

Revisit the Gibbs-Thomson Equation Fitting of Poly(butylene succinate) Based on Oligomer Extended-Chain Crystals

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 Electronic Supplementary Information

Abstract The equilibrium melting point (T_m^0) is a crucial thermodynamic parameter for characterizing the crystallization and melting behavior of semi-crystalline polymers. However, the direct measurement of T_m^0 poses a significant challenge because of the difficulty in physically fabricating fully-extended chain crystals of high-molecular-weight polymers. Therefore, various extrapolation equations for T_m^0 have been proposed that utilize the thermal properties of ordinary folded-chain lamellae. Among these, the Gibbs-Thomson equation is one of the most commonly employed for modeling. Despite its widespread use, there are notable variations in the T_m^0 values obtained by different research groups, even when based on similar samples. This raises questions about the validity and accuracy of using the Gibbs-Thomson equation to linearly extrapolate T_m^0 . In this study, we prepared a series of oligomer extended-chain crystals (ECCs) of poly(butylene succinate) (PBS) and used their properties for Gibbs-Thomson fitting. The results reveal a perfect linear relationship, with an extrapolated T_m^0 value of 136.08 °C. The basal surface free energy of the oligomer ECCs was calculated as 0.084 J/m², which is approximately twice that of folded-chain lamellae. This difference is attributed to the aggregation of highly mobile free tails on the crystal surface. The two structural features of oligomer ECCs—large thickness and fixed surface—better fulfill the conditions for applying the Gibbs-Thomson equation, ensuring its validity and accuracy. Therefore, we believe that the Gibbs-Thomson fit can produce reliable results when sufficient high-quality data are used.

Keywords Equilibrium melting point; Extended-chain crystal; Gibbs-Thomson equation; Inclusion complex

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INTRODUCTION

The equilibrium melting temperature (T_m^0) is theoretically important for determining the driving force of semi-crystalline polymers. However, the direct fabrication of polymer crystals with a defined T_m^0 is challenging because melt or solution crystallization typically results in the formation of folded-chain lamellae with thicknesses ranging from a few to a dozen nanometers. Consequently, various methods have been employed to assess the T_m^0 values of semi-crystalline polymers. Among them, Gibbs-Thomson extrapolation^[1–3] and Hoffman-Weeks extrapolation^[2–5] are traditionally the most widely used and simplest. The Hoffman-Weeks method assumes negligible variation in lamellar thickness during thermal measurements, which can lead to significant biases and thus has limitations. Alternatively, the Gibbs-Thomson equation (Eq. 1) offers another approach for estimating T_m^0 by linearly fitting the relationship between the reciprocal lamellar thickness (L^{-1}) and melting temperature (T_m) of folded-chain lamellae crystallized at various temperatures. In this equation, ΔH_v and σ_e represent the melt-

ing enthalpy per unit volume and basal surface energy, respectively.^[1–3] According to the Gibbs-Thomson equation, the accuracy of the estimated of T_m^0 value heavily relies on the measured data of L . However, the typical thickness of folded-chain lamellae is so small that even slight experimental inaccuracies can result in significant shifts in the extrapolating intercept value (i.e., T_m^0). For instance, the estimated T_m^0 of poly(butylene succinate) (PBS) has been reported in the literature from 127 °C to 151 °C based on lamellar data.^[3,6–9]

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H_v \cdot L} \right) \quad (1)$$

The fluctuating T_m^0 results raise questions regarding the applicability and accuracy of the Gibbs-Thomson equation. To address extrapolation inaccuracies, several modified or non-linear versions of the Gibbs-Thomson equation have been proposed.^[10–12] However, these variations introduce additional parameters and complicate the calculation process. In fact, if we consider a series of thick crystals, known as extended-chain crystals (ECCs), we may have a better chance of validating this equation. ECCs are anticipated to be more thermodynamically stable polymer crystalline structures, characterized by high melting temperatures and crystallinity,^[13–19] owing to their crystal thickness. Typically, polymer ECCs are produced

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via melt-crystallization under ultra-high-pressure conditions (>200 MPa). Unfortunately, the effective adjustment of the ECC thickness remains a challenge that is yet to be overcome.

Recently, we devised a novel approach to fabricate polymer ECCs by utilizing polymer/urea inclusion complexes as intermediate structures. In this structure, the polymer chains serve as isolated guest molecules, whereas urea molecules build host frameworks.^[17–19] The ultimate thickness of the ECCs is influenced by the thickness of the inclusion complex. Furthermore, research has shown that the thickness of inclusion complexes in oligomer/urea systems can be regulated by adjusting the molecular weight of the oligomers.^[20] Therefore, in this study, we employed a range of PBS oligomers to produce ECCs of varying thicknesses. Subsequently, we utilized these data to investigate the validity of Gibbs-Thomson fitting.

EXPERIMENTAL

Materials

Succinic acid (SA, AR grade), 1,4-butanediol (BDO, GC grade), tetra-*n*-butyltitanate (TBT, purity ≥99%), hexafluoroisopropanol (HFIP, AR grade), and urea (U, AR grade) were purchased from Shanghai Aladdin Reagent Co. Dichloromethane (AR grade) and methanol (AR grade) were supplied by Beijing Chemical Reagent Factory. All the reagents were used as received.

