Biodegradable thermoplastic copolyester elastomers: Methyl branched PBA\textsubscript{m}T

Abstract: A series of novel biodegradable copolymers named poly(3-butylene 3-methyl adipate co-terephthalate) (PBA\textsubscript{m}T) were synthesized from the monomers of 3-methyl adipic acid (\textit{AA}\textsubscript{m}), 1,4-butandiol (BD), and terephthalic acid (TPA) through a process of esterification and polycondensation. \textsuperscript{1}H NMR analysis shows that they are random copolymers whose composition can be well controlled by the feed ratio of monomers. From the results of DSC and XRD, the introduction of methyl group successfully destroys the crystallizability of the PBA\textsubscript{m} chains, thus making it become a relative soft segment compared to PBA, while these random PBA\textsubscript{m}T copolymers constructed by soft segment PBA\textsubscript{m} and rigid segment PBT change from semi-crystalline polymers to nearly amorphous polymers as the feed ratio of \textit{A}\textsubscript{m} increases. Especially, mechanical tests reveal that the copolymers show outstanding elasticity and rebound resilience with excellent strength. These thermoplastic copolyester elastomers with good performance by simply introduction of branched methyl group on polybutylene adipate terephthalate (PBAT) copolymer chains may well explore the potential application of biodegradable PBAT-based material.

Keywords: poly(butylene 3-methyl adipate co-terephthalate), 3-methyl adipic acid, thermoplastic copolyester elastomers, biodegradable, crystallizability

1 Introduction

Recently, the development and application of biodegradable plastics are more and more concerned by researchers and enterprises attributed to the problem of “white pollution” caused by the plastic products (1–4). From the first generation of biologically fermented poly(hydroxyvalerate)\textsubscript{s} (PHAs) (5,6) to the later chemically synthesized biodegradable polyester poly(lactic acid) (PLA) (7–9), poly-caprolactone (PCL) (10), and poly(butylene succinate) (PBS) (11,12), etc. (13–15), the biodegradable polyester family is booming. While all these polyesters are kinds of rigid degradable plastic, people pay little attention on the soft degradable thermoplastic copolyester elastomers (TPEE).

As a novel class of thermoplastic elastomers, TPEE are copolymers consisting of glassy or crystalline hard segments and amorphous soft segments. In the past few decades, the commercial growth of TPEE has continuously increased because of their unique advantages: first, TPEE have a similar synthetic feature as polyesters, which can be easily synthesized through a process of esterification and polycondensation (16–18); second, TPEE with different physical properties can be easily designed by variation in the species of the hard and soft segments and their ratios (13–15,19,20). Generally speaking, in the TPEE, the hard segments are generally aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) while the soft segments are aliphatic polyethers or polyesters with long chains such as poly(ethylene glycol) (PEG), poly(tetramethylene glycol) (PTMG), and poly(sebacate ethylene glycol) (21–24). The introduction of long aliphatic flexible soft segments is the most common...
strategy to construct polyester elastomers although very few TPEE are also constructed by introducing branched chain or stereo isomers (25–28).

Polybutylene adipate terephthalate (PBAT) is a new generation of bio-degradable aliphatic-aromatic copolyesters synthetic from the monomers of adipic acid (AA), 1,4-butane diol (BDO), and terephthalic acid (TPA). Combining the biodegradability of aliphatic polyester with excellent mechanical properties and thermal stability of aromatic polyester, PBAT possesses excellent strengths both on softness and toughness (29–32). The mechanical properties of PBAT are similar to that of low-density polyethylene, thus making it suitable for biodegradable and flexible applications such as agricultural films and various packaging material. The contents of aromatic TPA and aliphatic AA have a significant influence on the solid-state structures and properties of PBAT copolyester (33,34). As the content of aromatic TPA increases, the rigidity and crystallinity of PBAT increase, while as the content of AA increases, the elasticity of PBAT increases, which indicates that it is very possible to make PBAT into thermoplastic elastomer, where PBA unit can act as a role of soft segment, and PBT acts as a role of hard segment.

