Dependence of Crystallization Behavior of Interacting Telechelic Poly(butylene succinate) Oligomer on Molecular Weight

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Abstract: A large spherulite structure deteriorates the mechanical properties of crystalline polymers, and therefore various methods have been explored to increase primary nucleation density. Recently, chain-end modification has been proposed as an effective approach for regulating polymer crystal nucleation. However, the relevant nucleation mechanism still requires investigation. Therefore, in this work, 2-ureido-4[H]-pyrimidinone (UPy) units, which can form stacks via quadruple hydrogen bonds with each other, are introduced as end groups for the preparation of interacting telechelic poly(butylene succinate) (PBS-UPy) oligomers with different molecular weights ($M_n$). The crystallization, especially the nucleation behavior of PBS-UPy, is studied in detail by comparing with the corresponding pre-polymer, the hydroxyl-terminal PBS (PBS-OH). The thermal properties of PBS-UPy exhibit similar $M_n$-dependent tendency to those of PBS-OH, but with weaker total crystallization rate. The spherulite growth rate is significantly reduced, whereas the primary nucleation density is highly promoted, after introducing UPy groups. Further investigation reveals that the mechanism of UPy stacks’ influence on nucleation ability changes from inhibition to promotion with respect to $M_n$. Even under an inhibition of nucleation ability, the final nucleation density is obviously increased because of a significant decline of the growth rate. In addition, the change in the impact of UPy stacks on nucleation ability is speculated to originate from the memory expression feasibility of ordered conformation in the melt during crystallization.

Keywords: poly(butylene succinate); crystallization; telechelic polymer; nucleation; melt memory effect

1. Introduction

Poly(butylene succinate) (PBS), as one of the promising and extensively investigated biodegradable aliphatic polyesters, exhibits a high melting point, excellent processing properties and thermal stability [1–3]. It possesses comparable thermal and mechanical properties to polyolefin [4,5] but has some drawbacks, including large spherulite structure (i.e., poor primary nucleation density) and low melt strength, which limit its versatile application [6,7].

Various methods have been carried out to overcome the drawbacks. Copolymerization by introducing comonomeric units can decrease the spherulite size of PBS by raising the randomness of the polymer chains [8]. However, the thermal properties including melting point and enthalpy are highly degraded at the same time [9,10]. On the other hand, the incorporation of nucleating agent is generally used to increase the nucleation density of PBS, so as to reduce spherulite size and shorten the process period [11–14]. While nucleating agents can improve the properties of PBS, some new problem might be introduced—for instance, the uneven distribution of nucleating agent in the polymer matrix would lead to increased embrittlement [12]. Therefore, the development of new strategies for PBS is
still desired. Recently, chain-end modification has been proposed to be a viable method for controlling polymer crystal nucleation [15]. Consequently, it is interesting to regulate the crystallization of PBS by forming interacting telechelic chains.

The achievement of an interacting telechelic polymer is commonly realized by linking specific chemical groups that can form various hydrogen bonds with each other to the chain ends, such as quadruple hydrogen bonds of 2-ureido-4-[1H]-pyrimidinone (UPy) [16–19], multiple hydrogen bonds of thymine (THy) [20,21] and double hydrogen bonds of bis-(monomethyl malonyl) dihydrazide (BMMH) [22]. By bonding BMMH units to polylactide (PLA) chain ends with a number-average molecular weight of about \( \sim 1.1 \times 10^4 \) g/mol, the crystallization ability was improved and the nucleation density was notably raised in [22]. However, when introducing UPy units to the chain ends of poly(\( \varepsilon \)-caprolactone) (PCL) with molecular weight ranging from \( 1.3 \times 10^3 \) to \( 7.6 \times 10^3 \) g/mol, the crystallization ability of PCL was weakened [17]. The use of UPy units as end groups of PLA with various molecular weights and architectures lowers the crystallization rate and decreases the nucleation density [18,19]. During the heating of a quenched amorphous sample, THy end groups enhanced the crystallization of PLA, exhibiting a lower cold crystallization peak temperature in [20]. Interacting end groups can obviously change the crystallization behavior of polymer backbones (either promoting or inhibiting), and the polymer molecular weight plays an essential role. Previous research has shown that the spherulite growth rates of most telechelic polymers are slower than those of their counterparts without interacting end groups, especially in low-molecular-weight polymers (i.e., oligomers) [18]. Meanwhile, the effect of interacting end groups on the nucleation behavior of backbones is quite complicated and rarely investigated.

