

Thermal diffusivity and secondary crystallisation kinetics in poly(lactic acid)

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DOI:

[10.1016/j.polymer.2019.121595](https://doi.org/10.1016/j.polymer.2019.121595)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Jenkins, M, Turner, R, Marsh, J & Carter, J 2019, 'Thermal diffusivity and secondary crystallisation kinetics in poly(lactic acid)', *Polymer*, vol. 179, 121595. <https://doi.org/10.1016/j.polymer.2019.121595>

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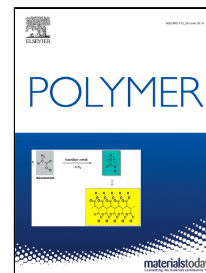
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Accepted Manuscript

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PII: S0032-3861(19)30579-8
DOI: 10.1016/j.polymer.2019.121595
Article Number: 121595
Reference: JPOL 121595
To appear in: *Polymer*
Received Date: 04 April 2019
Accepted Date: 19 June 2019

Please cite this article as: J.J. Marsh, R.P. Turner, J. Carter, M.J. Jenkins, Thermal diffusivity and secondary crystallisation in poly(lactic acid), *Polymer* (2019), doi: 10.1016/j.polymer.2019.121595

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1 Thermal diffusivity and secondary crystallisation in 2 poly(lactic acid) 3

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7

8 **Abstract**

9 The non-steady state technique of laser flash analysis (LFA) was used to record
10 the variation of thermal diffusivity with time during the cold-crystallisation of
11 poly(lactic acid), a grade containing 4% D stereoisomer content. The measured
12 diffusivity data was analysed in terms of the Avrami and Hoffman-Lauritzen
13 models for polymer crystallization. Within the temperature range 88 to 109°C,
14 mechanistic 'n' values of 2.0 ± 0.1 were calculated and a nucleation constant of 6.58
15 $\times 10^{-5} \text{ K}^2$ was determined; the LFA technique yielded kinetic data that was
16 comparable to that which originated from DSC. Measurements of thermal
17 diffusivity were also recorded over a longer time-scale to determine whether
18 thermal diffusivity was a useful indicator of secondary crystallization and this data
19 was analysed using a modified Avrami equation that includes a root-time
20 dependence of the secondary process. Secondary crystallisation rate constants
21 (k_s) increased with crystallisation temperature and yielded an activation energy
22 for the secondary crystallisation process of 40 kJ/mol.
23

24 **Keywords**

25 Poly (lactic acid), laser flash analysis, diffusivity, secondary crystallisation
26

27 **1. Introduction**

28 Heat-transfer is of key importance in the modelling of injection moulding
29 processes in polymeric materials and the thermo-physical properties of
30 conductivity, diffusivity and heat capacity are key parameters in this respect [1,
31 2]. These thermo-physical properties of polymers have also been the subject of
32 previous reviews [3, 4]. The thermal diffusivity and conductivity of polymers can
33 be measured in a wide variety of ways, which have been developed over a

1 considerable number of years. Examples of equilibrium or steady-state methods
2 to measure thermal conductivity include the guarded hot plate method (ASTM
3 C177-63) [5] and the split-bar method [6]. The thermal diffusivity and
4 conductivity of a wide range of polymers have been studied using these
5 techniques. Example polymers measured with these types of steady-state
6 methods include rubbers, thermosets and thermoplastics. [6]. However, steady-
7 state methods are slow. The typical timescale of measurement for the guarded hot
8 plate is of the order of 1 hour to ensure the sample is at equilibrium temperature.
9 Therefore, their applicability to time-resolved measurements is limited.

10

11 Non-equilibrium thermal conductivity and diffusivity measurement methods
12 allow for much more rapid data collection, thus enabling non-isothermal
13 measurements to be undertaken. Non-equilibrium measurement methods include
14 the Powell Comparator [7], rapid Differential Scanning Calorimetry [8], the Hot-
15 line source technique [9, 10, 11], and updated versions of Lee's disc apparatus
16 [12]. However, due to difficulties in controlling the test conditions (contact
17 between sample and apparatus, heat losses, accuracy in thermal readings), and
18 with sample preparation and degradation, non-equilibrium thermo-physical
19 property measurement is challenging [12].