Synthesis and Purification of PBS Oligomers

PBS oligomers with different molecular weights were synthesized using a conventional two-step reaction of successive bulk esterification and polycondensation of SA and BDO. To obtain the hydroxyl group terminal chains, the feeding ratio of SA: BDO was set constant at 1.4. TBT was used as a catalyst with a 0.5% added amount relative to the total weight of the reactants. Specifically, esterification was conducted by step heating from 135 °C to 190 °C under a flowing nitrogen atmosphere and holding at 135, 150, 175 and 190 °C for 30 min. Then, the reacting system was further switched to 220 °C under a pressure lower than 100 Pa and maintained for various times to prepare different PBS products. The as-polymerized products were dissolved in chloroform at a concentration of approximately 5 wt% and centrifuged at a rate of 10000 r/min for 10 min to remove insoluble impurities. The clear solutions were then precipitated with an excess amount of methanol to obtain the final oligomers. The oligomers were dried under vacuum at 50 °C for 48 h before use and were named *asp*-PBS.

Fractionation of PBS Oligomer

A chloroform solution of the PBS oligomer with a concentration of 5 wt% was first prepared at 25 °C. Then, a mixed solvent of chloroform and methanol (3:7 by mass) was slowly dropped into the PBS solution under gentle stirring. Once turbidity appeared in the solution and did not disappear with stirring, the addition of the mixed solvent was stopped, and the solution was left to equilibrate for 12 h. The precipitate was separated, and the remaining solution was further fractionated by repeated operations. Finally, all the fractions were dried under vacuum at 50 °C for 48 h and stored for further use. For convenience, the fractionated oligomers were labeled with *f*-PBS.

Preparation of ECCs of PBS Oligomers

Inclusion complexes between the PBS oligomer as the guest

chain and urea as the host molecule (PBS/U-ICs) were fabricated by electrospinning on an instrument (Beijing Ucalery, HD-X1) and then treating at 120 °C for 1 min^[17] for the fractionated samples or melt blending at 120 °C in desktop twin-screw extruder (Shanghai Xinshuo Company, WLJ-10G) for the as-polymerized samples.^[18] The PBS/U-ICs were washed with deionized water with gentle stirring for 24 h to remove urea, and the released PBS chains coalesced to form crystals (*c*-PBS crystals), which were expected to be ECCs according to previous work.^[17–19,21]

Characterization

The average number molecular weights (M_n s) of the samples were determined based on ¹H nuclear magnetic resonance (NMR) spectra obtained using a JEOL JNM-ECA 600 M spectrometer. Chloroform-*d* (CDCl₃) was used as the solvent, and tetramethylsilane (TMS) was used as the internal reference. The polydispersities (*Đ*) of fractionated samples were determined by a WATERS 1515 gel permeation chromatograph (GPC) using HPLC grade chloroform as the elution solvent and the calibration curve of polystyrene standards (Fluka) as references. The thermal properties, including the melting point (T_m) and melting enthalpy (ΔH_m) of the samples, were measured on a NET-ZSCH 204 F1 differential scanning calorimeter (DSC) equipped with an intercooler system under a nitrogen atmosphere. The samples were weighed to approximately 5 mg and sealed in aluminum pans, and the heating rate during the measurement was set at 10 °C/min. The microstructures of the samples were investigated using a HITACHI SU8010 scanning electron microscope (SEM). The samples were sputtered with thin layers of gold before scanning and the working accelerating voltage was set to 5 kV. The scattering vector of the samples was obtained using France Xenocs small-angle X-ray scattering (SAXS) operated at 50 kV and 0.6 mA. The sample-to-detector distance was selected as 2513 mm and the effective range of the scattering vector (*q*) was 0.1–2.5 nm^{−1}. Each SAXS pattern obtained at the center of the sample was collected for 10 min, background-corrected, and normalized using the standard procedure. The lamellar thickness (*d*, including the crystalline layer and amorphous surface) was calculated using the following equation:

$$d = \frac{2\pi}{q} \quad (2)$$

RESULTS AND DISCUSSION

The M_n s of *asp*-PBS determined by ¹H-NMR ranges from 1.13×10³ g/mol to 6.75×10³ g/mol and are tabulated in Table 1. DSC thermographs of *asp*-PBS are shown in Fig. 1(a). Melt crys-

Table 1 Number-average molecular weights and thermal properties of the *asp*-PBS samples.

Sample	M_n (g/mol)	<i>Đ</i>	$T_{m,asp}$ * (°C)	$T_{m,c}$ ** (°C)
<i>asp</i> -PBS1.1k	1130	2.10	104.7	106.4
<i>asp</i> -PBS1.7k	1660	1.69	109.2	107.5
<i>asp</i> -PBS2.3k	2300	1.78	110.5	106.1/108.4
<i>asp</i> -PBS2.9k	2930	1.53	111.4	111.1/118.7
<i>asp</i> -PBS6.8k	6750	1.74	113.8	111.0/127.3

* $T_{m,asp}$ indicates the highest melting point of *asp*-PBS sample prepared using a conventional melt-crystallization process. ** $T_{m,c}$ reveals all the melting points of *c*-PBS crystals coalesced from *asp*-PBS/U-IC.