As we know, common PBA and PBT are both crystallized polymers, while to guarantee the resilience, the soft segment in elastomer should be noncrystallizable (21–24). A well-performance elastomer based on PBAT structure can only be obtained if the crystallization of PBA or PBT segments is destroyed. To realize the idea in this paper, a short branched 3-methyl AA (AAm) was introduced instead of AA to synthesize a series of novel poly(butylene 3-methyl adipate co-terephthalate) (PBAmT) copolymers with different mole ratio of AAm and BT. We expect that the short branch 3-methyl in AA can effectively decrease the crystallizability of PBAmT segment. Then the flexible soft PBAm segments together with PBT rigid segments can construct a thermoplastic elastomer with good mechanical property and elastic resilience. The copolyesters are characterized by 1H NMR, GPC, DSC, XRD, tensile tests, and their enzymatic degradation test. The experimental results confirm our assumption, and we get a series of TPEE with good performance by simply introducing branched methyl group on PBAT copolymer chains.

2 Materials and methods

2.1 Materials

AAm, TPA, BDO, tetrabutyl titanate (TBT), polyphosphoric acid (PPA), and other reagents were analytically pure and purchased from Aladdin Reagent Co. Ltd and used as received. Lipase from porcine pancreas (30–90 units mg−1) was purchased from Sigma Aldrich Co. Ltd.

2.2 Synthesis

The synthesis of PBAmT was performed via a two-stage melt polycondensation adapted as esterification at atmospheric pressure and polycondensation at reduced pressure. According to the molar percentage of AAm in total acid feed, the PBAmT were labeled as PBAmT55, PBAmT60, PBAmT70, PBAmT75, and PBAmT80. Melt esterification and polycondensation were performed in a 250 mL four-neck round bottom flask with mechanical stirring. In a typical experiment of preparing PBAmT70, 19.94 g PTA, 44.85 g AAm, 54.07 g BDO (diol:diacid molar ratio 1.5:1), 0.07 g TBT (0.5 mmol mol−1 diacid, TBT is proved to significantly accelerate the esterification reaction of aromatic dicarboxylic acid), and 0.07 g PPA (0.5 mmol mol−1 diacid, PPA is believed to prevent side reactions such as etherification and thermal decomposition) were added into the flask. In the first step, the esterification reaction was conducted at 190–210°C for 4 h with a N2 inlet. In the second step, another part of 0.14 g TBT (1.0 mmol mol−1 diacid) was added, and the polycondensation reaction was conducted at 220–250°C for 4 h under a reduced pressure of 30 Pa.

2.3 Characterization

Gel permeation chromatography (GPC) was used to measure material molecular weight and polydispersity at a rate of 1 mL min−1 at 35°C. Chloroform was used as the solvent and the data were calibrated with polystyrene standard samples.

On the Bruker-AMX-300 device, with CDCl3 as the solvent of PBAmT, the 1H NMR spectrum was recorded. The chemical shift was based on one part per million of tetramethylsilane.

The thermal behaviors of materials were characterized by a Mettler-DSC1 differential scanning calorimeter (DSC) model. Five milligrams of sample was used to test through conventional heating/cooling/heating procedures from −70°C to 120°C at a temperature change rate of 10°C min−1, and the first heating run served to erase the thermal history.

At room temperature, wide-angle X-ray diffraction (WAXD) patterns were recorded on the Rigaku RAD-IIIB.
system, nickel filtered Cu-Kα radiation (λ = 0.154 nm, 40 kV, and 110 mA) in the 2θ range from 6° to 60°, and the step size was 0.02° s⁻¹. Using a 0.1 mm thick polytetrafluoroethylene film as a spacer layer, the polymer sample was sandwiched between polytetrafluoroethylene sheets, and then heated at a temperature of about 2°C higher than the melting temperature under a pressure of 15 kg cm⁻² for 2 min to prepare melt crystallized PBAmT copolyester film. The molded polymer film was then transferred to an oven at the desired temperature for isothermal crystallization. After the crystallization was completed, the polymer film was separated and subjected to X-ray diffraction.

Tensile testing and cyclic tensile testing were performed at room temperature (25°C) using an Instron tensile testing machine. The dumbbell-shaped samples with effective length 25 mm, width 4.0 mm, and thickness 2.0 mm were prepared by melt-pressing under a hot press at 30 MPa for 30 s and the temperatures ranged from 100°C to 190°C. In the tensile testing, all samples were stretched at a stretching rate of 50 mm min⁻¹ at 25°C. At least five specimens were tested for each sample, and the average values were reported.