20

21 Thermal diffusivity can be measured using a non-steady-state technique that
22 utilizes a short-duration flash of heat energy, an example of which is the technique
23 commonly referred to as Laser Flash Analysis (LFA). The timescale of measurement
24 in this technique is much shorter than that of the steady-state method and
25 measurements of thermal diffusivity can be made within a period of minutes. This
26 enables a time-resolved approach to the measurement of diffusivity and a range
27 of commercially available polymers have been studied in this respect. In the
28 amorphous polymers PS, PMMA, PES and PEI, a. c. joule heating has been used to
29 record the variation of diffusivity on heating. Through the T_g region, a decrease in
30 diffusivity was observed in all polymers. [13]. In the semi-crystalline polymers PE,
31 PP, PA6, PVDF it has been shown that the variation in diffusivity in the melting
32 regions correlated well with the specific heat capacities that were determined
33 using differential scanning calorimetry (DSC) [14] and in PET, PE and PP, the

1 measured thermal conductivity was related to the proportion of amorphous and
2 crystalline phases in the polymer and the orientation of the crystalline lamellae
3 has been considered [15, 16]. Diffusivity measurements from the LFA technique
4 have been compared with other techniques such as hot-wire method, but in these
5 instances, the number of diffusivity measurements are limited and cannot be
6 related to any thermal transitions and relaxations in the polymer [17].

7

8 An aspect that has not received a great deal of attention is the effect of re-
9 crystallisation on thermal diffusivity. The cold-crystallisation of PET has been
10 studied using flash radiometry and the variation of diffusivity with time has been
11 analysed in terms of the Avrami equation [18]. Mechanistic n values in the range
12 1.6 to 3.2 were reported for primary crystallisation process, but no secondary
13 process was detected. To study cold-crystallisation, the sample must be rapidly
14 quenched to render the sample amorphous, but the creation of a fully amorphous
15 sample is a non-trivial undertaking because unless exceedingly high cooling rates
16 are achieved, primary nucleation may occur on cooling such that the re-
17 crystallization on heating is more rapid due to the pre-existing nuclei [19, 20]. This
18 behavior can be limited through the selection of a polymer that exhibits relatively
19 slow crystallization kinetics and a variant of poly (_L-lactic acid) (PLA) containing
20 less than 10% d-isomer content is ideal in this respect.

21

22 PLA is a biodegradable linear polyester derived from corn starch or sugarcane and
23 is used in biomedical and packaging applications [21, 22]. PLA is a semi-crystalline
24 polymer with a degree of crystallinity of approximately 40% [23]. Semi-crystalline
25 PLA exhibits a glass to liquid transition temperature in the region of 50°C and
26 melts in the region of 165°C. The addition of small quantities of the D-lactide to
27 the otherwise L-lactide chain has been found to hinder the crystallization process
28 and retard the timescale of crystallization to such an extent that glassy PLA
29 without pre-existing nuclei can be formed through quenching [24]. Study of the
30 variation of thermal conductivity with temperature in PLA has been limited to the
31 glass transition region of a PLA/expanded graphite nanocomposite system
32 containing 3.0 wt% to 6.75 wt% graphite [25].

33

1 In this work, laser flash analysis was used to record the variation of thermal
2 diffusivity with time during the cold-crystallisation of PLA (a grade that contains
3 4.2% D-isomer) and the measured data is analysed in terms of the Avrami and
4 Hoffman-Lauritzen models for polymer crystallization. Measurements of thermal
5 diffusivity are also recorded over a longer time-scale to determine whether
6 thermal diffusivity is a useful indicator of secondary crystallization. This data is
7 analysed using a modified Avrami equation that describes both the primary and
8 secondary crystallisation processes and an activation energy for the secondary
9 process is reported.