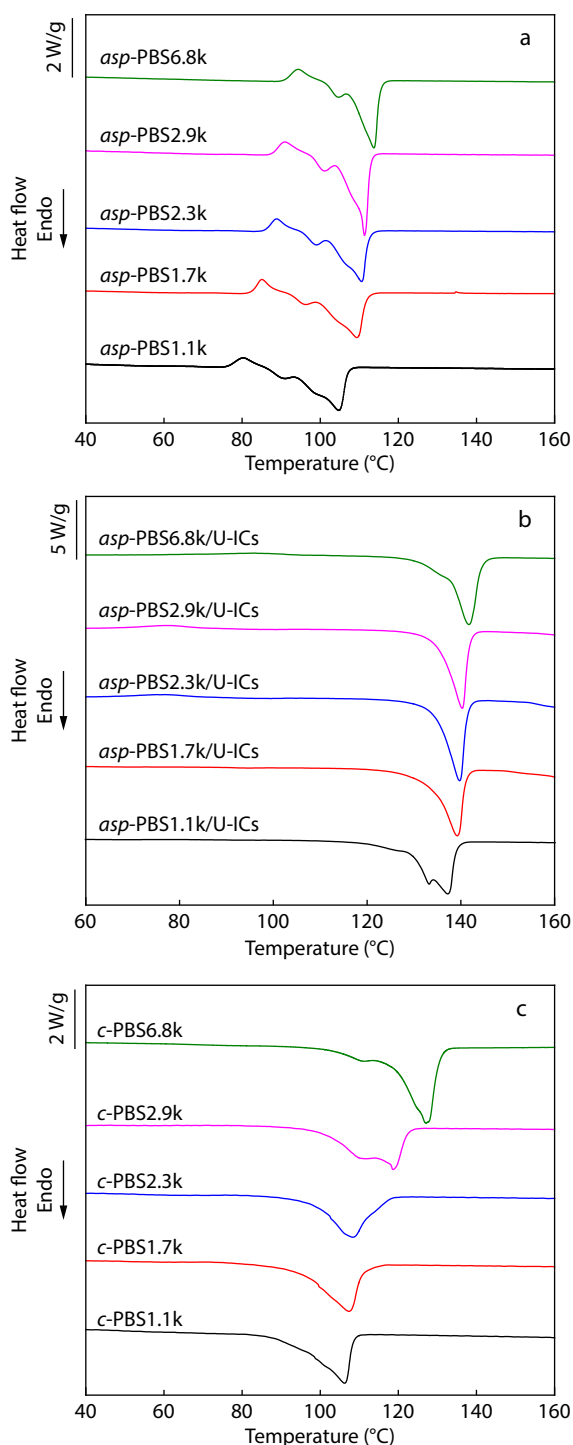


Fig. 1 DSC heating thermograms of the *asp*-PBS samples (a), their inclusion complexes with urea (b) and the coalesced crystals after washing by water (c).

tallization and multiple melting behaviors existed in all *asp*-PBS samples, and it was found that the melting point ($T_{m,asp}$, the highest one in each curve) gradually increased with increasing M_n . The T_m elevated from 104.7 °C of *asp*-PBS1.1k to 113.8 °C of *asp*-PBS6.8k, which could be ascribed to the content decline of terminal group in chains. The terminal groups play as defect roles and thus depress $T_{m,asp}$. After inclusion complexing with

urea molecules, all samples, as presented in Fig. 1(b), display a sharp endothermic peak at around 140 °C, which was much higher than the $T_{m,asp}$ of *asp*-PBS, and the melting point of pure urea (~133 °C). Thus, *asp*-PBS/U-ICs were successfully obtained.^[17,18] The slight elevation of the melting point of *asp*-PBS/U-IC with respect to the M_n of *asp*-PBS could be due to the increase in the persistence length of the urea channels.^[17,20] Note that an additional endothermic peak at around 133 °C appeared in *asp*-PBS1.1k/U-IC, which corresponded to excess urea that did not form an inclusion complex. Because the terminal group content that is not conducive to forming complexes in such low M_n PBS oligomers is quite high, leading to the remaining uncomplexed urea component.

The *c*-PBS crystals were obtained by washing *asp*-PBS/U-ICs with water at 25 °C. The DSC thermographs of *c*-PBS crystals are shown in Fig. 1(c), and the melting point temperatures ($T_{m,c}$) are tabulated in Table 1. The *c*-PBS6.8k crystals exhibited a main $T_{m,c}$ at 127.3 °C with a small lower-temperature shoulder peak at ~111 °C. The much higher $T_{m,c}$ of *c*-PBS6.8k crystals in comparison to the *asp*-PBS6.8k might reveal the formation of ECCs.^[17] The shoulder peak corresponds to the melting of folded-chain lamellae, which is almost the same as the original *asp*-PBS6.8k ($T_{m,asp}$ =113.8 °C). With a decrease in M_n of PBS, the enthalpy proportion of higher $T_{m,c}$ became weaker, while the lower $T_{m,c}$ became stronger in *c*-PBS2.9k and *c*-PBS2.3k crystals. It is reasonable to consider that PBS chains with ordered conformations were first released from the urea frameworks and then packed together to crystallize when the inclusion complexes were washed. The degree of conformation preservation is very important for the successful formation of ECCs. With a decrease in molecular weight, the molecular chain relaxation time shortens and, thus, the conformation maintenance ability weakens, which is not conducive to the formation of ECCs. Consequently, only $T_{m,c}$ with a value close to $T_{m,asp}$ of the corresponding *asp*-PBS sample appeared for both *c*-PBS1.7k and *c*-PBS1.1k crystals.