To better understand the crystallization behavior of interacting telechelic polymers and provide efficient guidance for raising the nucleation density of PBS, a series of UPy-terminal PBS oligomers are synthesized and studied. The crystallization, especially the nucleation behavior, is systematically demonstrated using NMR, DSC, POM, and WAXD, and the molecular-weight-dependent nucleation ability is established in detail.

2. Experimental

2.1. Materials

1,4-Butanediol (BDO, AR grade), succinic acid (SA, AR grade), 2-amino-4-hydroxy-6-methylpyrimidine (UPy, AR grade), 1,6-hexyldiisocyanate (HDI, AR grade), dibutyltindilaurate (DBTD, AR grade), tetrabutyl titanate (TBT, AR grade) and silica were purchased from Shanghai Aladdin Industrial Inc. (Shanghai, China). Petroleum ether (AR grade), methanol (AR grade) and chloroform (AR grade, predried over molecular sieves) were purchased from Beijing Chemical Factory (Beijing, China). All reagents were used as received.

2.2. Synthesis of UPy-NCO

Synthesis of 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[H]pyrimidinone (UPy-NCO) was carried out according to the following procedure [23]: a solution of 0.10 mol UPy in 0.70 mol HDI was heated to 100 °C for reaction lasting 16 h. Then, petroleum ether was added and the resulting precipitate was filtered and further washed with more petroleum ether. The as-received white powder was dried at 50 °C in a vacuum oven for 48 h to remove any residual solvent and then stored in a dryer.

2.3. Synthesis of PBS-OH

Hydroxyl-terminated poly(butylene succinate) (PBS-OH) was synthesized by a two-step reaction of esterification and polycondensation in a molten state, as reported in a previous paper [24]. The ratio of diol/diacid was set constant at 1.5 to ensure the obtainment of PBS-OH, and the polycondensation time was adjusted to regulate the molecular weight. The products were purified through a procedure consisting of dissolution in chloroform and precipitation in excess cold methanol.
2.4. Synthesis of PBS-UPy

UPy-terminated PBS (PBS-UPy) was prepared by the following procedure: 5 mmol UPy-NCO was added into the 50 mL chloroform solution containing 1 mmol PBS-OH, followed by the addition of 2 drops of DBTD. The resulting solution was stirred at 60 °C for 16 h, and 2 g of silica and 1 drop of DBTD were added to the solution for further reaction lasting 1 h. Then, 50 mL more chloroform was added and the mixture was filtered. The clear solution was further centrifuged at 1000 rpm for 20 min to remove impurity and then precipitated in an excess amount of cold methanol. The precipitate was collected and dried in a vacuum oven at 50 °C for 2 days.

2.5. Characterization

The chain structures of all products were determined by a $^1$H nuclear magnetic resonance ($^1$H NMR) spectrometer (JEOL, ECA-300M, Tokyo, Japan). Chloroform-$d$ and tetramethylsilane (TMS) were used as the solvent and reference, respectively.

The Fourier-transform infrared (FTIR) spectroscopy was conducted using a Bruker Hyperion FTIR spectrometer (Karlsruhe, Germany). The number of scans was set at 32 and the wavenumber range was obtained from 4000 to 800 cm$^{-1}$.

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 instrument (Kyoto, Japan). The samples with weight of ~10 mg were heated from 40 °C to 550 °C at a rate of 10 °C/min with a nitrogen purge flow rate of 20 mL/min.