In the cyclic tensile test, dumbbell-shaped samples were stretched to 100% strain at a tensile rate of 20 mm min⁻¹ at room temperature. Then, the clamp began to return at a speed of 20 mm min⁻¹ until the force acting on the sample is 0. After the above two steps, a cycle was completed. Three samples were tested to calculate the mean and standard deviation. Each sample was subjected to five cycles, and the shape recovery rate (Rₙ) was calculated according to Eq. 1:

\[ Rₙ = \frac{Lₘ - Lₙ}{Lₘ - Lₙ₋₁} \times 100\%, \]  

where \( n \) is the number of cycles, \( Lₘ \) is the maximum strain applied to the material, \( Lₙ \) and \( Lₙ₋₁ \) are the strain of the sample in two consecutive cycles when the force applied to the sample is 0, and \( Rₙ \) is based on two consecutive cycles.

The enzymatic degradation performance was studied using lipase in porcine pancreas. Using the same molding method as above, samples of 10 × 10 × 0.3 mm films were prepared by melting and pressing in a square mold (thickness of 0.3 mm), and then placed in a phosphate buffer solution (pH = 7.2) with 0.1 mg mL⁻¹ lipase at 37°C. After a specific incubation period, the film was removed, rinsed with distilled water, and weighed until a constant weight was reached. The degree of biodegradation was estimated by weight loss. Hitachi S-4300 scanning electron microscope was used to observe the morphology of the film before and after enzyme degradation.

### Table 1: Molecular weight and polydispersity characteristics of PBAm and PBAmT

<table>
<thead>
<tr>
<th>Sample</th>
<th>GPC</th>
<th>BAₘ ratio</th>
<th>²H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Mₘ ) (g mol⁻¹)</td>
<td>( M_w ) (g mol⁻¹)</td>
<td>PI</td>
</tr>
<tr>
<td>PBAm₅₅</td>
<td>49,614</td>
<td>80,946</td>
<td>1.63</td>
</tr>
<tr>
<td>PBAm₆₀</td>
<td>47,866</td>
<td>78,971</td>
<td>1.65</td>
</tr>
<tr>
<td>PBAm₇₀</td>
<td>45,738</td>
<td>78,311</td>
<td>1.72</td>
</tr>
<tr>
<td>PBAm₇₅</td>
<td>44,016</td>
<td>71,539</td>
<td>1.63</td>
</tr>
<tr>
<td>PBAm₈₀</td>
<td>41,811</td>
<td>71,605</td>
<td>1.72</td>
</tr>
<tr>
<td>PBAm</td>
<td>40,689</td>
<td>78,068</td>
<td>1.92</td>
</tr>
</tbody>
</table>

3 Results and discussion

#### 3.1 Chain structure and sequence of PBAmₘT

As the physical properties of PBAmₘT copolymers depend strongly on their chain structure and sequence including molecular weight and composition, they have been synthesized by a two-stage melt polycondensation from TPA, AA, and BDO, through the same and efficient process, which can guarantee a relatively high molecular weight and well-controlled composition. The chemical activity of the branched dicarboxylic acid AAₘ shows no significant difference with AA. All the copolyesters with different proportion of BAₘ and BT were synthesized within an identical time.

The molecular weights of PBAmₘT were measured by GPC. As listed in Table 1, number average molecular weight (\( Mₙ \)) ranging from 40,689 to 49,614 g mol⁻¹ and weight average molecular weight (\( M_w \)) ranging from 71,539 to 80,946 g mol⁻¹ are obtained with polydispersity range.
\( PI = M_w/M_n \) from 1.63 to 1.92, as expected for the synthetic method used. This result indicates that a high molecular weight of copolymer can be obtained using the two-stage melt polycondensation method.

