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Enhancing Toughness of Poly(L-lactic acid) for 3D-Printing Applications by Utilizing Long-chain Branching

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Lack of toughness is a well-known limitation of poly(L-lactic acid) (PLLA) materials in additive manufacturing. To address this challenge, this study systematically explores the effect of long-chain branching on the crystallization behavior, the micrometer-scale structure, and mechanical properties of printed single strands. The measurements showed that long-chain branching does not significantly influence the overall crystallization kinetics. The critical cooling rate to obtain an amorphous sample (CR1) increases slightly due to long-chain branching, but is independent of the degree of branching. Increasing the number of branch points per chain from 0 to 3.3 increased the critical cooling rate for nucleation suppression (CR2) continuously from 5 to 100 K/s, indicating an increasing nucleation rate. In contrast, the spherulite growth rate decreased with increasing branching, explaining the nearly unaffected overall crystallization kinetics. Owing to these complex nucleation and crystallization behaviors, long-chain branched PLLA tends to form finer and denser crystalline structures as the number of branch points per polymer chain increases. Mechanical tests further showed that introducing long-chain branches significantly improves mechanical performance, particularly the strain at break (ductility) and the toughness (integrated area under the stress-strain curve). In conclusion, long-chain branched structures effectively enhance the ductility and toughness of printed single PLLA strands by inducing finer and denser crystalline morphologies, which should also hold under typical 3D-printing conditions.

Poly(L-lactic acid) (PLLA) is the most widely used polymer in extrusion-based 3D-printing due to its favorable processing characteristics.¹ However, a persistent challenge is that 3D-printed PLLA parts are typically brittle, significantly limiting their applications in engineering fields.^{2–5} The brittleness of 3D-printed PLLA parts mainly comes from two sides: 1) Typically, slow crystallization of PLLA causes low crystallinity of the printed parts after 3D-printing, which allows physical aging in amorphous regions at ambient conditions.^{6–9} Physical aging is accompanied by an obvious increase in modulus as well as brittleness.^{7–10} The effect of physical aging of 3D-printed PLLA is found to reduce crystallinity.¹¹ 2) Due to slow crystal nucleation in PLLA, the spherulites in PLLA products typically exhibit large sizes,^{12–16} significantly increasing the brittleness.¹⁷ Based on these characteristics, increasing the nuclei density in PLLA can improve the toughness of 3D-printed parts and broaden their application range.

A common approach to enhance nucleation is the addition of nucleating agents.^{18–20} Heterogeneous nucleation in polymers refers to a crystallization initiation mechanism in which foreign substances present in the system (such as impurities, additives, or substrate surfaces) serve as active centers for crystal nucleation. These centers lower the activation barrier for nucleation and facilitate the immediate growth of crystals.^{21,22} However, the effectiveness of heterogeneous nucleation depends on the energy barrier reduction and the number of

heterogeneous nucleation centers. Compared to homogeneous nucleation, the improvements in nuclei density remain relatively low, as demonstrated for PLLA^{13,14} and other polymers.^{23–27} Homogeneous nucleation describes the process in which, in regions free of heterogeneous nuclei, polymer melts spontaneously aggregate through the thermal motion of molecular segments, forming crystal nuclei of at least critical size, which initiate the growth of crystals.^{23–26, 28} Homogeneous nucleation kinetics of polymers depends strongly on temperature^{23–28} and largely on the molecular chain topology.^{29,30} Long-chain branched architectures represent one such structural feature that has been shown to significantly alter crystal nucleation and crystallization behavior in PLLA^{31,32} and other polymers.^{33–36} Because branch points cannot be incorporated into the folded-chain structure of polymer crystals, they cannot act as active centers for heterogeneous nucleation. It is assumed that the accelerated nucleation kinetics in long-chain branched PLLA is due to the enhancement of homogeneous nucleation by the long-chain branches.²⁹ Since homogeneous nucleation can achieve much higher nuclei densities compared to heterogeneous nucleation, this feature can significantly enhance the nucleation process of PLLA under 3D-printing conditions. Under extruder-based 3D-printing conditions, PLLA typically crystallizes at high supercooling, between T_g -15 K and T_g +45 K (T_g : glass transition temperature),^{37,38} where homogeneous nucleation is dominant.^{13–16}

With the growing importance of the circular economy, the crystallization behavior of long-chain branched PLLA has received long-lasting interest across multiple applications, as PLLA is an important biodegradable plastic.³⁹ Nofar et al. systematically investigated the non-isothermal melt-crystallization, cold-crystallization, and isothermal crystallization kinetics of long-chain branched PLLA and its composites with talc.⁴⁰ The long-chain branched architecture was found to accelerate the crystallization of PLLA under all conditions. However, long-chain branched PLLA showed less influence on crystallization in the presence of talc. Although the mechanism of crystallization acceleration was not investigated, based on the authors' results, the acceleration of crystallization by long-chain branching and by talc should involve two different mechanisms.

Liu et al. synthesized long-chain branched PLLA with different amounts of "Three or Four Arms" and "Stretched H-Shaped". They linked the crystallization behavior of PLLA to the different types of long-chain branching.⁴¹ By measuring the crystallization kinetics and structural development of such samples, they found that long-chain branching accelerates PLLA crystallization. Specifically, the "Stretched H-Shaped" architecture increases nucleation density to a greater extent than the "Three or Four Arms" architectures.

Meanwhile, Wang et al. investigated the effect of branch length on the crystallization of long-chain branched PLLA.⁴² They found that the higher nuclei density of long-chain branched PLLA results in a shorter induction time of the isothermal crystallization process at 373 K ($\approx T_g + 40$ K). Bai et al. separately studied the crystal nucleation and crystal growth of long-chain branched PLLA.⁴³ They found that the long-chain branched architecture improves nucleation kinetics but slows crystal growth. This opposing effect agrees well with observations on other polymers, such as polyethylene and polypropylene.³³ However, due to limitations in instrumentation to evaluate nucleation over a wide range of supercooling, the authors suggested that the acceleration in nucleation is caused by heterogeneous structures at branch points acting as active nucleation centers. This viewpoint has been refuted by recent studies, which show that branch points cannot be included in crystals and therefore cannot serve as active nucleation interfaces.^{31,32} The acceleration in nucleation kinetics by long-chain branching can be observed over a very wide range of supercooling, even at deep supercooling, where commonly homogeneous nucleation dominates.^{31, 32} Based on the above literature, it appears that long-chain branching influences the nucleation and crystal growth rate of PLLA and may alter the brittleness of 3D-printed PLLA parts.

In extruder-based processing, long-chain branched PLLA is found to crystallize faster than linear PLLA.^{44, 45} In our previous work, we showed that materials with a high crystallization rate and a relatively long relaxation time are beneficial for forming oriented crystal structures during 3D-printing.⁴⁶ Furthermore, shearing is found to significantly enhance nucleation even without requiring the formation of oriented structures.⁴⁷ For long-chain branched PLLA, chain relaxation requires a longer time, and oriented structures require even longer times to recover after introducing shear.^{48, 49} As such, branching reduces the entropy of the melt after shear and accelerates crystallization.

In this study, one linear and three long-chain branched industrial-grade PLLA samples were investigated to verify the concept that introducing a long-chain branched structure can enhance the

toughness of 3D-printed PLLA products by refining the crystalline morphology due to increased crystal nuclei density, thereby overcoming the inherent brittleness of 3D-printed PLLA parts. Unlike conventional long-chain branched PLLA samples prepared primarily for fundamental studies of crystallization and nucleation, the three long-chain branched PLLA grades investigated here contain relatively few branch points per molecular chain. Consequently, their melt-flow behavior remains suitable for extrusion-based 3D-printing. As shown in Tab. 1, the melt flow index decreases only moderately, from 4.0 to 1.5 g/10 min (463 K/2.16 kg), with increasing number of branch points. Whether such low density of long-chain branch points is sufficient to enhance nucleation and generate a finer crystalline morphology is first investigated. The underlying mechanism is then examined in printed single strands to evaluate the potential of long-chain branching to produce a fine and dense crystalline structure in 3D-printed PLLA, thereby improving its toughness.