The thermal properties and melt memory effect of samples were investigated by a differential scanning calorimeter (DSC, NETZSCH 204 F1, Berlin, Germany) equipped with an intercooler as the cooling system under nitrogen atmosphere. The instrument was calibrated with indium and tin standards before use, and samples of ~5 mg were used. In a non-isothermal procedure, the samples were first heated to 160 °C and held for 20 min to eliminate previous thermal history, and then cooled to 30 °C. Subsequently, the samples were reheated to 160 °C. The protocol for melt memory effect evaluation is as follows: samples were heated to 160 °C and held for 20 min, follow by being cooled to 30 °C and held for 2 min, then the samples were reheated to a set melting temperature ($T_s$) for 5 min, and afterwards cooled to 30 °C for 2 min. The protocol was repeated by changing the value of $T_s$ to get enough data for evaluation of the melt memory effect. The heating and cooling rates in all measurements were set at 10 °C/min.

The crystal structures of samples were detected using a Bruker D8 Focus X-ray diffractometer equipped with Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm) at room temperature. The $2\theta$ scanning range was set as 5°–30° with a rate of 2°/min. The measuring voltage and current were set at 40 kV and 200 mA.

The spherulite morphology and nucleation ability of samples were observed with a polarized optical microscope (POM, Leica DM-2500P, Wetzlar, Germany) equipped with a temperature-controlled hot-stage (Linkam, THMS600, Surrey, UK). The samples sandwiched between glass slides, with thickness of 10 µm, were melted at 160 °C for 5 min and then were fast switched to the desired temperatures for isothermal crystallization.

3. Results

3.1. Chain Structure

The $^1$H NMR spectra and peak identifications of PBS-OH and PBS-UPy chains are presented in Figure 1. In the $^1$H NMR spectrum of PBS-OH, peaks $a$ and $b$ (located at 2.62 and 3.65 ppm, respectively) are assigned to protons in the CH$_2$ of succinate units and the CH$_2$ covalently linked to the terminal –OH groups [24]. Based on Equation (1), the number-average molecular weights ($M_n$s) of PBS-OH samples were calculated and are tabulated in Table 1.
CH2 covalently linked to the terminal –OH groups [24]. Based on Equation (1), the number-average molecular weights ($M_n$) of PBS-OH samples were calculated and are tabulated in Table 1.

Three peaks located at 10.10, 11.92 and 13.11 ppm are ascribed to the characteristic protons in the terminal UPy units [23]. Consequently, the $M_n$s of PBS-UPy samples were calculated and are listed in Table 1 according to Equation (2).

$$M_n(PBS - OH) = 90 + \frac{I_{peaka}}{2I_{peakb}} \times 172$$

$$M_n(PBS - UPy) = 292 + 88 + \frac{I_{peakc}}{4I_{peakc}} \times 172$$

where “I” represents the integral intensity of peak in the $^1$H NMR spectrum.

The $M_n$ of PBS-UPy is slightly higher than the counterpart of PBS-OH. Considering the polydispersity feature of polycondensation polymers and the fact that the reaction feeding ratio of UPy-NCO/PBS-OH was sufficiently high, it is reasonable to conclude that the chain ends of PBS were completely terminated with UPy units in the as-prepared PBS-UPy. To facilitate the subsequent description, the samples are discriminatively named by referring to their $M_n$s.

To further confirm the chemical structure of PBS-UPy, FTIR spectra of PBS-OH, UPy-NCO and PBS-UPy were collected for comparison. As shown in Figure 2, PBS-OH does not show an FTIR absorption band in the wavenumber range 1700–1500 cm$^{-1}$, while new absorption bands at 1669, 1588 and 1527 cm$^{-1}$ appear in PBS-UPy. The three bands are respectively assigned to the characteristic C=O stretching, C=C stretching and N–H bending vibrations of UPy [25,26], which are also observed in the FTIR spectrum of UPy-NCO. The wavenumber positions of C=O stretching and N–H bending also confirm the
formation of quadruple hydrogen bonds among UPy groups [16–19]. The slight shifting behavior of absorption bands between PBS-UPy and UPy-NCO indicates the different chemical environment and proves that the as-obtained PBS-UPy was not a simple blend between PBS-OH and UPy-NCO. Therefore, we conclude that telechelic PBS chains with interacting UPy end groups were obtained.