To better understand the sequence structures of polymer chains, \(^1\text{H} \) NMR was conducted for all the PBA\(_m\)T copolymers. The \(^1\text{H} \) NMR spectrum of PBA\(_m\)T70 is shown as the example in Figure 1. The two different dicarboxylic acids both have their typical proton with totally different chemical shifts. The shift appearing at 8.09 ppm belongs to \( \text{C}_6\text{H}_6 \) units of TPA and 0.96 ppm belongs to \( \text{CH}_3 \) units of AA. The composition of BA\(_m\) and BT can be easily calculated by the integrated intensity of peaks c and d. The mole ratio of calculated \(^1\text{H} \) NMR are well fitted with the feed ratio of AA when synthesis. The chemical shifts of \(-\text{CH}_2-\) in BDO close to different ester bonds resulting from copolycondensation show different chemical shifts appear at 4.09 ppm (a), 4.14 ppm (h), 4.37 ppm (k), and 4.43 ppm (e), respectively. From the spectrum, the number-average sequence length of BT and BA\(_m\) units \( (L_{n,\text{BT}} \text{ and } L_{n,\text{BA}_m}) \), and the degree of randomness \( (R) \) are calculated using Eqs 2–4, respectively, where the integrated intensity of chemical shift \( I \) is abbreviated as \( I_i \). The multipeaks fitting function of MestReNova software was used to calculate the integrated intensity of the partially peaks: a, h, k, e. The results of PBA\(_m\)T70 are listed as \( L_{n,\text{BT}} = 1.53 \) and \( L_{n,\text{BA}_m} = 2.83 \), \( R = 1.01 \). The \(^1\text{H} \) NMR data and the calculated results of other copolymer are listed in Table 1. The degree of randomness close to 1.0 indicates a random structure of all the synthesized copolyesters (35).

\[
L_{n,\text{BA}_m} = 1 + \frac{2I_a}{I_h + I_k},
\]
\[
L_{n,\text{BT}} = 1 + \frac{2I_e}{I_h + I_k},
\]
\[
R = 1/L_{n,\text{BT}} + 1/L_{n,\text{BA}_m}.
\]

### 3.2 Thermal properties of PBA\(_m\)T

The thermal properties and melt crystallization behaviors of the copolymers have direct influence on their using and processing performance, which can also reflect their crystallization properties. The glass transition temperature \( (T_g) \), melting temperature \( (T_m) \), and crystallization temperature \( (T_c) \) of PBA\(_m\)T copolymers as well as PBA\(_m\) were investigated by DSC as seen in Figure 2. Different from the semi-crystalline PBA that shows obvious melt and crystallization peaks as reported by literature, the methyl branched PBA\(_m\) is amorphous and shows that the glass transition point is only \(-55^\circ\text{C}\). The introduction of methyl group significantly reduces the crystallinity of the PBA\(_m\) chain, so that it becomes flexible chains compared to rigid PBA chains. With the introduction of more and more PBT blocks that play a role as hard segment into the copolymer, the \( T_g \) increases continuously and reaches to a higher temperature of \(-30^\circ\text{C}\) when the content of PBT increases to 45%. The increase in \( T_g \) is probably because of that the flexibility of the copolymer chains are restricted greatly. All the copolyesters with only one glass transition temperature means that they

![Figure 1: \(^1\text{H} \) NMR spectrum and chain structures of PBA\(_m\)T70.](image-url)
are all random copolymers, which is in agreement with the results of the proton NMR spectra (36,37).

For \( T_c \) and \( T_m \), there are no melting and melt crystallization peaks appearing for PBA\(_m\), PBA\(_m\)T80, PBA\(_m\)T75, and PBA\(_m\)T70 during the heating and cooling scan when composition of PBA\(_m\) is higher. As explained above, the copolymers show nearly amorphous condition when the proportion of PBA\(_m\) is high, and the crystallization rate is so slow that we cannot observe the peaks within the experimental time region. As the content of PBT increases further, the crystallization of PBA\(_m\)T60 is improved, leading to a melting peak appearing at 90°C. Although the cooling scan curve still shows no peaks under this condition, a cold crystallization peak at 21°C is clearly observed in the next heating run (38,39). As the PBT composition increases higher, the crystallization of PBA\(_m\)T55 increases further and shows obvious melting peak at 108°C and melt crystallization peak at 62°C. These results well support our explanations about the influence of methyl group of PBA\(_m\) on the crystallization property of copolymers. With the increase in PBA\(_m\) content, the crystallinity of copolyester transfers from semi-crystalline to amorphous, and it tends to become a better thermoplastic elastomer.