To further confirm the formation of the ECCs, the microstructures of *c*-PBS6.8k crystals were examined using SEM. As shown in Fig. 2(a), the *c*-PBS6.8k sample consisted of periodic crystalline stacks with an average thickness of 41.34 nm (Gaussian fit in Fig. 2b), based on the statistical calculation of over 100 crystals. PBS6.8k with M_n of 6750 g/mol means an average number of repeating unit (172 g/mol) in a molecular chain of 39.2, which equals to a thickness of 42.73 nm when adopting ECCs of α crystal modification. The *c*-axis of α PBS crystal is 1.09 nm,^[22] and the *c*-PBS crystals have been proven to take α crystal modification.^[17] The fact that the experimental and calculated values were very close (only a ~3% difference) directly suggested the successful formation of ECCs. The slightly smaller value of the SEM result in comparison with the theoretical calculation might be due to the disturbance of the chain terminals, which could not be included in the lattices. Because the chain lengths of other *asp*-PBS samples were shorter than that of PBS6.8k, the energy barrier for the formation of ECCs from ordered chains released from PBS/U-ICs was lower. Therefore, the higher $T_{m,c}$ s values of both *c*-PBS2.3k and *c*-PBS2.9k are ascribed to the melting of their ECCs. The SAXS profiles of the three melt-crystallized *asp*-PBS samples are shown in Fig. 2(c). The appearance peri-

ods at approximately $q=1.6 \text{ nm}^{-1}$ can be observed, which demonstrates the formation of folded-chain lamellae with an average thickness $d < 4 \text{ nm}$, which is much thinner than the stacks in Fig. 2(a).

Based on the above results, it seems that PBS with M_n higher than 2300 kg/mol can be used to obtain ECCs via the inclusion complexing approach. Therefore, PBS6.8k was fractionated, and the resulting oligomers with M_n ranging from 2600 g/mol to 9040 g/mol (Table 2) were utilized. Fig. 3(a) displays DSC thermographs of the fractionated PBS oligomers (*f*-PBS). The melting points ($T_{m,r}$) of *f*-PBS samples gradually in-

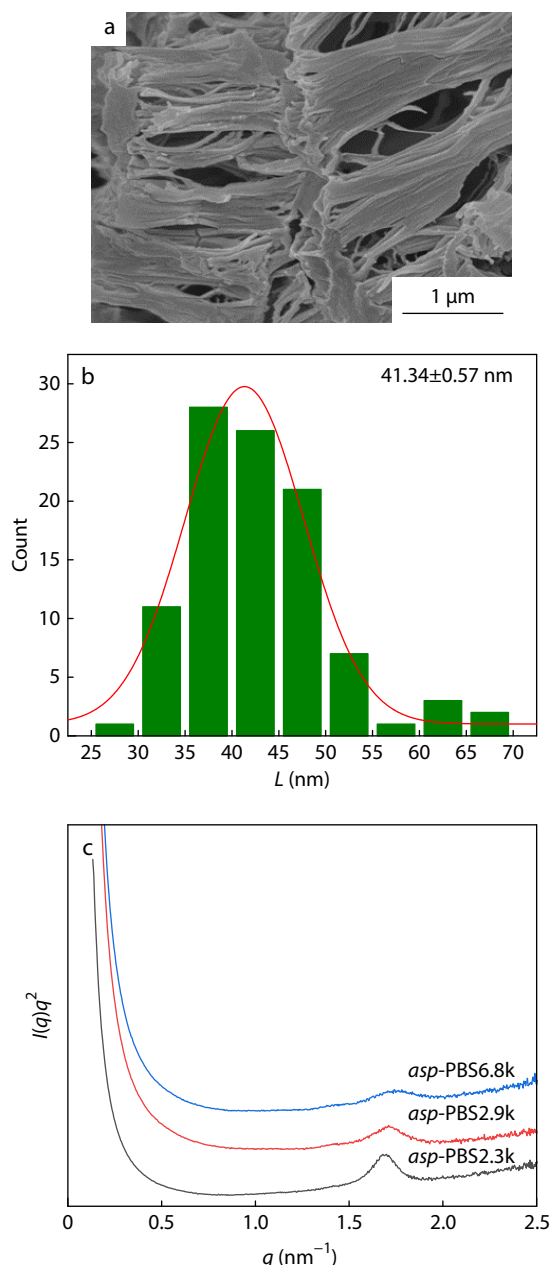


Fig. 2 SEM images of the *c*-PBS6.8k crystals (a), the thickness distribution and Gaussian fitting curves of 100 crystals, $41.34 \pm 0.57 \text{ nm}$ (b), and one-dimensional scattering intensity distribution profiles of *asp*-PBS2.3k, *asp*-PBS2.9k and *asp*-PBS6.8k (c).

Table 2 Number-average molecular weights and thermal properties of the fractionated PBS samples.