![FTIR spectra](image)

**Figure 2.** FTIR spectra of PBS-OH-4.4k, UPy-NCO and PBS-UPy-4.5k.

Before the investigation of the crystallization behavior of PBS-UPy, it is important to become clear on the thermal stability, though it is known that PBS-OH (or PBS) has a thermal degradation temperature higher than 200 °C [27]. Hence, a TGA analysis of PBS-UPy was carried out (Figure 3). The PBS-UPy samples showed comparable or even better thermal stability, as they displayed a higher \( T_{5\%} \) (the temperature at a weight loss of 5%) than PBS-OH. Therefore, it is suitable to study the thermal properties of PBS-OH and PBS-UPy in the temperature range not exceeding 160 °C, which was used to eliminate the thermal history of samples here.

![TGA curves](image)

**Figure 3.** TGA curves of PBS-OH-1.0k and PBS samples at a heating rate of 10 °C/min.

### 3.2. Non-Isothermal Crystallization

To investigate the effect of \( M_n \) on the crystallization behavior of telechelic polymers of PBS-UPy, conventional non-isothermal DSC characterization was carried out at a rate of 10 °C/min. As shown in Figure 4A and Table 2, the crystallization peak temperature (\( T_c \)) of PBS-UPy decreased with the decrease of \( M_n \), displaying the same changing tendency as PBS-OH. The decline of the total crystallization rate could be attributed to the increase of end-group...
defect, and similar phenomena have been commonly observed in other polymers [17,19]. The $T_c$ and crystallization enthalpy ($\Delta H_c$) of PBS-UPy were apparently lower than the counterpart values of PBS-OH, revealing that the interaction of hydrogen bonding between UPy end groups imposed rather strong confinement on the crystallization of PBS backbones. The gap of $T_c$ for the counterparts with the highest $M_n$ ($\Delta T_c = 70.5 - 57.5 = 13 ^\circ C$) was smaller than that of the counterparts with the lowest $M_n$ ($\Delta T_c = 57.5 - 41.6 = 15.9 ^\circ C$) as a result of the weaker confinement action on the longer chains.

Table 2. Crystallization peak temperatures ($T_c$), crystallization enthalpy ($\Delta H_c$), melting temperatures ($T_m$) and melting enthalpy ($\Delta H_m$) of PBS-OH and PBS-UPy samples during the melt-cooling and reheating process with a rate of 10 $^\circ C$/min. The enthalpy values of PBS-UPy samples were obtained by dividing the as-measured enthalpies by the mass fraction of PBS in PBS-UPy.

| Sample            | $T_c$ ($^\circ C$) | $\Delta H_c$ (J/g) | $T_m$ ($^\circ C$) | $\Delta H_m$ (J/g) |
|-------------------|--------------------|--------------------|--------------------|--------------------|
| PBS-OH-1.0k       | 57.5               | 70.4               | 98.7               | 70.8               |
| PBS-OH-2.1k       | 63.9               | 71.2               | 108.0              | 73.9               |
| PBS-OH-4.4k       | 70.5               | 73.2               | 114.2              | 74.3               |
| PBS-UPy-1.1k      | 41.6               | 38.6               | 101.6              | 47.1               |
| PBS-UPy-2.6k      | 49.8               | 46.7               | 107.6              | 53.7               |
| PBS-UPy-4.5k      | 57.5               | 43.3               | 109.8              | 47.5               |

During the subsequent heating process, the melting temperatures ($T_m$) of both PBS-UPy and PBS-OH series increased with the increase of $M_n$ (Figure 4B). However, the degree of change was lower in the PBS-UPy series than that in the PBS-OH series. This could also have stemmed from the confinement effect of hydrogen-bonding interaction between UPy units, hindering the re-crystallization process and lamellar thickening of PBS chains during heating. Therefore, the incorporation of interacting UPy as end groups obviously suppressed the total crystallization ability of PBS oligomer with a molecular weight of several thousand g/mol.