10

11

12

13 **2. Experimental**

14 *2.1 Materials and sample preparation*

15 PLA 2002D was supplied in pellet form by NatureWorks LLC (Nebraska, USA). It
16 is a semi-crystalline grade with a typical heat of fusion of 93 J/g [26]. This grade
17 exhibits a glass transition temperature and melting point of 59 and 154 °C
18 respectively. PLA2002D has a molecular weight (M_w) of 194,000 (manufacturers
19 data). The 2002D grade is essentially a random co-polymer containing 3%
20 monomeric D stereoisomer in an otherwise L polymer chain.

21

22 Prior to processing, PLA pellets were dried at 70 °C in an oven for 4 hours to
23 remove moisture. Dried PLA pellets were then formed into plaques using a heated
24 press (melt temperature was 200 °C and a load of 10 tons was applied). On
25 removal from the press, the plaques were air cooled. Assuming Newtonian
26 cooling, the cooling rate experienced by the plaque as it cooled through the
27 temperature range of crystallization was greater than 50°C/min and through T_g it
28 was approximately 40 °C/min.

29

30 For thermal diffusivity measurements, disc shaped samples of thickness 1.1 ± 0.1
31 mm and diameter 12.6 ± 0.1 mm were cut from the amorphous PLA plaque. To
32 facilitate measurement of diffusivity, samples were coated on all sides with
33 $\sim 3.5 \pm 0.5$ μm of graphite (Kontakt Chemie Graphit 33) which was applied in the

1 form of a spray coat. To facilitate adhesion of the graphite coating to the polymer,
2 a very thin layer of high-vacuum grease was applied to the polymer disc. For
3 thermal analysis, discs of 5 mm in diameter with a typical mass of 4 ± 2 mg were
4 cut from the PLA plaques.

5

6 2.2 Measurement of thermal diffusivity

7 A Netzsch laser flash apparatus (LFA) was used to determine the thermal
8 diffusivity of the PLA discs. Nitrogen was used as a purge gas to prevent oxidation
9 of the samples and a flow rate of 100 mL/min was adopted for all experiments.
10 The laser pulse width and voltage were 0.4 ms and 400V respectively and three
11 laser pulses at each measurement point (ie time or temperature) were used to
12 determine a measurement of thermal diffusivity which was calculated from the
13 following equation [27],

14

$$15 \alpha = \frac{-\ln(1/4)L^2}{\pi^2 t_{1/2}} = 0.139 \frac{L^2}{t_{1/2}} \quad \text{Equation 1}$$

16

17 Where L is the sample thickness and $t_{1/2}$ is the time required for the top surface of
18 the sample to rise to half of the maximum temperature reached. Corrections for
19 heat losses from the front and rear surface of the sample along with the disc edges
20 are considered to be radiated heat losses. The Cape-Lehman [28] method was
21 used to correct for these.

22

23 Given that the LFA control thermocouple was mounted approximately 10mm
24 from the sample, the apparatus was modified to enable the inclusion of an
25 additional thermocouple (k-type) which was mounted in close proximity to the
26 upper surface of the polymer sample (as illustrated in figs 1a and 1b). The
27 temperature data was logged at 2 data points per second using National
28 Instruments signal conditioning and data acquisition systems controlled by
29 LabView. The inclusion of an additional thermocouple enabled a more accurate
30 measurement of sample temperature and it also enabled the instrument
31 temperature to be calibrated, the equation $T = 1.05(T_{LFA})+3$ was used in this
32 respect. Furthermore, the additional thermocouple also provided a more accurate

1 measure of the variation of sample temperature with time during the laser pulses.
2 The variation of sample temperature with time (recorded using the additional
3 thermocouple) showed that the laser pulse caused a near instantaneous increase
4 in temperature of approximately 1.5°C and the subsequent decay occurring over
5 150 to 200 seconds; a typical thermal response is shown in fig. 1c. It was apparent
6 that the baseline temperature drift over the duration of the experiment was
7 insignificant. This sample time-temperature profile informed the selection of the
8 measurement intervals, therefore, a time of 200s between measurements was
9 adopted.