Results and Discussion

Isothermal Crystallization

Isothermal crystallization was investigated in the temperature range from 350 K to 420 K through fast scanning calorimetry (FSC, device details see Methods) measurements, following the temperature-time protocol shown in Fig. 1. Prior to crystallization, the thermal history of the sample was erased by annealing at 500 K for 0.1 s. The sample was then rapidly cooled to the pre-set isothermal crystallization temperature and annealed for different durations to allow crystallization. After isothermal crystallization, the sample was cooled to 120 K and finally reheated to the molten state to reveal information about the preceding crystallization from the melting enthalpy.

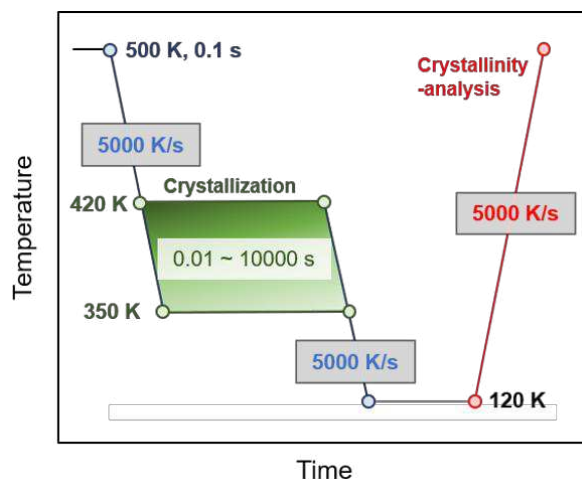


Fig. 1 | Temperature-time protocol for studying isothermal crystallization between 350 and 420 K using fast scanning calorimetry.

Fig. 2 displays the FSC heating scans corresponding to the crystallinity-analysis segment (red trace in Fig. 1). As expected, the melting peak area increases with increasing annealing time from 0.01 s to 10000 s.

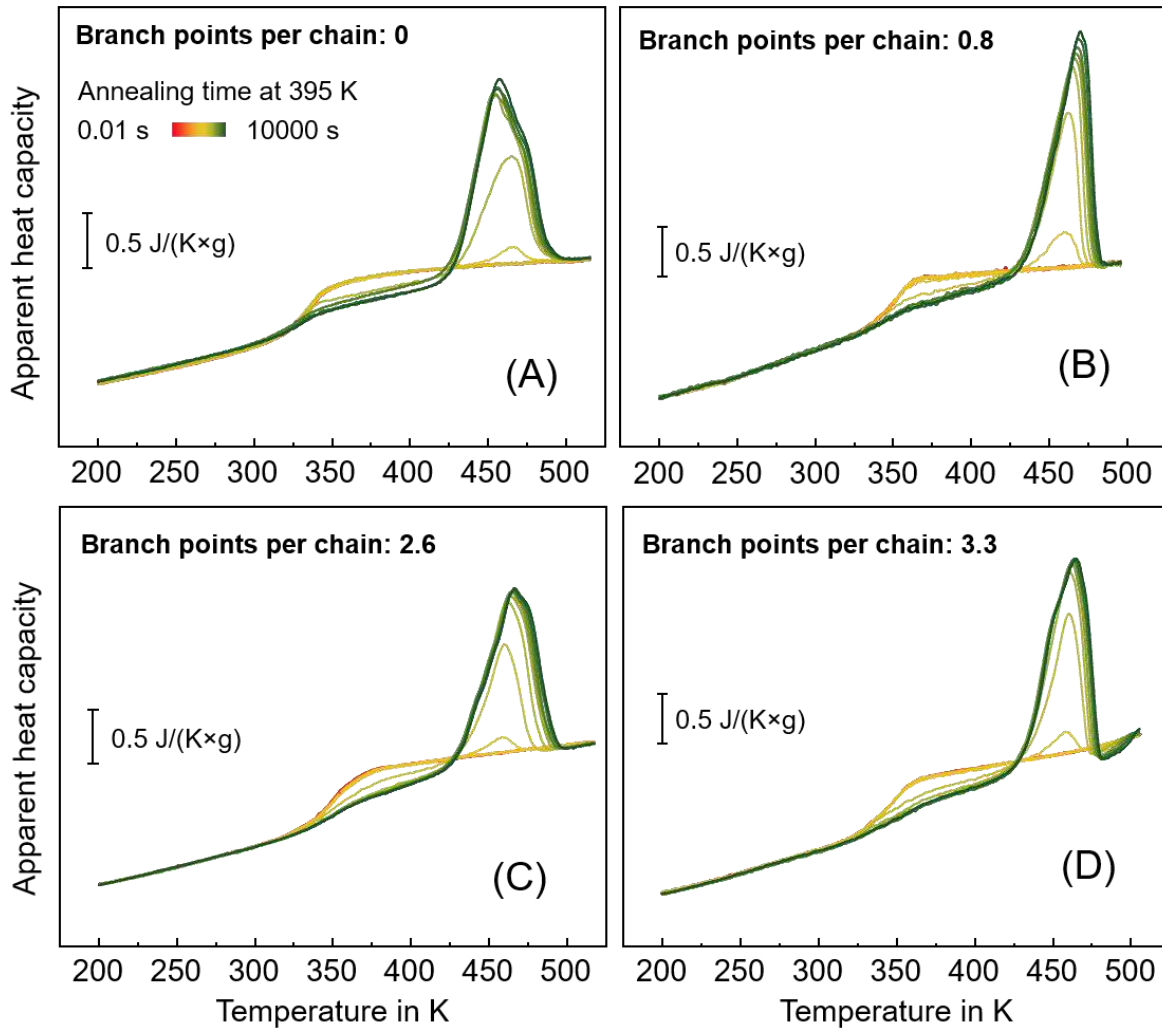


Fig. 2 | Representative FSC heating scans (5,000 K/s). After isothermal annealing at 395 K for different times (0.01–10,000 s) for linear PLLA (A), and branched PLLA samples containing 0.8 (B), 2.6 (C) and 3.3 (D) branch points per chain.

The melting peak area is shown in Fig. 3A as a function of crystallization time. In the figure, the melting enthalpy of all PLLA samples shows an initial sharp increase followed by a gradual rise, corresponding to primary and secondary crystallization, respectively. The half-time of primary crystallization is estimated using an Avrami-like equation (Eq. 1) that accounts for both primary and secondary crystallization. The superposition of these two processes was already discussed by Wunderlich,⁵⁰ and subsequently widely applied in FSC analysis^{27,51–54}:

$$\Delta h(t) = A \left(1 - \exp \left(-\frac{t}{t_{1/2}} \ln 2 \right) \right)^n + B \left(\ln(t - t_{1/2}) \right) \times \left(\frac{1}{2} \left(\frac{t - t_{1/2}}{t - t_{1/2}} + 1 \right) \right) \quad (1)$$

where $\Delta h(t)$ is the specific enthalpy of melting determined from FSC heating curves obtained after isothermal crystallization for a predefined crystallization time t , A is the melting enthalpy at the end of primary crystallization, and B is an empirical constant describing the contribution from secondary crystallization, $t_{1/2}$ is the half-time of primary crystallization, and n is the Avrami-like exponent. The crystallization half-time is then plotted as a function of the crystallization temperature in Fig. 3B. As temperature increases, the

crystallization half-time first decreases and then increases, being similar for both linear and long-chain branched PLLA. The minimum half-time of primary crystallization ranges from 67 to 93 s as the number of branch points increases from 0 to 3.3. Given the data's uncertainty, the half-times of crystallization for all four PLLA samples appear similar.