3.3. Crystalline Structure and Morphology

PBS is a kind of polymorphic polymer [28], thus the crystal modification of PBS-UPy was determined by comparing it to PBS-OH. It is clear in Figure 5 that all melt-crystallized PBS-UPy samples adopted the same $\alpha$-form crystal modification as PBS-OH, exhibiting four main peaks at $2\theta = 19.7^\circ$, $22.1^\circ$, $22.9^\circ$ and $29.0^\circ$, which are respectively assigned to the diffraction signals of (020), (021), (110) and (111) crystallographic planes. The UPy end groups did not change the crystal modification. Besides, the PBS-UPy samples showed an additional weak peak at around $2\theta = 8.8^\circ$, whose intensity decreased with respect to the
M\textsubscript{n} of PBS oligomers. The new diffraction peak is attributed to the interplanar distance of stacked UPy groups driven by the hydrogen-bonding interaction between cytosine alkene protons and carbonyl moieties of neighboring cytosine molecules [17]. The stacks of UPy units would provide a confinement environment for PBS chains, and thus depress their crystallization ability, as revealed in DSC.

Figure 5. Wide angle X-ray diffractograms of PBS-OH series (A) and PBS-UPy series (B).

The crystalline morphology of all six samples is depicted in Figure 6, though UPy stacks hindered the crystallization ability of PBS (Figure 4). The primary nucleation density significantly increased in PBS-UPy samples in comparison with the corresponding PBS-OH. Consequently, the PBS-UPy samples crystallized into much smaller spherulites. The confinement effect of UPy stacks on PBS chains should be the promoting origin for nucleation density. However, the nucleation density of PBS-UPy showed similar M\textsubscript{n}-dependent tendency as PBS-OH—that is, the degree of promotion increased as the confinement effect weakened. Therefore, the value of M\textsubscript{n} seems to play an essential and complicated role in the specific conflict phenomenon of PBS-UPy, hindering crystallization rate versus improving primary nucleation density.

Figure 6. POM images of PBS-OH and PBS-UPy samples isothermally crystallized at 85 °C. (A) PBS-OH-1.0k, (B) PBS-OH-2.1k, (C) PBS-OH-4.4k, (D) PBS-UPy-1.1k, (E) PBS-UPy-2.6k and (F) PBS-UPy-4.5k. The images were captured at a suitable crystallization level to clearly show the primary nucleation density. The scale bars are all 100 µm in length.
As the polymer total crystallization rate consists of primary nucleation and spherulite growth rate \( G \), the values of \( G \) were measured during isothermal crystallization processes. From the data plotted in Figure 7, it is confirmed that the \( G \) declined with the decrease of \( M_n \) in both PBS-UPy and PBS-OH series, and that of PBS-UPy was much lower than that of PBS-OH. For example, the \( G \) of PBS-UPy-1.1k was as low as 0.08 \( \mu \)m/s and only about one-twentieth that of PBS-OH-1.0k at 85 °C. The dependence of the decline of \( G \) on \( M_n \) after introducing UPy end groups was consistent with the aforementioned DSC result (i.e., the lower the \( M_n \) of the PBS chain, the stronger the restriction of interacting UPy stacks on spherulite growth), which plausibly stems mainly from the inhibition of the diffusion ability of PBS chains in the melt.

![Figure 7. The spherulite growth rates of PBS-OH and PBS-UPy samples at different crystallization temperatures.](image)

3.4. Nucleation Behavior and Melt Memory Effect

Although UPy stacks suppressed the total crystallization ability and spherulite growth rate, the confinement effect promoted the primary density of PBS. Yet, at the same time, Figure 6 shows that the weakening of confinement benefited the primary nucleation density. Therefore, the effect of UPy stacks on the nucleation of PBS-UPy oligomer is quite complicated and needs detailed investigation. The amounts of spherulites were counted at different times while the samples were being isothermally crystallized at various temperatures. The normalized data are plotted in Figure 8. The steady-state nucleation rate \( (J_{st}) \) and the introduction period before nucleation \( (t_{ind}) \) were calculated by fitting the relationship between the volume-based nucleus density \( (N_V(t)) \) at a specific time \( (t) \) using Equation (3) [29]. The results are summarized in Table 3. For the counterparts of PBS oligomers with the lowest \( M_n \), the PBS-UPy-1.1k showed both lower \( J_{st} \) and longer \( t_{ind} \) than PBS-OH-1.0k. Therefore, the UPy stacks not only inhibited the spherulite growth but also weakened the nucleation ability of PBS. The higher nucleation density of PBS-UPy-1.1k in comparison to PBS-OH-1.0k was due to the significant reduction of spherulite growth rate after introducing UPy units, which needed much more time to finish the crystallization, thus providing more opportunity for the occurrence of primary nucleation. The longer \( t_{ind} \) values of PBS-UPy-1.1k also reveal the suppression of nucleation ability. A similar conclusion can be drawn based on the results of the counterparts of PBS-OH-2.1k and PBS-UPy-2.6k.