Sample	M_n (g/mol)	$\bar{D}$	$T_{m,f}^*$ (°C)	$T_{m,c}^{**}$ (°C)
<i>f</i> -PBS2.6k	2600	1.26	110.8	108.6/112.4
<i>f</i> -PBS3.6k	3550	1.14	113.0	112.8/118.6
<i>f</i> -PBS3.9k	3860	1.22	113.2	113.1/120.5
<i>f</i> -PBS5.4k	5440	1.19	113.9	113.7/124.6
<i>f</i> -PBS9.0k	9040	1.22	114.7	111.9/129.3

* $T_{m,f}$ indicates the highest melting point of *asp*-PBS sample prepared using a conventional melt-crystallization process. ** $T_{m,c}$ reveals all the melting points of *c*-PBS crystals coalesced from *f*-PBS/U-IC.

creased with respect to M_n . When the *f*-PBS samples formed inclusion complexes with urea molecules, sharp melting points over 140 °C (Fig. S1 in the electronic supplementary information, ESI) demonstrated the successful formation of the PBS/U-ICs.

After being washed completely with water, the melting processes of *c*-PBS crystals were recorded, as shown in Fig. 3(b), and the higher $T_{m,c}$ s, which are obviously higher than the corresponding $T_{m,r}$ s and can be assigned to the melting of ECCs, are tabulated in Table 2.

Previously, we found that PBS ECCs, due to their high crystal stability, can tolerate chloroform and dichloromethane,^[23] which are good solvents for ordinary PBS samples. The *c*-crystals of *f*-PBS9.0k were then soaked in dichloromethane for 24 h at room temperature. Most of the crystals remained and were collected and measured using DSC (Fig. 3c). It was found that the small shoulder melting peak at 111.9 °C before being soaked in dichloromethane disappeared, indicating the dissolution of normal folded-chain lamellae in PBS. The main endothermic peak of *c*-PBS9.0k after soaking in dichloromethane remained due to the melting of ECCs.

The microstructures of *c*-PBS9.0k crystals after soaking in dichloromethane are shown in Fig. 4(a). Many crystalline stacks were clearly observed. Based on the statistical calculation of over 100 crystals, an average thickness of 57.09 nm was determined (Gaussian fit in Fig. 4b), which was close to the theoretical calculation value (57.29 nm, a crystal modification based^[17]). Thus, the formation of the ECCs of the PBS oligomers was confirmed.

When PBS oligomers were employed to prepare ECCs, terminal hydroxyl groups were located on the top and bottom surfaces of the crystals. That is, ECCs adopt the same surface structure and basal surface energy. Therefore, it is wise to use the Gibbs-Thomson equation (Eq. 1) to fit the relationship between the melting points (given in Table 2) and crystal thickness of the ECCs (L , calculated from the M_n values). The plotted data and the as-fitted " $T_{m,c}-L^{-1}$ " curve are presented in Fig. 5. It was demonstrated that the data fit very well linearly, with an adjusted R -squared of 0.9985. The fitted T_m^0 of PBS was 136.08 °C, which was the same as the directly measured melting point of ECCs of high-molecular-weight PBS.^[17] Thus, Gibbs-Thomson equation worked well here to extrapolate T_m^0 .

Because PBS is a popular semi-crystalline biodegradable polyester, its T_m^0 has been widely studied and used.^[3,6–9] Some of the values of T_m^0 were obtained by fitting the data of folded-chain lamellae using the Gibbs-Thomson equation,^[3,5,6,17] and they are summarized in Table 3 and plot-