Meanwhile, the temperature positions of the minimum in the curves are also similar. All these observations suggest that long-chain branching has a lesser influence on the overall crystallization process, consistent with the results from the non-isothermal crystallization experiments in Fig. 7 below. Unlike previous studies 40–45, here, no significant acceleration in crystallization kinetics was observed for long-chain-branched PLLA. To rule out instrumental influences, the same experiment was repeated on a second commercial fast-scanning calorimeter to verify the reproducibility of the data; further details are provided in the Supporting Information S1. Crystallization kinetics measured using commercial FSC and DSC. The most likely explanation for the observed difference with the literature data is that the cooling rates employed in the present study are significantly higher than those reported in previous literature.^{40–45}

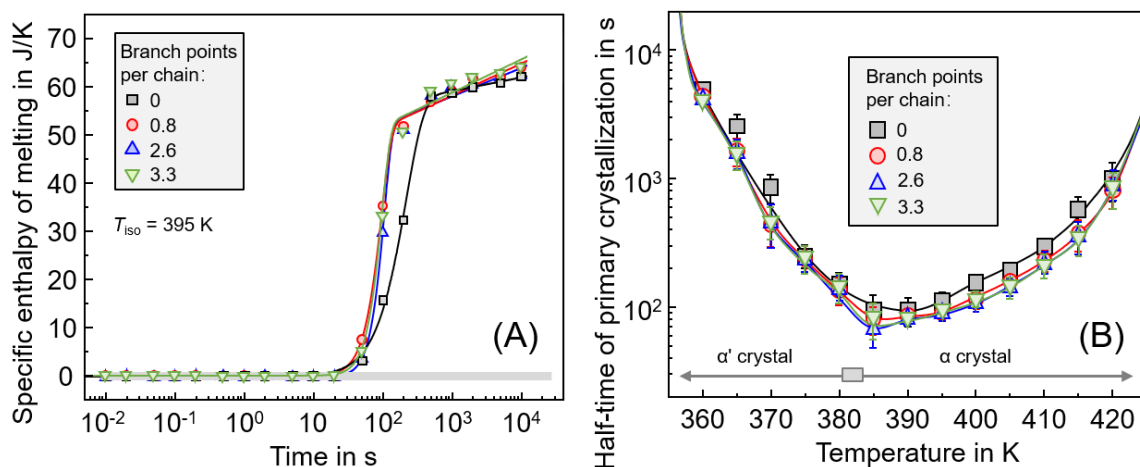


Fig. 3 | Crystallization kinetics analysis. (A) Specific melting enthalpy vs. time, fitted with the Avrami-like equation (Eq.(1)); (B) Half-time of primary crystallization vs. temperature.

Isothermal crystallization at 413 K was also monitored using POM. The samples were examined using a hot stage, with the thermal history removed at 498 K for 3 min, followed by cooling to 413 K at 0.83 K/s (50 K/min). Non-isothermal DSC analysis at this cooling rate did not show any crystallization during cooling to 413 K, indicating that 0.83 K/s (50 K/min) is sufficient to suppress crystallization during the approach of the target crystallization temperature. It is worth noting that the used device cannot cool the sample to lower temperatures without non-isothermal nucleation. Therefore, morphological studies at lower temperatures apply solely to

investigating crystal growth rates, which are independent of prior nuclei/crystal formation during cooling.

Fig. 4 illustrates the evolution of the semicrystalline morphologies of linear and long-chain branched PLLA samples by polarized-light optical microscopy (POM), with increasing crystallization time at 413 K. The most striking observation is that the number of crystals increases with increasing branch concentration, most clearly evident in micrographs collected after 60 min. As such, long-chain branched PLLA generally yields smaller spherulites compared to linear PLLA.

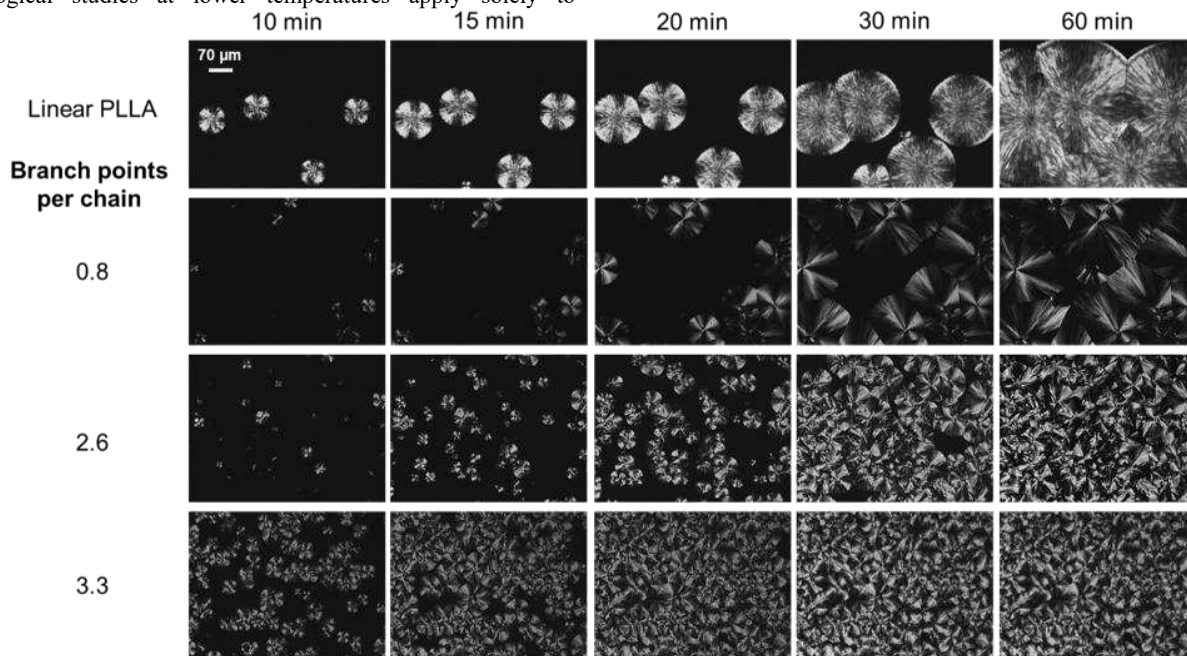


Fig. 4 | POM observation of structure formation in PLLA of different branch concentration during isothermal annealing at 413 K.

Spherulite growth rates determined from the POM images are plotted as a function of crystallization temperature for different branch concentrations in Fig. 5, with the growth rates obtained by linear fitting of the time-dependent spherulite radii. A dual dependence of the spherulite growth rate on temperature is observed, with a crossover point near 383 K. This behavior is frequently reported in the literature and related to the formation of α and α' crystals at high and low temperatures, respectively.^{55–58} More

important in the context of the present study is the observation that, as the branching degree increases, the spherulite growth rates decrease, indicating that long-chain branching hinders crystal growth. This result is in agreement with previous studies,^{31,32,41, 43} which demonstrated that the reduced crystal growth rate can be attributed to two effects of long-chain branching: (1) slower polymer chain diffusion caused by increased chain entanglement concentration, and (2) the exclusion of branch points from the crystalline lattice, where they act as structural defects requiring rejection from the growing lamellae.^{31–34,43,59,60}

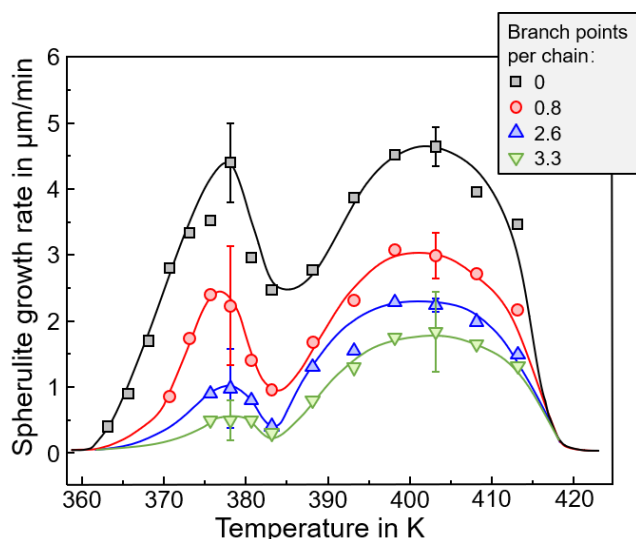


Fig. 5 | Spherulite growth rate of linear and long-chain branched PLLA as a function of the crystallization temperature, determined by POM.

The maximum spherulite growth rates and the corresponding temperatures were used to further analyze the influence of long-chain branching, as shown in Fig. 6. The values at low and high temperatures correspond to the α' and α crystal forms.^{55–58} Both α' and α crystal forms exhibit a consistent trend; the spherulite growth rate decreases with increasing branch-point number per molecular chain. Furthermore, the temperatures at which these two maxima occur remain nearly constant for both crystal forms and appear to be independent on the branch-point concentration.