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N_V(t) = J_{st}(t - t_{ind})
\] (3)
Our investigation of nucleation behavior suggests that the impact of UPy end groups on the changing of PBS’ nucleation ability is $M_n$-dependent. Generally, UPy units in a polymer matrix would aggregate and assemble into stacks via quadruple hydrogen bonds. The stacking of the end groups of PBS chains could limit the movement and diffusion of backbones, which helps polymer chains to keep some ordered conformation during and after melting. As a result, the melt memory effect would be enhanced, which usually presents as the promotion of nucleation ability (as seen with the PBS-UPy-4.5k sample). However, during crystallization, the conformation of polymer chains in melt—either with or without the memory effect—is different from that in crystalline structure, and still needs to be regulated in order to realize crystallization. Consequently, when the melt memory effect (i.e., confinement strength) is too strong, regulation of the pre-existing ordered conformation in the melt would become rather difficult, which is unfavorable for crystallization. For example, in PBS-UPy-1.1k and PBS-UPy-2.6k samples, the restriction of UPy stacks on PBS chains was sufficiently strong that the melt memory of the crystalline sample after melting could not be re-expressed as enhancing the nucleation behavior.

Furthermore, to evaluate the melt memory effect in the two series of PBS oligomers via a crystallization protocol, the samples were successively melted and crystallized in a DSC instrument by adjusting the self-nucleation temperature ($T_s$). The relevant cooling

When comparing PBS-UPy-4.5k with PBS-OH-4.4k, it is found that the incorporation of UPy units improved the $J_{st}$ (e.g., 6.44 versus 2.75 at 95 °C) and shortened the $t_{ind}$ (e.g., 32 versus 106 at 95 °C), that is, the nucleation ability of PBS was improved. As the temperature was elevated to 100 °C, the hydrogen-bonded UPy stacks were destroyed [18] and the difference between two kinds of PBS reduced.

Table 3. The steady-state nucleation rate ($J_{st}$) and induction time of nucleation ($t_{ind}$) of PBS-OH and PBS-UPy samples at various crystallization temperatures.

| Sample        | $T_c$ (°C) | $J_{st}$ (θ/(mm$^3$·s)) | $t_{ind}$ (s) |
|---------------|------------|-------------------------|---------------|
| PBS-OH-1.0k   | 80         | 34.9                    | 11            |
|               | 85         | 2.94                    | 53            |
| PBS-UPy-1.1k  | 80         | 4.12                    | 189           |
|               | 85         | 1.47                    | 473           |
| PBS-OH-2.1k   | 80         | 55.7                    | 32            |
|               | 85         | 47.8                    | 31            |
| PBS-UPy-2.6k  | 80         | 40.4                    | 62            |
|               | 85         | 2.52                    | 279           |
| PBS-OH-4.4k   | 95         | 2.75                    | 106           |
|               | 100        | 0.49                    | 480           |
| PBS-UPy-4.5k  | 95         | 6.44                    | 32            |
|               | 100        | 0.25                    | 402           |

Figure 8. Dependence of primary nucleation density on crystallization time for PBS-OH-1.0k and PBS-UPy-1.1k (A), PBS-OH-2.1k and PBS-UPy-2.6k (B) and PBS-OH-4.4k and PBS-UPy-4.5k (C) at various temperatures.
thermograms are presented in Figure S1 in the Supplementary Materials, and the “$T_{tr}$–$T_{c}$” curves are shown in Figure 9. For PBS-UPy-4.5k, the self-nucleation phenomenon emerged when $T_s$ was lower than 140 °C. This transition temperature ($T_{tr}$) is higher than that of PBS-OH-4.4k at 130 °C. Thus, the as-concluded melt memory effect in PBS-UPy-4.5k was stronger than that in PBS-OH-4.4k. UPy stacks promoted the maintenance of an ordered conformation of PBS chains in the melt and enhanced the primary nucleation ability.