### 3.3 Crystal structure

To further understand the influence of methyl branched AA on the crystallization property of the copolyesters, XRD was investigated for all of the synthesized PBA\(_m\)T. According to the XRD patterns shown in Figure 3, PBA\(_m\) segment with methyl branch is proved to be amorphous and shows no diffraction peaks compare to PBA. On the contrary, PBT units are crystallizable. When the BA\(_m\) content is less than 40%, both PBA\(_m\)T60 and PBA\(_m\)T55 behave as semi-crystalline polyesters and show five diffraction peaks at 16.1°, 17.2°, 20.2°, 23.2°, and 25.1°, which can be assigned to (011), (010), (101), (100), and (111) reflection planes of PBT, according to the literature (36,37). The intensity of diffraction peaks decreases as BA\(_m\) content increases but still appear at the same position, indicating that the branched BA\(_m\) segment shows no significant effect on the crystal form of PBT segment. On the contrary, as BA\(_m\) content increases, PBA\(_m\)T80, PBA\(_m\)T75, and PBA\(_m\)T70 show no diffraction peaks in their XRD patterns indicating that the crystallinity of copolyesters decreases dramatically. The decreased crystallization ability attributes a large part to the randomization of the main chain structure and the influence of amorphous PBA\(_m\) units. The introduction of branched

![Figure 2: DSC thermograms of PBA\(_m\) and PBA\(_m\)T copolyesters. The curves were obtained during the second heating (a) and cooling runs (b), while the first heating run was to erase thermal history.](image)

![Figure 3: XRD patterns of PBA\(_m\)T copolyesters and PBA\(_m\).](image)
PBAm chain reduces the regularity of the main chain, ultimately leading to the decrease in the degree of crystallinity of the copolyester, in which the microcrystalline structure acts as the cross-linking point to form thermoplastic. These results validate the DSC results mutually.

### 3.4 Mechanical properties

The mechanical properties of PBAmT copolymers depend mainly on the ratio of PBAm segments to PBT segments, and the crystallinity of PBT segments as the two segments are miscible in amorphous phase. Therefore, the effect of different contents of PBAm on their mechanical properties was checked by tensile strength measurements. Tensile strength and elongation at break are tested and presented in Table 2. The PBAm samples are amorphous polymers and almost have no available mechanical properties. For PBAmT, when the content of BA contents decreases from 80% to 55%, the tensile strength increases from 5.3 MPa to 20.8 MPa, which is because of not only the greater flexibility of PBAm chains than that of PBT, but also the low crystallinity of the copolymers. In contrast, the elongation at break obviously decreases from 1,480% to 1,071%, which is also because of the formation of greater phase separation with higher BA contents.

The crystallized PBT hard segments give strength to the copolymers, and the branched soft PBAm segments provide flexibility to the system. Furthermore, crystallized PBT segments act as junctions of a labile physical network in the materials to guarantee the elastic recovery. The PBAmT copolyesters obtain excellent elasticity and flexibility. Figure 4 shows the stress (δ)–strain (ε) curves. For PBAmT copolymers, their curves are typical elastic curves with large elongation at break but without yielding behaviors, and actually the deformation is reversible to some extent. Besides, their strain hardening is obvious, which is caused by the strain-induced crystallization and chain alignment. PBAmT exhibits obvious rebound resilience, while the rebound resilience of PBAmT75 is much better with the recoverable strain close to 1,500% and tensile strength of nearly 5.4 MPa.

To further study the elasticity of PBAmT, we took PBAmT70 as an example and carried out five times of tension recovery cyclic loading under 100% strain. The stress–strain curve for cyclic tension is shown in Figure 5, and the shape recovery rate data for the samples are summarized in Table 3. In the first cycle, the shape recovery rate of the sample is 82.6%, and it gradually increases above 97.6% in the following four cycles. These results confirm the sufficient level of elastic recovery of PBAmT. It is found that the tensile and recovery curves of the samples form a nonlinear hysteresis loop. In the first cyclic tension, the samples show a large hysteresis loop and a large residual strain. With the increase in the number of cycles, the tensile and recovery trajectories almost coincide, the hysteresis loop gradually decreases, and the total residual strain tends to be constant.

In fact, the area of hysterisis loop is equivalent to the work lost in the stretching recovery process of elastomer.
It is an obvious relaxation phenomenon when the polymer chain is hindered by the change in internal friction and strain, which cannot keep up with the change in stress. In addition to the large lag cycle in the first cycle, the tension recovery curves of the following cycles almost overlap, indicating that the friction to be overcome in the process is small, and the tension recovery process has obvious reversibility. In conclusion, PBAmT is a kind of elastomer with excellent elasticity and great development potential.