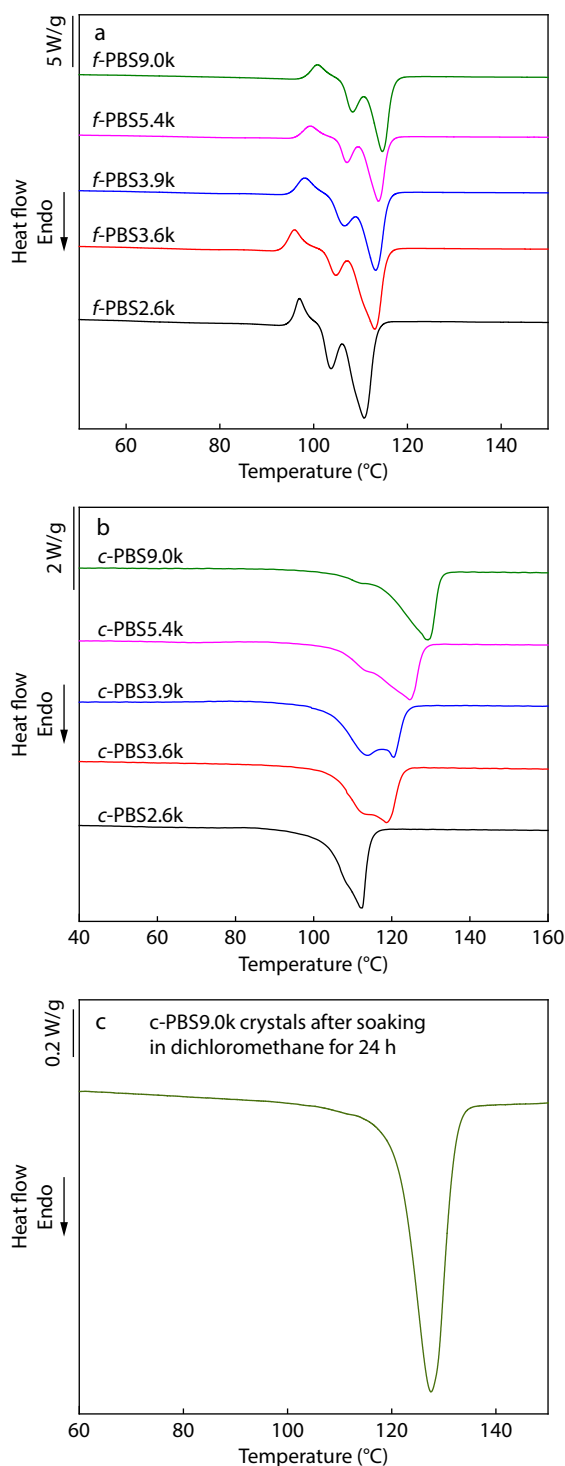


Fig. 3 DSC melting thermographs of the *f*-PBS samples (a), *c*-PBS crystals (b) and *c*-PBS9.0k after being soaked in dichloromethane for 24 h (c).

ted in Fig. 5. It was found that the as-fitted values of T_m^0 remarkably varied obviously from different literature, even though the ranges of lamellar thickness among them are only slightly different (ca. 3–6 nm).

This variable value of T_m^0 can be attributed to two important factors. First, the large gap between the experimental

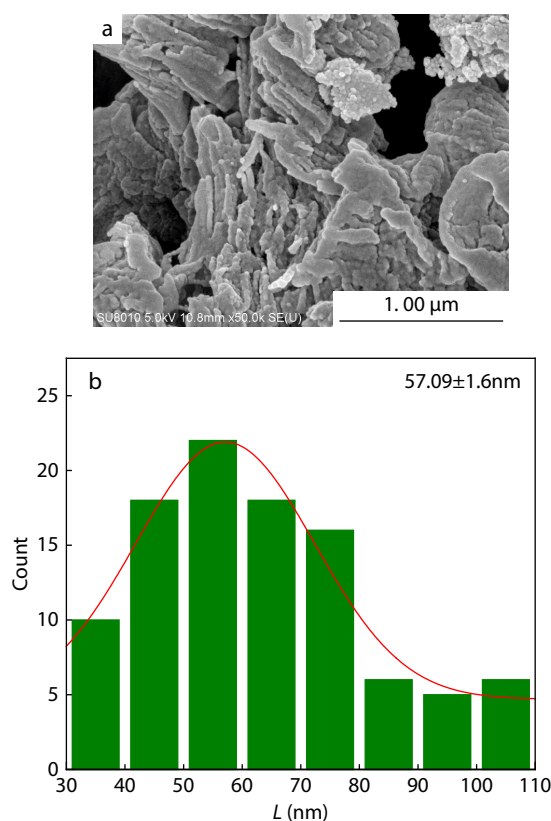


Fig. 4 SEM images of *c*-PBS9.0k crystals after soaking in dichloromethane for 24 h (a) and the thickness distribution and Gaussian fitting curves of over 100 crystals (b).

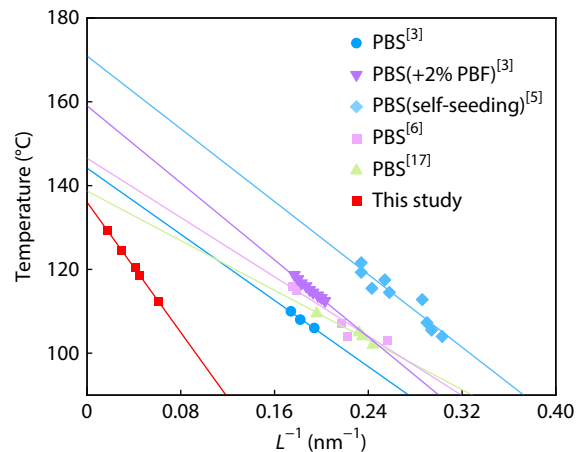


Fig. 5 Gibbs-Thomson plots of PBS oligomer ECCs in comparison with the data from literature.^[3,5,6,17]

data and extrapolated intercept is the data deficiency. In this case, a disturbance or variance in the measured data triggers a significant change in the intercept value (i.e., T_m^0). Second, the slope of the fitting line, which is related to the basal surface energy (σ_e) of the lamellae, might change when the lamellar structure changes. PBS has a typical three-phase model structure after ordinary crystallization, and a rigid-amorphous fraction (RAF) exists between the mobile amorphous region and the crystalline region.^[24,25] That is, RAF plays a key role in determining σ_e . In addition, it has been re-

Table 3 The fitting slopes (k) and calculated basal surface energy (σ_e) of PBS based on the fitting results in Fig. 5.

Source	Ref. [3]	Ref. [3]	Ref. [6]	Ref. [17]	Ref. [5]	This study
k (nm·K)	−197	−230	−177	−148	−217	−389
T_m^0 (°C)	144	159	147	139	171	136
σ_e (J/m ²)	0.042	0.047	0.037	0.032	0.043	0.084

vealed that RAF content increases with increasing crystallization temperature.^[25] Thus, when the lamellar thickness is regulated by changing the crystallization temperature (almost all), the surface state of the PBS lamellae will be somewhat altered, leading to inappropriate and inaccurate linear fitting results of the Gibbs-Thomson equation. However, the data of ECCs explored here can avoid these two deficiencies, leading to a reliable and accurate result.