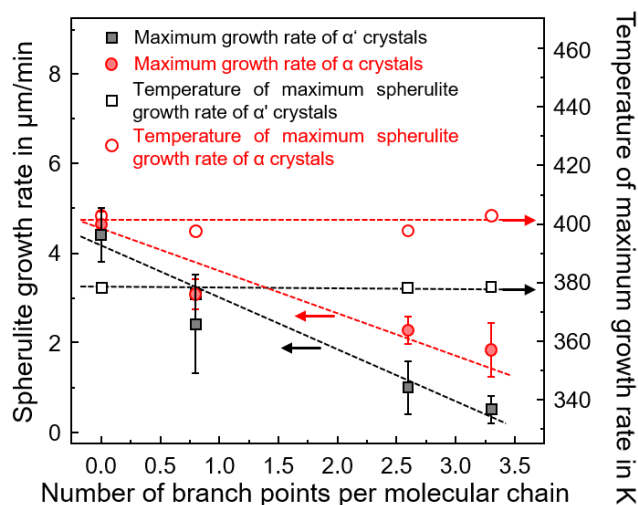


Fig. 6 | The influence of long-chain branching on spherulite growth rate (left axis) and temperature of maximum growth rate (right axis) for α and α' crystal forms.

Non-isothermal crystallization

The non-isothermal crystallization behavior of long-chain branched and linear PLLA was investigated using differential scanning calorimetry (DSC). PLLA samples were cooled from 498 K to 248 K at various cooling rates, and the enthalpy change due to crystallization was determined from the DSC cooling curves. The relationship between the crystallization enthalpy and cooling rate is

presented in Fig. 7. The cooling rate at which the crystallization enthalpy approaches zero is defined as the critical cooling rate for suppressing crystallization (CR1).^{24–26,28,50–52,61} For linear PLLA, CR1 was determined to be approximately 0.2 K/s (12 K/min). The CR1 values for linear PLLA with different molecular masses reported in the literature^{15,16,69–71} are shown at the bottom of Fig. 7 as short straight lines of different colors. As the molecular mass increases, CR1 decreases, indicating that lower-molecular-mass samples crystallize more readily during cooling. The CR1 value for linear PLLA (145 kDa) agrees well with the literature and is consistent with values reported for PLLA with a similar molecular weight (104 kDa, green).^{15,16} This agreement validates the accuracy of the CR1 determination in this study. In contrast, CR1 for long-chain branched PLLA is slightly higher than that of linear PLLA, with a value of approximately 0.83 K/s (50 K/min) for all long-chain branched samples.

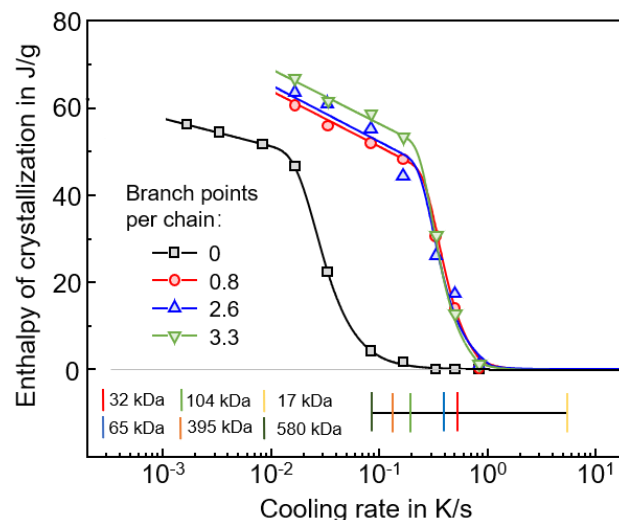


Fig. 7 | Enthalpy of crystallization for PLLAs cooled from 498 K to 248 K at different rates. Critical cooling rates of PLLA with different molecular masses are represented by short vertical lines on the cooling rate axis, with the data taken from references.^{15,16,62–64}

The formation of the semicrystalline morphology was observed using a POM equipped with a hot stage. The samples were cooled from 498 K to room temperature (298 K) at 0.17 K/s (10 K/min). Images were recorded during cooling, and those selected within the temperature range of 423 K to 383 K are presented in Fig. 8 to illustrate the differences in crystallization characteristics. For linear PLLA, no μm -scale structure was observed during cooling, which is consistent with the CR1-value result from the aforementioned DSC study. As the number of branch points per molecule increases, an increasing number of birefringent spots appear during cooling, particularly visible at 393 K and 383 K, suggesting that nucleation is enhanced by long-chain branching since the crystal growth rate follows an opposite trend.

The morphology of the PLLA samples after cooling to room temperature is shown in Fig. 9. The linear PLLA sample (A) exhibits no clearly discernible morphology, whereas the branched PLLA samples (B, C, and D) display similar morphological features after cooling. The images reveal that the fine structures densely cover the entire image. Moreover, the morphology becomes progressively finer with increasing branch concentration. The assumption of enhanced nucleation in long-chain branching PLLA is then further evaluated and quantified by calorimetry.

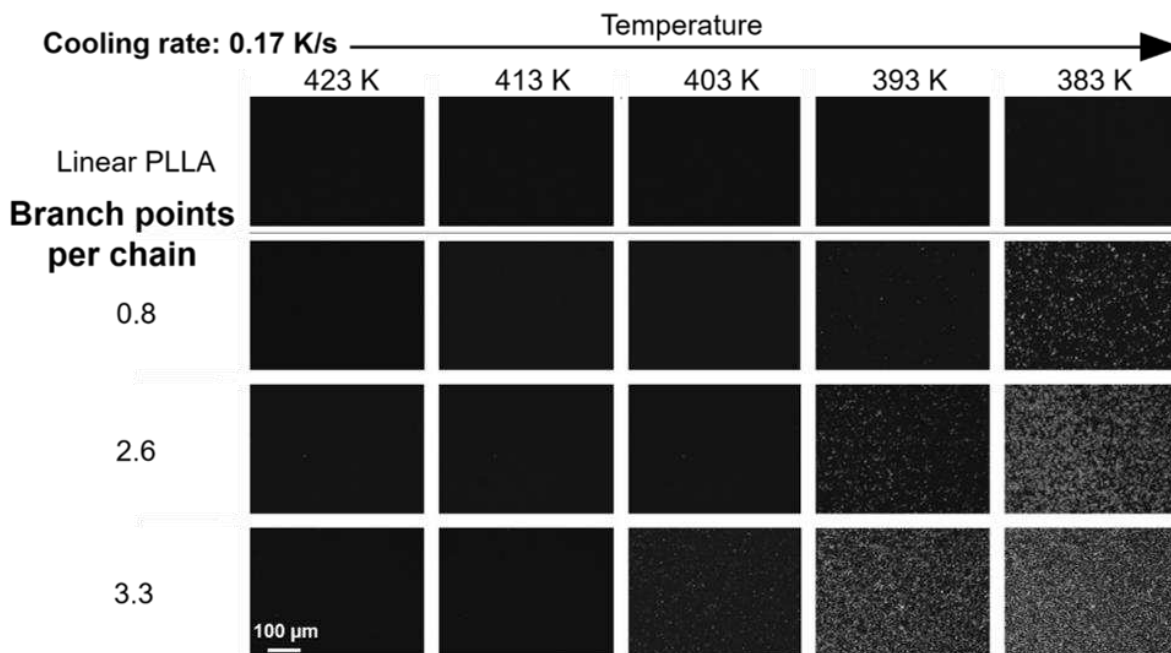


Fig. 8 | POM observation of structure formation of PLLA during cooling from 498 to 298 K at a rate of 0.17 K/s (10 K/min).

Crystal nucleation

To clarify the influence of long-chain branching on nucleation, we used Tammann's two-stage crystal nuclei development method,⁶⁵ which employs distinct nucleation and growth stages as part of the experimental protocol. Under carefully chosen and fixed growth-stage conditions, the variation in total crystallinity, as measured by the melting enthalpy, directly reflects differences in the kinetics of crystal nucleation. However, this approach necessitates precise control of the transfer and growth stages, as any unwanted additional nucleation or growth of nuclei prior to the designated growth stage must be avoided.⁶⁶ This requirement demands high scanning rates to ensure adequate temporal resolution. Consequently, FSC emerges as an ideal tool for implementing Tammann's two-stage crystal nuclei development method to study crystal nucleation kinetics, an approach that has been successfully applied for many polymers.^{23-28,52,53,56-59}

The temperature-time protocol for this experiment is illustrated in Fig. 10. The thermal history is removed by holding the sample at 500 K for 0.1 s. Subsequently, the sample is cooled from 500 K to 120 K at cooling rates ranging from 0.5 to 10000 K/s to facilitate or prevent nucleation during the cooling. Following nucleation, the sample is always heated to 395 K at 5000 K/s and annealed at this temperature for 50 s, to allow the formed nuclei to grow into crystals. Finally, an analysis scan is performed to record the melting behaviour of the sample after crystal nucleation and growth.