10

11 Samples of PLA were subjected to two temperature programmes, these are
12 referred to as isothermal and non-isothermal and are described as follows. In the
13 case of the non-isothermal temperature programme, measurements of diffusivity
14 were recorded at 2–5°C intervals on heating the sample from ambient
15 temperature to 85°C. Amorphous and partially crystalline samples were used in
16 this approach. In the case of the isothermal temperature programme, a two-step
17 heating profile was adopted. The samples of amorphous PLA were initially heated
18 at 5 °C/min (from ambient) to a point 5 °C below the target crystallisation
19 temperature (T_c). A heating rate of 0.5 °C/min was adopted for the approach to T_c .
20 Crystallisation temperatures in range 88.1 to 108.9°C were adopted. Samples
21 were maintained at the selected temperature for a period of up to 19 hours and
22 measurements of diffusivity were recorded at intervals of 200-400 seconds. The
23 rationale for the adoption of a relatively long hold at the crystallisation
24 temperature was to enable the effect of the secondary crystallisation process on
25 the diffusivity to be determined.

26

27 2.3 *Differential Scanning Calorimetry (DSC)*

28 A Mettler Toledo DSC 1 (Mettler-Toledo, Greifensee, Switzerland), calibrated with
29 indium and zinc standards, was used to record the thermal response of the PLA in
30 the region of the glass to liquid transition temperature. All experiments were
31 conducted under a nitrogen flow rate of 50 mL/min. A standard procedure was
32 adopted in which the samples were weighed into 40 µl aluminium DSC pans
33 hermetically sealed with aluminium DSC lids. Samples masses were in the region

1 of 10 mg \pm 0.5 mg. To produce amorphous material, samples were heated from 20
2 to 200 °C at 20 °C min⁻¹ and then cooled back to 20°C at a cooling rate of 50 °C/min,
3 thereby forming the glass at 50° C/min. Fig. 2 shows the thermal response of
4 PLA2002D on cooling at rates ranging from 50 to 0.2 °C/min. It is clear that
5 crystallisation on cooling only occurred at cooling rates of less than 1 °C/min. Fig
6 2 also shows the thermal response of the hot-pressed sample on heating (reheat
7 rate of 10 °C/min). No melting peak was observed which confirmed that this
8 sample preparation route enabled the production of amorphous samples. Partially
9 crystalline samples were created by heating the sample to a temperature of 200
10 °C and cooling rapidly to a temperature of 130 °C at 50 °C/min, at which point the
11 sample was held for a period of 4 hours prior to cooling back to 20 °C, again at
12 50°C/min. The melting peak was then recorded on re-heating at 10 °C/min and
13 the degree of crystallinity was determined to be 51%. The glass transition
14 temperatures of both amorphous and semi-crystalline morphologies were
15 recorded at a heating rate of 10 °C/min.

16
17

18 3. Results and Discussion

19 The non-isothermal variation of thermal diffusivity (α) in the glass transition
20 region of both amorphous and partially crystalline PLA is shown in fig. 3 (the
21 change in diffusivity is shown in order to facilitate comparison with DSC). In both
22 amorphous and partially crystalline morphologies, the diffusivity was found to
23 decrease on heating, markedly so in the glass to liquid transition region. In the
24 case of the amorphous sample, there is no long-range order and the associated
25 free volume in the system hinders phonon transport due to increased scattering.
26 Conversely, the presence of an ordered, closed-packed crystalline phase facilitates
27 phonon transport and the diffusivity is therefore increased (relative to the
28 amorphous sample). In both cases, the diffusivity decreases on heating due to the
29 thermal expansion in the glassy phases of the samples. This is then followed at a
30 temperature of 55 °C by the T_g in which there is a more significant increase in
31 volume and a correspondingly pronounced decrease in phonon transport. The
32 presence of a crystalline phase limits this effect and the size of the step-change in

1 diffusivity ($\Delta\alpha$) for the partially crystalline sample is reduced in comparison to the
2 amorphous sample.