With the relationship between the fitting slope k and σ_e shown in Eq. (1), the value of σ_e can be determined by employing $T_m^0=136.08$ °C and $\Delta H_v=177.56$ J/cm³. ΔH_v is equal to ΔH_m^0 (133.5 J/g)^[19] times crystalline density ($\rho=1.33$ g/cm³).^[22] The as-deduced values of σ_e from the data in the previous literature range from 0.032 J/m² to 0.047 J/m². However, the σ_e of oligomer ECCs reaches a much higher value of 0.084 J/m², which is approximately twice that of the folded-chain lamellae. The chemical structure contributing to σ_e includes chain folds, loops, and tails in common PBS lamellae, with the first two structures being the main contributors. In contrast, the chain tails (terminal hydroxyl groups here) are, ideally, contributors to the σ_e of oligomer ECCs. The tails have greater mobility than the chain folds and loops, which induce a significant increase in σ_e . As references, the σ_e values of folded-chain lamellae are most estimated as much smaller than 0.1 J/m².^[26–32] A similar set of phenomena have been reported in the investigation of poly(ethylene oxide) (PEO).^[33] The σ_e values of the folded-chain and extended-chain crystals are 0.098 and 0.275 J/m², respectively.^[33] Thus, a higher σ_e value is an intrinsic characteristic of ECCs and leads to a larger slope of the fitting line based on the Gibbs-Thomson equation.

CONCLUSIONS

In summary, we successfully fabricated a series of oligomer ECCs of PBS and leveraged their unique properties to reassess the validity of the classical Gibbs-Thomson equation. Our findings reveal a perfect linear relationship, with the extrapolated melting temperature (T_m^0) at 136.08 °C, aligning precisely with the previously directly measured value of ECCs of high-molecular-weight PBS. The σ_e of these oligomer ECCs was calculated to be 0.084 J/m², which is approximately twice that of the folded-chain lamellae. This disparity was attributed to the accumulation of highly mobile free tails on the basal surface of the crystal. The two defining structural characteristics of oligomer ECCs—their large thickness and fixed surface structure—are well suited for applying the Gibbs-Thomson equation, ensuring its validity and accuracy. Consequently, we are confident that the Gibbs-Thomson equation can yield reliable results when based on sufficient high-quality data. Thus, this study offers a precise method for determining the thermodynamic properties of semicrystalline polymers from their oligomer ECCs.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3270-5>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

- Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I. The Rate of Crystallization of Linear Polymers with Chain Folding. In *Treatise on Solid State Chemistry*; Springer: Boston, MA. **1976**, 497–614.
- Flory, P. J.; Vrij, A. Melting points of linear-chain homologs. the normal paraffin hydrocarbons. *J. Am. Chem. Soc.* **1963**, *85*, 3548–3553.
- Xu, J.; Heck, B.; Ye, H. M.; Jiang, J.; Tang, Y. R.; Liu, J.; Guo, B. H.; Reiter, R.; Zhou, D.-S.; Reiter, G. Stabilization of nuclei of lamellar polymer crystals: insights from a comparison of the Hoffman-weeks line with the crystallization line. *Macromolecules* **2016**, *49*, 2206–2215.
- Hoffman, J. D.; Weeks, J. J. Melting process and the equilibrium melting temperature of polychlorotrifluoroethylene. *J. Res. Natl. Bur. Stand A Phys. Chem.* **1962**, *66A*, 13–28.
- Xie, Z. N.; Ye, H. M.; Chen, T.; Zheng, T. Z.; Xu, J.; Guo, B. H. Melting and annealing peak temperatures of poly(butylene succinate) on the same Hoffman-Weeks plot parallel to $T_m=T_c$ line. *Chinese J. Polym. Sci.* **2021**, *39*, 745–755.
- 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*, 605–613.
- Miyata, T.; Masuko, T. Crystallization behaviour of poly(tetramethylene succinate). *Polymer* **1998**, *39*, 1399–1404.
- Qiu, Z.; Ikehara, T.; Nishi, T. Miscibility and crystallization in crystalline/crystalline blends of poly(butylene succinate)/poly(ethylene oxide). *Polymer* **2003**, *44*, 2799–2806.
- Papageorgiou, G. Z.; Bikiaris, D. N. Crystallization and melting behavior of three biodegradable poly(alkylene succinates). A comparative study. *Polymer* **2005**, *46*, 12081–12092.
- Höhne G. W. H. Another approach to the Gibbs-Thomson equation and the melting point of polymers and oligomers. *Polymer* **2002**, *43*, 4689–4698.
- Pandey, A.; Toda, A.; Rastogi, S. Influence of amorphous component on melting of semicrystalline polymers. *Macromolecules* **2011**, *44*, 8042–8055.
- Toda, A.; Taguchi, K.; Nozaki, K. Gibbs-Thomson, thermal Gibbs-Thomson, and Hoffman-Weeks plots of polyethylene crystals examined by fast-scan calorimetry and small-angle X-ray scattering. *Cryst. Growth Des.* **2019**, *19*, 2493–2502.