Fig. 11A shows heating scans (recorded at 5000 K/s) of samples that underwent nucleation at cooling rates ranging from 0.5 K/s (green) to 10000 K/s (red), followed by crystal growth at 395 K for 50 s, avoiding space filling. As the cooling rate increases, the melting-peak area decreases, eventually converging to a small residual peak. This remaining peak is likely caused by heterogeneous nuclei, but without any contribution from nucleation during the preceding non-isothermal stage. The additional melting peak area observed at lower cooling rates is attributed to crystals grown from nuclei generated during the prior cooling.

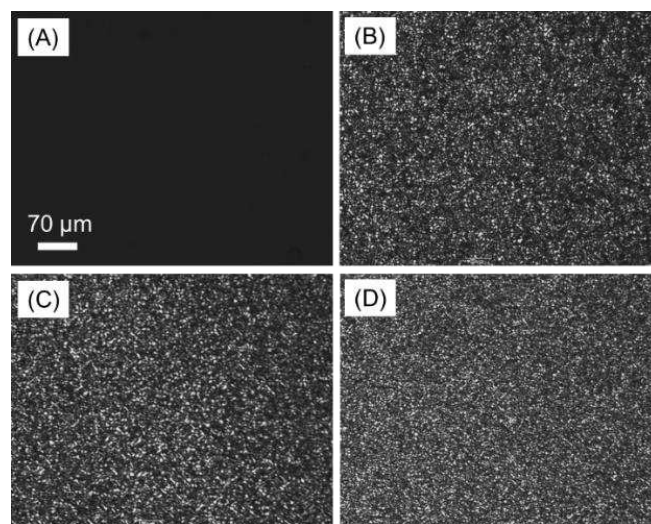


Fig. 9 | POM images observations of PLLA following cooling from 498 K to 298 K at a rate of 0.17 K/s (10 K/min). (A) linear, (B) 0.8, (C) 2.6, (D) 3.3 branch points per chain. The scale bar holds for all images.

The melting enthalpy, in excess of the residual peak at the highest cooling rates, is plotted as a function of cooling rate in Fig. 11B. The enthalpy of crystallization at the growth stage due to nucleation during cooling is determined as the difference between the measured melting enthalpy and the residual melting enthalpy at the highest cooling rates ($> CR_2$, the critical cooling rate for suppressing nucleation). The melting enthalpy measured at 0.5 K/s cannot be used for nucleation analysis (data points colored in grey), because 0.5 K/s is below CR_1 of all branched PLLA samples, and crystallization on cooling cannot be excluded. The CR_2 is defined as the cooling rate at which the excess enthalpy of melting is about zero, as indicated in Fig. 11B by the arrows on the cooling-rate axis. For linear PLLA, CR_2 is approximately 5 K/s, about 25 times higher than CR_1 . It is also observed that CR_2 increases systematically with branch concentration, reaching approximately 20, 60, and 100 K/s for 0.8, 2.6, and 3.3 branch points per chain, respectively. The CR_2 of 100 K/s for the sample with 3.3 branch points per chain is about 100 times higher than the corresponding CR_1 .

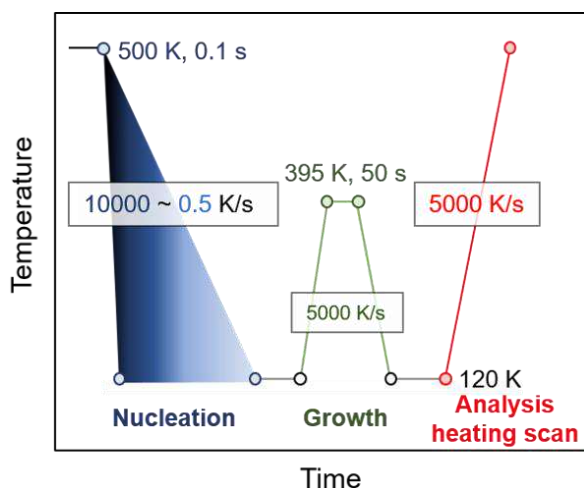


Fig. 10 | Temperature-time protocol for studying non-isothermal nucleation using FSC.

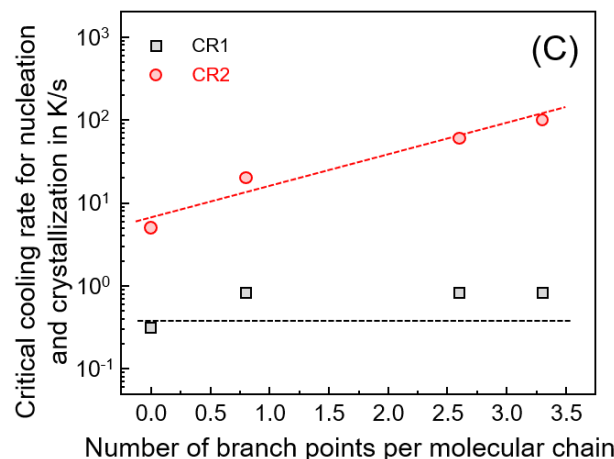
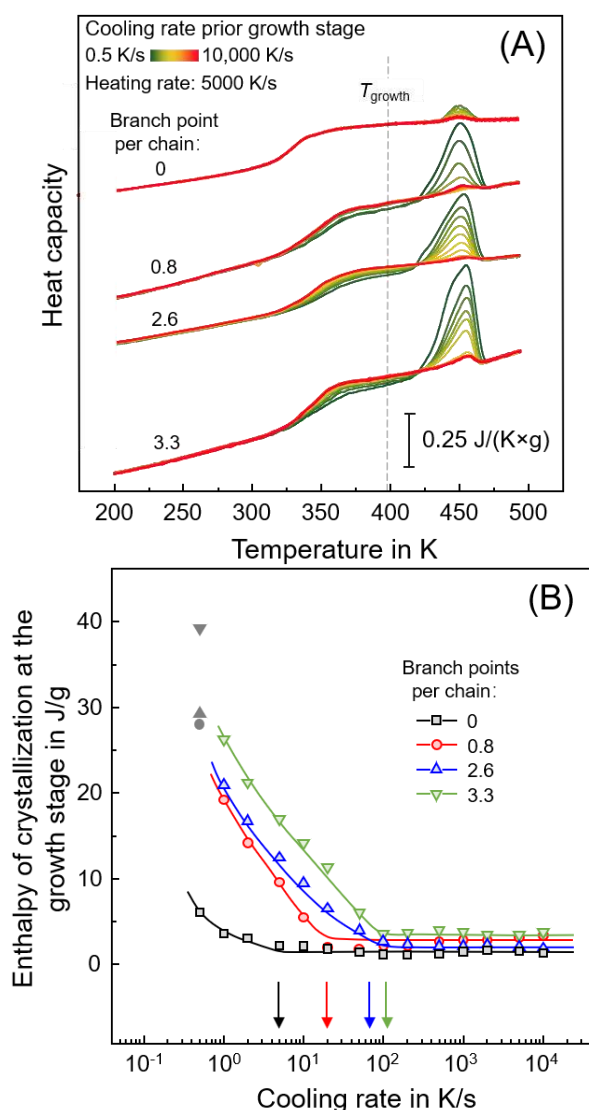


Fig. 11 | (A) FSC heating curves for the determination of the excess enthalpy of crystallization at the growth stage in Tamman's two-stage crystal development method. (B) Excess enthalpy of crystallization by nuclei formed during cooling at different rates. The data are used to determine the critical cooling rate for nucleation (CR2). (C) Critical cooling rate for suppressing crystallization (CR1, black) and nucleation (CR2, red) from the non-isothermal analysis.

