matzinos, P.; Pavlidou, E.; Vachliotis, D.; Panayiotou, C. Biodegradable aliphatic polyesters. part I. properties and biodegradation of poly(butylene succinate-co-butylene adipate). *Polym. Degrad. Stab.* 2006, 91, 367–376.
- 2 Gan, Z.; Kuwabara, K.; Abe, H.; Iwata, T.; Doi, Y. Metastability and transformation of polymorphic crystals in biodegradable poly(butylene adipate). *Biomacromolecules* 2004, 5, 371–378.
- 3 Xu, J.; Guo, B. H. Poly(butylene succinate) and its copolymers: research, development and industrialization. *Biotechnol. J.* 2010, 5(11), 1149–1163.
- 4 Gan, Z.; Abe, H.; Kurokawa, H.; Doi, Y. Solid-state microstructures, thermal properties, and crystallization of biodegradable poly(butylene succinate) (PBS) and its copolyesters. *Biomacromolecules* 2001, 2(2), 605–613.
- 5 Kint, D.; Munoz-Guerra, S. A review on the potential biodegradability of poly(ethylene terephthalate). *Polym. Int.* 1999, 48(5), 346–352.
- 6 Stein, R. S.; Misra, A. Morphological studies on polybutylene terephthalate. *J. Polym. Sci. Polym. Phys. Ed.* 1980, 18(2), 327–342.
- 7 Herrera, R.; Franco, L.; Rodríguez-Galán, A.; Puiggali, J. Characterization and degradation behavior of poly(butylene adipate-co-terephthalate)s. *J. Polym. Sci., Part A: Polym. Chem.* 2002, 40(23), 4141–4157.
- 8 Yokouchi, M.; Sakakibara, Y.; Chatani, Y.; Tadokoro, H.; Tanaka, T. Structures of two crystalline forms of poly(butylene terephthalate) and reversible transition between them by mechanical deformation. *Macromolecules* 1975, 9, 266–273.
- 9 Kai, W.; Zhu, B.; He, Y.; Inoue, Y. Crystallization of poly(butylene adipate) in the presence of nucleating agents. *J. Polym. Sci., Part B: Polym. Phys.* 2005, 43(17), 2340–2351.
- 10 Yang, J.; Pan, P.; Dong, T.; Inoue, Y. Crystallization kinetics and crystalline structure of biodegradable poly(ethylene adipate). *Polymer* 2010, 51(3), 807–815.
- 11 Vasanthan, N.; Ozkaya, S.; Yaman, M. Morphological and conformational changes of poly(trimethylene terephthalate) during isothermal melt crystallization. *J. Phys. Chem. B* 2010, 114, 13069–13075.
- 12 Yang, J.; Pan, P.; Hua, L.; Xie, Y.; Dong, T.; Zhu, B.; Inoue, Y.; Feng, X. Fractionated crystallization, polymorphic crystalline structure, and spherulite morphology of poly(butylene adipate) in its miscible blend with poly(butylene succinate). *Polymer* 2011, 52(15), 3460–3468.
- 13 Chen, Y. A.; Wu, T. M. Crystallization kinetics of poly(1,4-butylene adipate) with stereocomplexed poly(lactic acid) serving as a nucleation agent. *Ind. Eng. Chem. Res.* 2014, 53, 16689–16695.
- 14 Milani, A.; Galimberti, D. Polymorphism of poly(butylene terephthalate) investigated by means of periodic density functional theory calculations. *Macromolecules* 2014, 47(3), 1046–1052.
- 15 Androsch, R.; Rhoades, A. M.; Stolte, I.; Schick, C. Density of heterogeneous and homogeneous crystal nuclei in poly(butylene terephthalate). *Eur. Polym. J.* 2015, 66, 180–189.
- 16 Cui, Z.; Qiu, Z. Thermal properties and crystallization kinetics of poly(butylene suberate). *Polymer* 2015, 67, 12–19.

- 17 Park, S. S.; Chae, S. H.; Im, S. S. Transesterification and crystallization behavior of poly(butylene succinate)/poly(butylene terephthalate) block copolymers. *J. Polym. Sci., Part A: Polym. Chem.* 1998, 36(1), 147–156.
- 18 Nikolic, M. S.; Djonlagic, J. Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s. *Polym. Degrad. Stab.* 2001, 74, 263–270.
- 19 Kuwabara, K.; Gan, Z.; Nakamura, T.; Abe, H.; Doi, Y. Crystalline/amorphous phase structure and molecular mobility of biodegradable poly(butylene adipate-co-butylene terephthalate) and related polyesters. *Biomacromolecules* 2002, 3(2), 390–396.
- 20 Cranston, E.; Kawada, J.; Raymond, S.; Morin, F. G.; Marchessault, R. H. CocrySTALLIZATION model for synthetic biodegradable poly(butylene adipate-co-butylene terephthalate). *Biomacromolecules* 2003, 4, 995–999.
- 21 Gan, Z.; Kuwabara, K.; Yamamoto, M.; Abe, H.; Doi, Y. Solid-state structures and thermal properties of aliphatic-aromatic poly(butylene adipate-co-butylene terephthalate) copolyesters. *Polym. Degrad. Stab.* 2004, 83, 289–300.
- 22 Ren, M.; Song, J.; Song, C.; Zhang, H.; Sun, X.; Chen, Q.; Zhang, H.; Mo, Z. Crystallization kinetics and morphology of poly(butylene succinate-co-adipate). *J. Polym. Sci., Part B: Polym. Phys.* 2005, 43(22), 3231–3241.