### 3.5 Enzymatic degradation

The study of the enzymatic degradation behaviors of the copolyesters is indispensable to develop novel bio-based biodegradable. In this work, the enzymatic degradation behaviors of the copolymer by lipase from porcine pancreas were detected in phosphate buffer solution (pH 7.2) at 40°C. Figure 6 shows the SEM micrographs of PBAmT during enzymatic degradation after 0, 2, and 6 weeks. The surfaces of all the samples appear smooth initially.

### Table 3: Tensile properties of PBAmT70

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ (%)</th>
<th>$R_2$ (%)</th>
<th>$R_3$ (%)</th>
<th>$R_4$ (%)</th>
<th>$R_5$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAmT70</td>
<td>82.6 ± 1.8</td>
<td>97.6 ± 0.2</td>
<td>98.7 ± 0.3</td>
<td>99.1 ± 0.2</td>
<td>99.3 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 6: SEM micrographs of PBAmT80 ($a_1$–$a_3$), PBAmT75 ($b_1$–$b_3$), PBAmT70 ($c_1$–$c_3$), PBAmT60 ($d_1$–$d_3$), and PBAmT55 ($e_1$–$e_3$), during enzymatic degradation at several times; ($a_1$–$e_1$) 0 days, ($a_2$–$e_2$) 2 weeks, and ($a_3$–$e_3$) 6 weeks.
As time goes on, there is apparently a degradation emerging. After 2 weeks, they show some holes because of the degradation, and then small fragments because of extended surface erosion are revealed and large parts of the film surface are removed at last. It should be noted that the degradation behaviors of all PBA\textsubscript{m}T copolymers show apparently no difference in our experiments. They all behave as the characteristics of amorphous polymers and can degrade completely. The relatively higher biodegradation rate compared with PBAT can be well explained that the introduction of branched BA\textsubscript{m} decreases the crystalline and melting point.

In other words, the acceleration to degradation caused by the decrease in crystalline and melting point exceeds the resistance to degradation caused by increasing the BT units, thus accelerating the adsorptive binding of the lipase at the PBA\textsubscript{m}T surface.

4 Conclusion

High molecular weight poly(butylene adipate co-terephthalate) thermoplastic elastomer with methyl branch introduced into the main chains were obtained by an esterification and polycondensation process using TBT as catalyst. The introduction of methyl group successfully destroys the crystallizability of the PBA\textsubscript{m} chains, thus changing it into a relative soft segment compared to PBA. Thus the random PBA\textsubscript{m}T copolymers constructed by soft segment PBA\textsubscript{m} and rigid segment PBT change from semi-crystalline polymers to nearly amorphous polymers as the feed ratio of Am increases. They are random copolymers whose composition can be well controlled by the feed ratio of monomers. According to the DSC and XRD, their enzymatic degradation behaviors are also investigated. The PBA\textsubscript{m} blocks are proved to be amorphous and will decrease the crystallization ability of the copolymers. With the increase in the BT units’ content, the amorphous copolymers change to semi-crystalline copolymers. As a result of the rigid segment increasing, the copolymers have excellent strength, while the increase in soft segments makes them have excellent elasticity, and the recovery rate in the first cycle can reach 82%. All in all, the biodegradable PBA\textsubscript{m}T can be potentially used in biodegradable elastomers or modifiers for other polymers. Furthermore, this work may provide new ideas for the design and synthesis of new elastomer materials.

Acknowledgment: The authors are thankful to Dr Huang Dan, National Engineering Research Center of Engineering Plastics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, China, for her help in experimental testing.

Funding information: The authors would like to thank the National Natural Science Foundation of China (Project No. 51973228) and Youth Innovation Promotion Association, CAS (2018033) for financial support.

Author contributions: Wen-Bo Neng: writing – original draft, writing – review and editing, methodology, formal analysis; Wen-Guang Xie, Bo-Lu, and Zhi-Chao Zhen: writing – original draft, formal analysis, visualization, project administration; Jun-Long Zhao, Ge-Xia Wang, and Jun-Hui Ji: resources.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: All data generated or analysed during this study are included in this published article.

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