Based on the analysis of nucleation and crystallization behaviors shown in Fig. 7 and Fig. 11A and B, the CR1 and CR2 values are presented in Fig. 11C. As shown, except for the linear chain, branching has a negligible effect on the CR1, whereas at the highest branch concentration, the CR2 is increased by an order of magnitude. In other words, the branch architecture of PLLA molecules has a much stronger influence on nucleation than on overall crystallization.

Overall, an increasing number of branching points in long-chain branched PLLA enhances nucleation while simultaneously reducing the spherulite growth rate. Despite these changes in nucleation and crystal growth rate, the overall crystallization rate of the long-chain branched samples in this study remains nearly unchanged in the temperature range from 360 to 420 K.

Enhancing the toughness and semicrystalline morphology of printed single strands

Linear and long-chain branched PLLA were printed, as described in Method. The single-layer printed parts were continuously annealed at the print-bed temperature of 393 K for 2 hours to allow crystallization to complete. The annealing time of 2 hours was selected because it corresponds to the standard processing time for 3D-printed parts with a printing length of 10000 mm,^{70–72} which is representative of typical applications. It should be noted that the thermal history under actual printing conditions is considerably more complex and depends on factors such as the bed temperature, the layer position, and reheating caused by the deposition of subsequent layers. The present study does not aim to reproduce the complete layer-dependent thermal history but rather focuses on systematically elucidating the influence of intrinsic material properties under a representative, simplified thermal protocol. Furthermore, at a bed temperature of 393 K, a moderate number of crystals can be observed in microscope images. Well-separated crystals facilitate the analysis of the influence of long-chain branching on nucleation. Differences in crystal morphology are clearly distinguishable. The single deposited strands were cut from the printed part and used for structural characterization and mechanical testing, as described and discussed below.

The two-dimensional wide-angle X-ray diffraction (2D-WAXD) patterns and the corresponding azimuthally averaged one-dimensional wide-angle X-ray diffraction (1D-WAXD) pattern of printed single strands of linear and long-chain branched PLLA are shown in Figure 13A and B, respectively. In 2D-WAXD patterns, the data reveal the absence of crystal orientation, which agrees with our previous research that PLLA does not orient under 3D printing

conditions.⁴⁶ This is explained by the competition between relaxation time and crystallization kinetics.^{46,73,74} Worth noting, even if orientation is negligible, the shear rate can accelerate crystallization through shear-induced nuclei.^{75–81} In addition, the 1D-WAXD profiles exhibit three prominent diffraction peaks at 16.6–16.8°, 18.9–19.2°, and 22.2–22.5°, with slight shifts observed between the linear and long-chain-branched PLLA samples. These results indicate that all samples possess the same crystalline polymorph,¹⁶ with slight differences in crystal perfection.

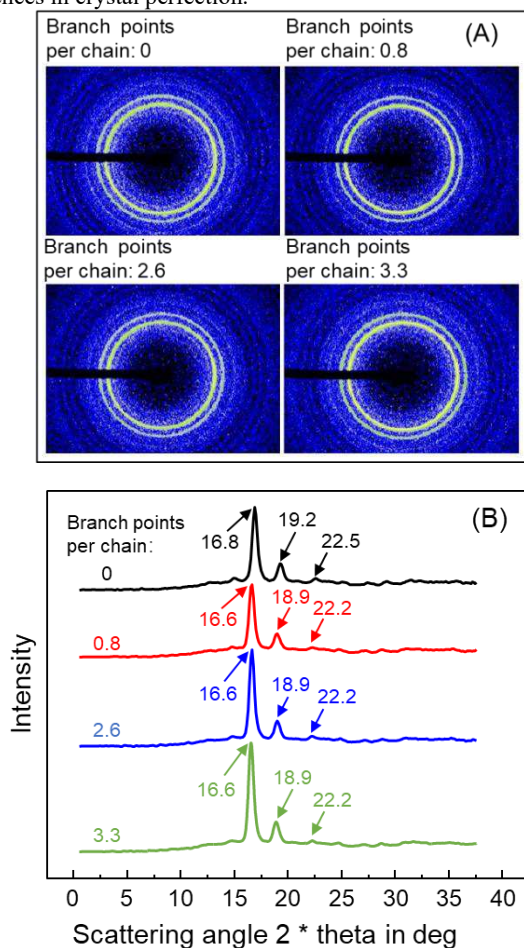


Fig. 12 | (A) Two-dimensional and (B) one-dimensional (azimuthally averaged) X-ray diffraction patterns of the printed single strands.

Fig. 13 presents the DSC melting curves of printed single strands obtained at a heating rate of 0.33 K/s (20 K/min). In these curves, a broad melting peak following the glass transition step is observed in all four samples. The melting peak occurs at around 443–449 K for all samples. In addition, the melting enthalpy is similar across all samples, ranging from approximately 48 to 54 J/g, corresponding to a crystallinity of about 50% when normalized using a bulk enthalpy of melting of 105 J/g for 100% crystalline PLLA.⁸² This result is consistent with the values at the end of primary crystallization at a similar temperature (395 K) for the four PLLA samples; see Fig. 3A.

In Fig. 14, the microstructures of the printed PLLA single strands were examined using POM in both the printing and cross directions. Both directions exhibit similar microstructural features, with no evidence of shear-induced oriented structures. The morphology observed in these images agrees well with the material properties shown in Fig. 12. No orientation structure was observed. In the linear PLLA sample, spherulitic structures were observed. Similar structures were also present in the sample with 0.8 branch points per chain, although the morphology was slightly finer. In contrast, the PLLA samples with higher numbers of branch points per chain (2.6 and 3.3) exhibit a distinctly finer structure, indicating a high nuclei density. Across the images shown in Fig. 14, the characteristic

structural size decreases from approximately 30 to 2 μm . Crystal morphology, including crystal size and number density, directly influences the mechanical properties.^{83,84}

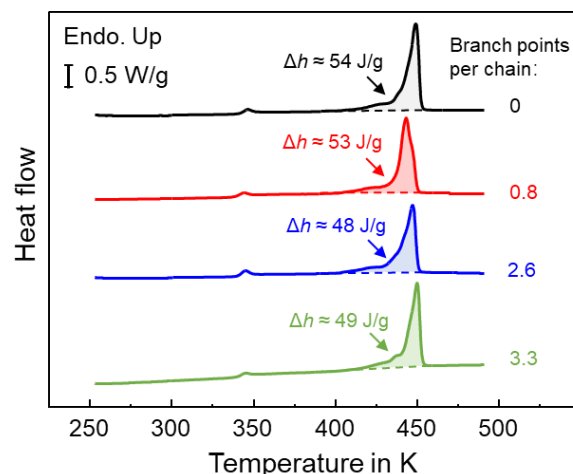


Fig. 13 | Differential scanning calorimetry melting scans of the printed single strands.

In Fig. 14, flow-line-like features, appearing as linear alignments of granular particles, are observed and become more pronounced as the crystalline morphology is refined. These features are not ascribed to shear-induced orientation, but instead originate from the sample geometry or from artifacts generated during sectioning. This interpretation is further supported by morphological observations of the same sample obtained using an inserted λ plate.

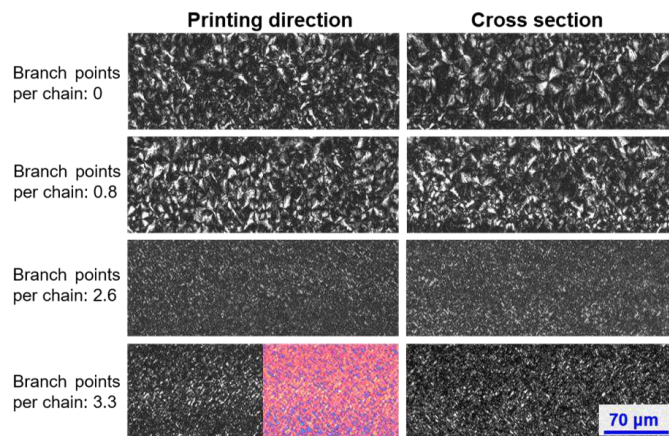


Fig. 14 | Optical microscopy images of printed single strands in printing and cross directions.