- 13 Wunderlich, B.; Arakawa, T. Polyethylene crystallized from the melt under elevated pressure. *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2*, 3697–3706.
- 14 Geil, P. H.; Anderson, F. R.; Wunderlich, B.; Arakawa, T. Morphology of polyethylene crystallized from the melt under pressure. *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 3707–3720.
- 15 Li, Y.; Tang, S.; Pan, M. W.; Zhu, L.; Zhong, G. J.; Li, Z. M. Polymorphic extended-chain and folded-chain crystals in poly(vinylidene fluoride) achieved by combination of high pressure and ion-dipole interaction. *Macromolecules* **2015**, *48*, 8565–8573.
- 16 Siegmann, A.; Harget, P. J. Melting and crystallization of poly(ethylene terephthalate) under pressure. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *18*, 2181–2196.
- 17 Ye, H. M.; Chen, X. T.; Liu, P.; Wu, S. Y.; Jiang, Z.; Xiong, B.; Xu, J. Preparation of poly(butylene succinate) crystals with exceptionally high melting point and crystallinity from its inclusion complex. *Macromolecules* **2017**, *50*, 5425–5433.
- 18 Ye, H.-M.; Chen, X.-T.; Li, H.-F.; Zhang, P.; Ma, W.; Li, B.; Xu, J. Industrializable and sustainable approach for preparing extended-chain crystals of biodegradable poly(butylene succinate) and their applications. *Polymer* **2019**, *160*, 93–98.
- 19 Tian, Y. P.; Wu, T.; Meng, X.; Ye, H. M. Thermodynamic features of extended-chain crystals of poly(butylene succinate) and its random copolymers with adipic acid. *Macromolecules* **2022**, *55*, 5669–5674.
- 20 Ye, H. M.; Song, Y. Y.; Xu, J.; Guo, B. H.; Zhou, Q. Melting behavior of inclusion complex formed between polyethylene glycol oligomer and urea. *Polymer* **2013**, *54*, 3385–3391.
- 21 Ye, H. M.; Li, H. F.; Wang, C. S.; Yang, J.; Huang, G.; Meng, X.; Zhou, Q. Degradable polyester/urea inclusion complex applied as a facile and environment-friendly strategy for slow-release fertilizer: Performance and mechanism. *Chem. Eng. J.* **2020**, *381*, 122704.
- 22 Ichikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. Crystal structures of α and β forms of poly(tetramethylene succinate). *Polymer* **2000**, *41*, 4719–4727.
- 23 Chen, J. Y.; Li, N.; Wang, S.; Wu, T.; Meng, X.; Ye, H. M. Boosting solvent resistance and structure stability of degradable polyester through extended-chain crystal structure: A preliminary case of oil/water separation membrane. *J. Environ. Chem. Eng.* **2024**, *12*, 113507.
- 24 Yao, S. F.; Chen, X. T.; Ye, H. M. Investigation of structure and crystallization behavior of poly(butylene succinate) by Fourier transform infrared spectroscopy. *J. Phys. Chem. B* **2017**, *121*, 9476–9485.
- 25 Righetti, M. C.; Di Lorenzo, M. L.; Cinelli, P.; Gazzano, M. Temperature dependence of the rigid amorphous fraction of poly(butylene succinate). *RSC Adv.* **2021**, *11*, 25731–25737.
- 26 Chen, S. H.; Su, C. H.; Su, A. C.; Sun, Y. S.; Jeng, U.; Chen, S. A. Gibbs-Thomson analysis of crystalline poly(9,9-di-*n*-octyl-2,7-fluorene). *J. Appl. Cryst.* **2007**, *40*, s573–s576.
- 27 Baratian, S.; Hall, E. S.; Lin, J. S.; Xu, R.; Runt, J. Crystallization and solid-state structure of random polylactide copolymers: poly(L-lactide-co-D-lactide)s. *Macromolecules* **2001**, *34*, 4857–4864.
- 28 Supaphol, P.; Spruiell, J. E.; Lin, J.-S. Isothermal melt crystallization and melting behaviour of syndiotactic polypropylene. *Polym. Int.* **2000**, *49*, 1473–1482.
- 29 Wang, C.; Cheng, Y. W.; Hsu, Y. C.; Lin, T. L. Lamellar morphology and equilibrium melting temperature of syndiotactic polystyrene in β -crystalline form. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1626–1636.
- 30 Yamada, K.; Hikosaka, M.; Toda, A.; Yamazaki, S.; Tagashira, K. Molecular weight dependence of equilibrium melting temperature and lamellar thickening of isotactic polypropylene with high tacticity. *J. Macromol. Sci., Part B: Phys., Part B-Phys.* **2003**, *42*, 733–752.
- 31 Hocquet, S.; Dosière, M.; Thierry, A.; Lotz, B.; Koch, M. H. J.; Dubreuil, N.; Ivanov, D. A. Morphology and melting of truncated single crystals of linear polyethylene. *Macromolecules* **2003**, *36*, 8376–8384.
- 32 Schönherr, H.; Frank, C. W. Ultrathin films of poly(ethylene oxides) on oxidized silicon. 2. *In situ* study of crystallization and melting by hot stage AFM. *Macromolecules* **2003**, *36*, 1199–1208.
- 33 Yin, J.; Raegen, A.; Idziak, S. H. J.; Forrest, J. A. Crystallization and melting of highly monodisperse poly(ethylene-oxide). *Soft Matter* **2020**, *16*, 7958–7969.