3

4 The variation of diffusivity in this temperature range strongly resembles the
5 thermal response of PLA as detected by DSC, and as shown in fig. 3, there appears
6 to be good correlation between the LFA and DSC. Treating the variation of
7 diffusivity with temperature (in fig. 3) as a conventional DSC T_g curve, it is
8 apparent that the onset of the transition is similar in both cases (approx. 55.0°C),
9 as is the T_g at the $\frac{1}{2}\Delta\alpha$ point (approx. 56.8 °C), where $\Delta\alpha$ is the difference between
10 the diffusivity of the liquid and glass i.e. the LFA equivalent of $\frac{1}{2}\Delta C_p$. However, in
11 the case of the partially crystalline sample, the breadth of the glass transition is
12 slightly increased, and as noted above, it is also apparent that the $\Delta\alpha$ term is
13 greater for the amorphous sample.

14

15 The isothermal variation of diffusivity with time for an (initially) amorphous PLA
16 sample is shown in fig. 4 (a crystallisation temperature of 98.5°C is shown). The
17 progressive increase in diffusivity is related to the development of crystallinity in
18 the samples. The initial section of the curves represents the primary
19 crystallisation process which involves the radial growth of spherulitic
20 superstructures. Instead of reaching a plateau, the diffusivity continues to
21 increase with time. This is due to the presence of a secondary crystallisation
22 process. It is interesting to observe that LFA and the measurement of diffusivity
23 seems to be sensitive to both the primary and secondary crystallisation processes.

24

25 Although the primary and secondary processes are likely to occur over an
26 overlapping timescale, the transition between them was estimated from the point
27 of intersection between tangents drawn to the primary and secondary
28 crystallisation regions (fig. 4), this defined the diffusivity equivalent of the $X_{p,\infty}$
29 parameter (the relative crystallinity achieved at the end of the primary
30 crystallisation process), and from this, the relative crystallinity, X_b , for the primary
31 process was defined as follows,

32

$$X_t = \frac{\alpha_t - \alpha_{p,\infty}}{\alpha_{p,\infty} - \alpha_0} \quad \text{Equation 2}$$

2

3 Where α_t is the diffusivity at time t , $\alpha_{p,\infty}$ is the diffusivity at the end of the primary
4 crystallisation process and α_0 is the initial diffusivity. The variation of relative
5 crystallinity with time in fig. 5 shows a clear temperature dependence with the
6 crystallisation half-life. Also, this data was amenable to an Avrami analysis with
7 plots of $\log[-\ln(1-X_c)]$ against $\log t$ yielding a series of near parallel lines (shown
8 in fig. 6). The mechanistic 'n' value was determined from the slope of the line and
9 the rate constant from y intercept. The half-life was calculated from $t_{1/2} = (\ln 2)/K^n$.

10

11 The temperature dependence of the half-life and rate constant are shown in fig. 7,
12 and as indicated above, the rate of crystallisation increases with increasing
13 temperature indicating that the crystallisation is occurring in the cold-
14 crystallisation region. What is particularly interesting is the mechanistic 'n' values
15 shown in table 1. Analysis of the data shows that the 'n' value was nearly constant
16 over the temperature range studied: 'n' values of 2.0 ± 0.1 were calculated.
17 Comparison with crystallization data on PLA generated using DSC shows that
18 there is good agreement between the techniques: over the temperature range 90
19 to 130 °C, the n value was found to vary from 1.99 to 2.11, the mean being 2.1 ± 0.1
20 (note that the PLA used in that particular study contained 4.24% D content) [29].
21 Further analysis of the crystallisation half-life data is possible by using a modified
22 Hoffman-Lauritzen theory (modified such that the growth rate, G, is replaced with
23 the reciprocal of the half-life [30]) such that,

24

$$G = G_0 \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \exp\left(-\frac{K_g}{T\Delta T f}\right) \quad \text{Equation 3}$$