In Fig. 15, the stress–strain diagrams for linear and long-chain branched PLLA samples are shown, measured by a universal tensile testing machine. The inset shows the experimental tensile testing setup and specimen placement between two clamps. Generally, as the branch concentration increases, tensile performance improves, with yield strength and ductility increasing. Starkweather and Brooks showed that, for polyamide 6,6, the yield point is inversely proportional to the size of visible spherulites,⁸⁴ suggesting that crystal morphology plays an important role in determining toughness. In isotactic polypropylene (iPP),⁸⁵ experimental results showed that samples with a fine granular/nodular structure, initially melt-crystallized during cooling at 750 K/s, exhibited superior toughness compared to samples with large spherulitic structures, initially melt-crystallized at 0.1 K/s. Variations in crystal morphology are, therefore, an important factor contributing to differences in toughness. In addition, it has been reported for long-chain-branched iPP that the toughness increases because branching enhances the nuclei density,

thereby promoting the formation of finer and more crystalline structures.⁸⁶ As described above, all PLLA deposited strands consist of α -crystals. Therefore, polymorphic superstructures, which may also influence toughness,^{85,87–90} are excluded as the main reason for the observed differences in stress–strain behavior. Instead, these differences must be attributed to variations in the semicrystalline morphology (see Fig. 14)

The mechanical properties derived from the data shown in Fig. 15 are presented in Fig. 16A–D, showing tensile strength, strain at break, toughness, and Young's modulus, respectively. Figure 17A demonstrates that long-chain branched PLLA exhibits higher tensile strength compared to linear PLLA. While the difference in tensile strength of PLLA containing different amounts of branch points is less pronounced, there is a slight increase in maximum tensile strength with increasing number of branch points.

Fig. 16B and C present strain at break (ductility) and toughness obtained from the stress–strain curves, respectively.⁸⁷ It is worth noting that the ductility and toughness discussed here are intrinsic properties of the material, as evaluated using printed single strands, rather than properties of the complete 3D-printed part. As the number of branch points per chain increases from 0 to 3.3, the strain at break (ductility) rises from approximately 1.6% to 5.2%, while the

toughness, estimated from the area under the stress–strain curves, increases from about 0.2 to 2.3 MPa.

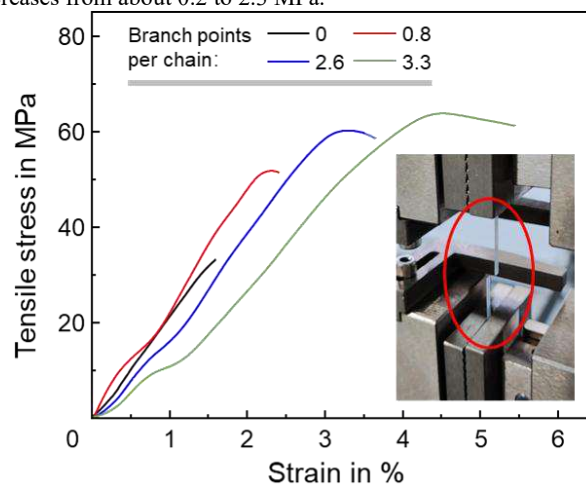


Fig. 15 | Tensile stress as a function of strain, with an inset showing the experimental setup and specimen placement between two clamps.

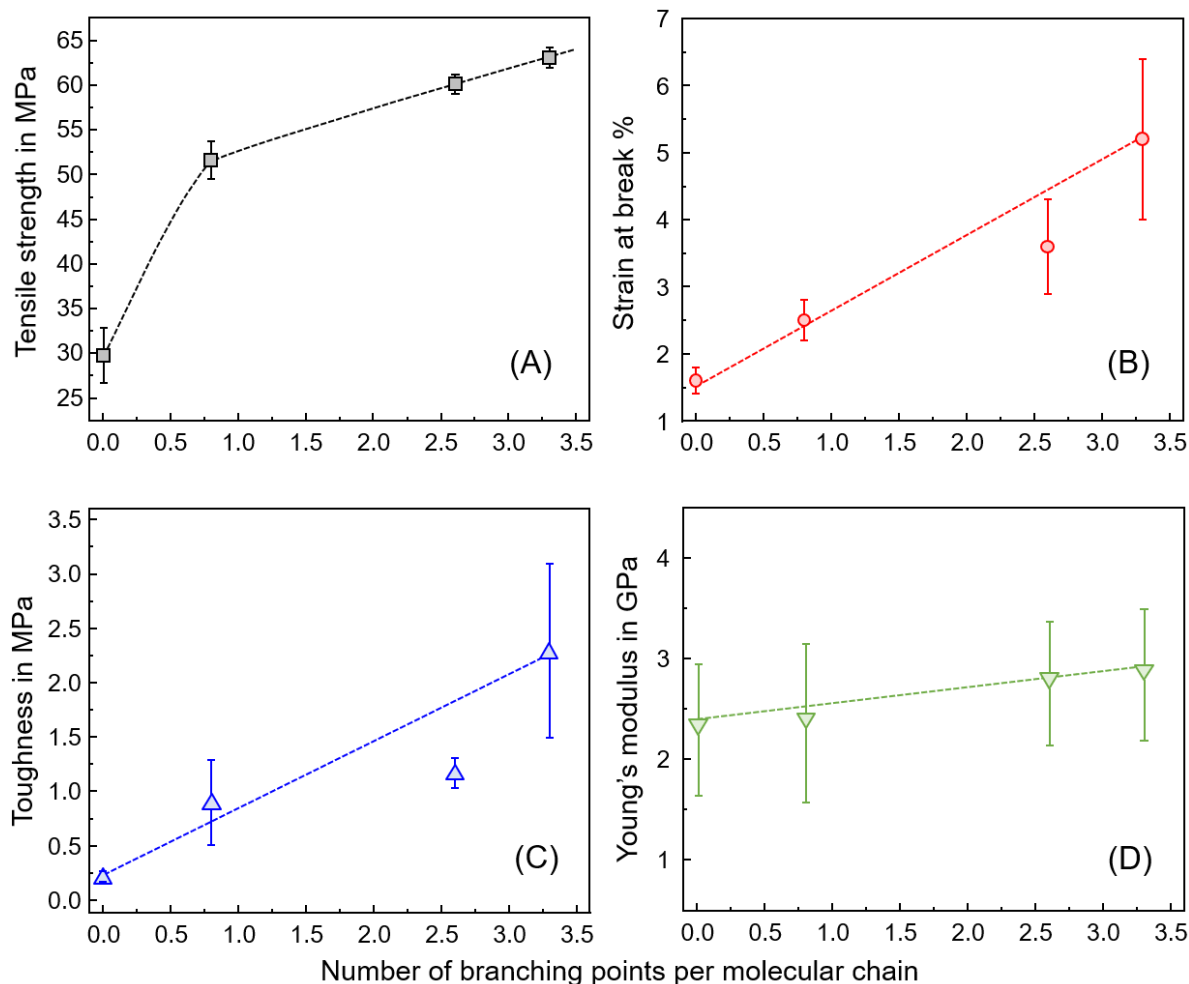


Fig. 16 | Mechanical test results. (A) Tensile strength; (B) strain at break; (C) toughness (estimated through the area under the stress–strain curve); (D) Young's modulus. The dashed lines serve as visual guides to facilitate data interpretation. The data plotted in these figures are the average values obtained from five specimens.

Fig. 16D shows Young's modulus of linear and long-chain branched PLLA samples, as estimated through the linear region of the curves in Fig. 16. In general, Young's modulus increases slightly with

the number of branch points per chain. This result is consistent with observations for long-chain branched metallocene polyethylene.⁹¹

Conclusions

Analysis of the crystallization kinetics, morphology, crystal structure, and mechanical properties of linear and long-chain branched PLLA samples and their corresponding printed single deposited strands yields the following conclusions:

- (1) Long-chain branching of PLLA has a limited effect on the overall crystallization kinetics. Interestingly, it enhances crystal nucleation but reduces the spherulite growth rate. Enhanced nucleation, driven by an increasing number of branch points per polymer chain, leads to finer crystalline structures.
- (2) The morphology of printed single deposited strands confirms that finer and denser crystalline structures form as the number of branch points per chain increases. Meanwhile, no detectable crystal orientation was observed in the printed lines. Furthermore, mechanical testing demonstrates that introducing long-chain branching significantly improves the ductility and toughness of printed strands.