- 23 Shi, X. Q.; Ito, H.; Kikutani, T. Characterization on mixed-crystal structure and properties of poly(butylene adipate-co-terephthalate) biodegradable fibers. *Polymer* 2005, 46, 11442–11450.
- 24 Qiu, Z.; Yan, C.; Lu, J.; Yang, W.; Ikehara, T.; Nishi, T. Various crystalline morphology of poly(butylene succinate-co-butylene adipate) in its miscible blends with poly(vinylidene fluoride). *J. Phys. Chem. B* 2007, 111(11), 2783–2789.
- 25 Hwang, S. Y.; Jin, X. Y.; Yoo, E. S.; Im, S. S. Synthesis, physical properties and enzymatic degradation of poly(oxyethylene-*b*-butylene succinate) ionomers. *Polymer* 2011, 52(13), 2784–2791.
- 26 Ojijo, V.; Sinha Ray, S.; Sadiku, R. Role of specific interfacial area in controlling properties of immiscible blends of biodegradable polylactide and poly[(butylene succinate)-*co*-adipate]. *ACS Appl. Mater. Interfaces* 2012, 4(12), 6690–6701.
- 27 Wang, X.; Shi, J.; Chen, Y.; Fu, Z.; Shi, Y. Nonisothermal crystallization kinetics of poly(butylene adipate-co-terephthalate) Copolyester. *China Pet. Process. Petrochemical Technol.* 2012, 14(1), 74–79.
- 28 Dil, E. J.; Carreau, P. J.; Favis, B. D. Morphology, miscibility and continuity development in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *Polymer* 2015, 68, 202–212.
- 29 Liu, F.; Zhang, J.; Wang, J.; Liu, X.; Zhang, R.; Hu, G.; Na, H.; Zhu, J. Soft segment free thermoplastic polyester elastomers with high performance. *J. Mater. Chem. A* 2015, 3, 13637–13641.
- 30 Brunelle, D. J.; Jang, T. Optimization of poly(1,4-cyclohexylidene cyclohexane-1,4-dicarboxylate) (PCCD) preparation for increased crystallinity. *Polymer* 2006, 47(11), 4094–4104.
- 31 Berti, C.; Celli, A.; Marchese, P.; Marianucci, E.; Barbiroli, G.; Di Credico, F. Influence of molecular structure and stereochemistry of the 1,4-cyclohexylene ring on thermal and mechanical behavior of poly(butylene 1,4-cyclohexanedicarboxylate). *Macromol. Chem. Phys.* 2008, 209(13), 1333–1344.
- 32 Gigli, M.; Lotti, N.; Vercellino, M.; Visai, L.; Munari, A. Novel ether-linkages containing aliphatic copolyesters of poly(butylene 1,4-cyclohexanedicarboxylate) as promising candidates for biomedical applications. *Mater. Sci. Eng. C Mater. Biol. Appl.* 2014, 34, 86–97.
- 33 Gigli, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Finelli, L.; Munari, A.; Dalla Rosa, M. Fully aliphatic copolyesters based on poly(butylene 1,4-cyclohexanedicarboxylate) with promising mechanical and barrier properties for food packaging applications. *Ind. Eng. Chem. Res.* 2013, 52(36), 12876–12886.
- 34 Commereuc, S.; Askanian, H.; Verney, V.; Celli, A.; Marchese, P.; Berti, C. About the end life of novel aliphatic and aliphatic-aromatic (co)polyesters after UV-weathering: structure/degradability relationships. *Polym. Degrad. Stab.* 2013, 98(7), 1321–1328.
- 35 Berti, C.; Binassi, E.; Celli, A.; Colonna, M.; Fiorini, M.; Marchese, P.; Marianucci, E.; Gazzano, M.; Credico, F. D. I.; Brunelle, D. J. Poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate): influence of stereochemistry of 1,4-cyclohexylene units on the thermal properties. *J. Polym. Sci., Part B: Polym. Phys.* 2008, 46, 619–630.
- 36 Chen, L. P.; Yee, A. F.; Goetz, J. M.; Schaefer, J. Molecular structure effects on the secondary relaxation and impact strength of a series of polyester copolymer glasses. *Macromolecules* 1998, 31(16), 5371–5382.
- 37 Gong, Y.; Hu, C. W.; Li, H.; Huang, K. L.; Tang, W. Isomer transformation and photoluminescence in novel coordination polymers constructed from 1,4-cyclohexanedicarboxylic acid and imidazole. *J. Solid State Chem.* 2005, 178(10), 3152–3158.
- 38 Liu, F.; Qiu, J.; Wang, J.; Zhang, J.; Na, H.; Zhu, J. Role of *cis*-1,4-cyclohexanedicarboxylic acid in the regulation of the structure and properties of a poly(butylene adipate-co-butylene 1,4-cyclohexanedicarboxylate) copolymer. *RSC Adv.* 2016, 6(70), 65889–65897.
- 39 Qiu, J.; Liu, F.; Zhang, J.; Na, H.; Zhu, J. Non-planar ring contained polyester modifying polylactide to pursue high toughness. *Compos. Sci. Technol.* 2016, 128, 41–48.
- 40 Celli, A.; Marchese, P.; Sullalti, S.; Berti, C.; Barbiroli, G. Eco-friendly poly(butylene 1,4-cyclohexanedicarboxylate): relationships between stereochemistry and crystallization behavior. *Macromol. Chem. Phys.* 2011, 212(14), 1524–1534.