![Figure 9](image)

**Figure 9.** $T_{tr}$–$T_{c}$ curves of PBS-OH-1.0k and PBS-UPy-1.1k (A), PBS-OH-2.1k and PBS-UPy-2.6k (B) and PBS-OH-4.4k and PBS-UPy-4.5k (C).

At lower $M_n$, the $T_{tr}$ of PBS-UPy became lower than that of PBS-OH. PBS-UPy-2.6k and PBS-OH-2.1k started to show self-nucleation at $T_s$ of 120 °C and 125 °C, respectively. PBS-UPy-1.1k did not exhibit self-nucleation behavior, while PBS-OH-1.0k showed this behavior at $T_s$ of 115 °C. Therefore, for these two PBS-UPy samples, the plausible ordered conformation of PBS chains in the melt as restricted by UPy stacks could not be expressed as a melt memory effect through the crystallization process. The restriction delayed the chain mobility and acted in opposition to the transition of the pre-existing ordered conformation in the melt to a crystalline conformation, leading to the depression of nucleation ability.

Therefore, in the primary nucleation process, the balance between keeping an ordered conformation and the chain mobility of PBS-UPy was in the $M_n$ range between $2.6 \times 10^3$ and $4.5 \times 10^3$ g/mol. When the $M_n$ was higher, the ordered conformation could enhance the nucleation, and thus a better melt memory effect was observed. When the $M_n$ was lower, due to the reduction of chain mobility, restriction became the major function; regulation of chain conformation, and thus the nucleation ability, were hindered. Therefore, the ordered conformation restricted by UPy stacks (i.e., memory in melt) could not be expressed via the crystallization process for PBS-UPy-1.0k and PBS-UPy-2.6k.

4. Conclusions

In this study, telechelic PBS oligomers with different $M_n$ were synthesized by introducing UPy units to the chain ends, and their crystallization behaviors—especially nucleation processes—were studied in detail. The UPy stacks formed via quadruple hydrogen bonding suppressed the total crystallization rate of PBS-UPy in comparison with PBS-OH. The spherulite growth rate was significantly reduced, whereas the primary nucleation density was strongly promoted for PBS after replacing the OH end group with UPy. Further investigation of the nucleation behavior revealed that the mechanism for increasing the nucleation density of PBS after the introduction of UPy end groups changed with respect to $M_n$. When the $M_n$ was low (e.g., $1.1 \times 10^3$ and $2.6 \times 10^3$ g/mol), both growth ability and nucleation ability were reduced due to the confinement effect of UPy stacks. The decline in the growth rate was much more obvious, providing more time and thus opportunity for the occurrence of primary nucleation, leading to a higher nucleation density. As the $M_n$ increased to $4.5 \times 10^3$ g/mol, the nucleation ability was strengthened. Consequently, the nucleation density increased. We speculate that the observed change from the inhibition to the promotion of nucleation for PBS-UPy with increasing $M_n$ can be explained as follows. At low molecular weight, chain mobility was reduced and the melt memory effect could not be expressed. At higher molecular weights the UPS stacks could limit the movement
of polymer chains and the ordered confirmation of the melt could be preserved (the melt memory effect could be expressed), enhancing nucleation.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11121530/s1, Figure S1: The cooling DSC curves of PBS-OH-1.0k (A), PBS-UPy-1.1k (B), PBS-OH-2.1k (C), PBS-UPy-2.6k (D), PBS-OH-4.4k (E) and PBS-UPy-4.5k (F) after being melted at different $T_s$.

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