In the context of 3D-printing manufacturing, this study confirms that long-chain branching effectively improves crystal nucleation in PLLA, which is important for enhancing the ductility and toughness of individually printed strands, regardless of further factors such as filament-fusion, exposure to thermal cycling etc. effective in production of three-dimensional parts.

Long-chain branching sometimes introduces additional limitations, most commonly reduced processability due to increased melt viscosity. However, this challenge can be readily addressed by blending long-chain-branched PLLA with low-molecular-weight PLLA, which acts as a plasticizer, allowing adjustment of the system viscosity and achieving a suitable melt viscosity for printing. In summary, introducing long-chain branching is an effective strategy to improve the mechanical performance of PLLA materials for 3D-printing applications.

Methods

Materials

PLLA pellets were supplied by Anhui BBBCA Biomaterials Co., Ltd. (Bozhou, China). Three long-chain branched PLLA samples, here named FY 43, FY 45, and FY 48, were manufactured by the supplier via reactive processing with a chain extender. A linear PLLA reference sample, FY801, with matching molecular weight and molecular weight distribution to the long-chain branched samples, was also provided. The molecular weight, polydispersity index, and the number of branch points per chain for all samples are summarized in Tab. 1. A more detailed description of the sample characteristics has been reported in our previous work.⁹²

It is worth noting that the increase in molecular weight will cause a decrease in crystallization kinetics, as illustrated in Fig. 7. As the molecular weight increases from 104 kDa to 395 kDa, the CR1 only decreases from 0.2 to 0.15 K/s, suggesting that the influence of molecular weight on crystallization of our samples is small. In addition, all grades used in this study comply with the European REACH Regulation, and the total residual additive content is below 0.1 mass%. Therefore, residual chain extenders and other additives are unlikely to significantly influence heterogeneous nucleation.

Tab. 1 | Molecular characteristics of the linear and branched PLLA samples used in this study.

Sample	M_n (kDa)	PDI	Melt flow index (g/min) (463 K/2.16 kg)	Branching point per chain (BP)
FY 801	145	1.37	4.0	N/A
FY 43	142	1.49	3.8	0.8
FY 45	167	1.33	2.1	2.6

FY 48	167	1.35	1.5	3.3
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Melt flow index for branched PLLA was obtained through personal contact with the supplier.

Printing Procedure

Samples were fabricated using a Fused Pellet Fabrication (FPF) 3D-printer (Tumaker Pro, Indart3D, Gipuzkoa, Spain), equipped with a 0.4 mm nozzle. The nozzle temperature for melting the PLLA pellets was set to 498 K, while the print bed temperature was maintained at 393 K. The cooling fan was set to its maximum, approximately 6000 rpm. The deposition speed was set to 2700 mm/min, while the pellet-feed rate was controlled automatically. Following the manufacturer's instructions, the nozzle-to-bed distance was manually adjusted to slightly above 0.3 mm, approximately corresponding to the nominal strand height of 0.3 mm.

A standard glass plate was used as the print bed. The geometry of the printed specimen is shown in Fig. 17. It consists of a rectangular pattern with separated line-to-line infill. These single deposited strands, used to fill the rectangular pattern, were cut from the printed part for the investigation of mechanical properties and semicrystalline morphology. Each line had approximate dimensions of 100 mm in length, 2 mm in width, and 0.2 mm in thickness. These dimensions differ from the nominal strand dimensions (width = 1 mm and height = 0.3 mm) because of spreading after deposition.

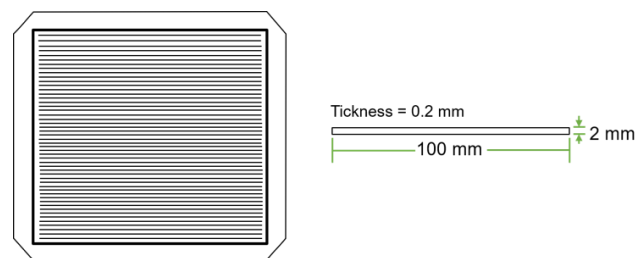


Fig. 17 | Schematic illustration of the geometry of the printed part.

Characterization

X-ray diffraction

Wide-angle X-ray diffraction (WAXD) measurements were performed to examine the crystalline structure of printed single strands using a custom-built microfocus X-ray system (Xenocs, Grenoble, France). The system was equipped with a multilayer-focused CuK α X-ray source (GeniX3D-Cu ULD, Xenocs SA, Grenoble, France; $\lambda = 0.154$ nm) and a high-intensity focusing mirror, allowing the X-ray beam to be focused at the sample position to a spot size of approximately $40 \times 60 \mu\text{m}^2$. 2D-WAXD patterns were recorded using a Pilatus 100K detector (Dectris, Switzerland) with an exposure time of 1 min for each measurement. After background subtraction, the 2D-WAXD patterns were azimuthally integrated to obtain 1D-WAXD profiles.

Polarized-light Optical Microscopy

POM was used to analyze the semicrystalline morphology of the PLLA samples and their corresponding printed single strands using a DMRX microscope (Leica, Wetzlar, Germany), operated in transmission mode. Sections of $10 \mu\text{m}$ thickness were prepared using a rotary microtome (Slee, Mainz, Germany) equipped with a tungsten carbide knife.

A Linkam THMS600 hotstage (Linkam Scientific Instruments, Tadworth, UK) was coupled with the POM to investigate both non-isothermal structure formation and isothermal spherulite growth rates in the samples. For cooling experiments, performed at rates above 30 K/min, liquid nitrogen was used at a constant flow rate of approximately 7 mL/min to assist with cooling.

Differential Scanning Calorimetry

DSC measurements were performed using a calibrated heat-flux DSC 1 (Mettler Toledo, Greifensee, Switzerland) fitted with an FRS5 sensor. The DSC instrument was coupled to a Huber TC100 intracooler (Huber, Offenburg, Germany) for precise temperature control and accessing temperatures below room temperature. Calibration was validated prior to sample analysis using an indium standard, confirming that both the melting temperature and enthalpy were within the accepted error ranges of ± 0.2 K and $< 2\%$, respectively. For all measurements, the DSC furnace was continuously purged with dry nitrogen at a constant flow rate of 60 mL/min. Approximately 4–7 mg of each sample was sealed in 20 μ L aluminum pans before testing.

Fast Scanning Calorimetry (FSC)

FSC measurements were carried out on a chip-based fast-scanning calorimeter manufactured by RoNa Tech GmbH (Rostock, Germany). The device was developed in the Polymer Physics group at the University of Rostock, as described elsewhere.^{28,93–95} An XI-395 chip sensor from Xensor Integration (Delfgauw, The Netherlands) was used for all measurements.⁹⁶ Liquid nitrogen was used as the cooling medium to maintain the system environment and the silicone frame of the chip-sensor at 83 K throughout testing. The instrument temperature scale was calibrated using indium and tin standards, following the protocol described elsewhere.⁹⁷ FSC samples with masses in the range of 3–10 ng were prepared by micro-cutting specimens from the original PLLA pellets with a scalpel. To ensure good thermal contact between the sample and the chip sensor surface, multiple consecutive heating-cooling cycles were performed before data collection.⁹⁸

Mechanical Testing

The tensile properties of printed single strands were evaluated using a universal tensile testing machine (UTM4000, Suntest, Shenzhen, China). The gauge length was set to 45 mm, and the crosshead speed was 5 mm/min. All other testing parameters were configured in accordance with ISO 527-2:2012 for the tensile testing of plastic films and sheets. For each test, the width and thickness of each strand were measured at five equally spaced positions along its length. The cross-sectional area was calculated at each position, and the mean of the five values was used as the representative cross-sectional area of the strand.

To minimize variations caused by physical aging, all samples used for mechanical testing were printed on the same day, stored under identical conditions, and tested exactly 21 days later. Therefore, the contribution of physical aging to the mechanical properties was assumed to be comparable among all samples.

Additional information

Supplementary information: the online version contains supplementary material available at <https://doi.org/10.1038/sXXXX-XXXX>.

Data availability

The data supporting the findings of this study are available from the corresponding author, Rui Zhang, upon reasonable request. The research data are stored in accordance with the data-retention requirements of the European Regional Development Fund (EFRE). For inquiries concerning data storage and archiving, please contact Rene Sattler.

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