26

27 Where U^* is the activation energy (6276 J/mol) [31], R is the universal gas
28 constant (8.314 J/mol), T_c is the crystallisation temperature and K_g is the
29 nucleation rate constant. T_∞ is a temperature where the motion of chains ceases
30 and is generally deemed to occur at temperatures 30 °C below T_g , ΔT is the
31 supercooling ($T_m - T_c$) and f is a correction factor ($2T_c/(T_m+T_c)$). A plot of
32 $\ln[(1/t_{1/2}) + U^*/R(T_c - T_\infty)]$ against $1/(T_c \Delta T f)$ is shown in fig. 8. The slope of the line

1 is related to the nucleation constant K_g and was determined to be $6.58 \times 10^{-5} \text{ K}^2$.
 2 As above, there is good agreement with existing literature in that for PLA, a K_g
 3 value of $6.02 \times 10^{-5} \text{ K}^2$ was reported [32] which suggests that the crystallization
 4 process in the temperature range adopted in this work is occurring in regime III.

5
 6 The diffusivity-time profile shown in fig. 4 is very similar to the peak area-time
 7 profile as recorded for the crystalline carbonyl band in poly(ethylene terephthalate)
 8 using the technique of infra-red spectroscopy; this technique enabled the primary
 9 and secondary crystallisation processes to be clearly resolved [33].
 10 Mechanistically, the secondary crystallisation process involves the formation of
 11 new thinner lamellae in the existing inter-lamellar gaps and localised thickening
 12 of the existing lamella. Both mechanisms for the secondary process will promote
 13 phonon transport across the inter-lamellar regions and increase diffusivity.

14
 15 The kinetics of the secondary process (in polycaprolactone) has been shown to fit
 16 a root-time dependence of the form,

$$17 \quad X_{s,t} = X_{p,\infty}(1 + k_s t^{1/2}) \quad \text{Equation 4}$$

18
 19 where $X_{s,t}$ is the relative crystallinity for the secondary stage of the crystallisation
 20 process, $X_{p,\infty}$ is the final fractional crystallinity at the end of the primary process
 21 and k_s is the rate constant for the secondary process [34]. Since the LFA technique
 22 is also able to resolve the secondary crystallisation process, this region of the
 23 diffusivity-time curves was analysed in terms of equation 3; $X_{p,\infty}$ was replaced
 24 with $\alpha_{p,\infty}$ and $X_{s,t}$ was replaced with the diffusivity values measured over the
 25 secondary process i.e $\alpha_{s,t}$. Plots $\alpha_{s,t}/\alpha_{p,\infty}$ (the diffusivity equivalent of $X_t / X_{p,\infty}$)
 26 were linear with a slope of k_s , as shown in fig. 9. The rate constants increased with
 27 increasing temperature which is consistent with the diffusion-controlled nature
 28 of the secondary process. The crystallisation temperatures and the associated rate
 29 constants are shown in table 2. The R^2 parameters were in the range 0.79 to 0.90
 30 but there was no systematic variation with crystallisation temperature.

31
 32

1 The secondary crystallisation process was found to obey an Arrhenius
2 dependence on temperature: a plot of $\ln(k_s)$ against $1/T_c$ was linear and gave an
3 activation energy of 40 kJ/mol. This value compares well with other reported
4 values of the activation energy for the secondary process; activation energies of
5 40 kJ/mol [34] and 35 kJ/mol [35] for PCL and 25 kJ/mol [36] have been reported
6 for polycaprolactone and polylactic acid (PLA 2002D, the same grade selected for
7 use in this work). It is worth noting that these activation energies were
8 determined over temperature ranges that were clearly in the 'hot-crystallisation'
9 regions, and in the case of PCL, close to the melting point. The significance of this
10 is that in this crystallisation region, the secondary process will be dominated by a
11 diffusion-controlled thickening of the 'fold-surface' rather than a process
12 involving infill which can occur at reduced crystallisation temperatures. The
13 temperature range adopted in this study is much reduced in comparison and may
14 not be dominated by lamella thickening. However, the root-time dependence still
15 appears to fit adequately well.

16
17

18 **4. Conclusion**

19 The relatively rapid measurement speeds associated with the laser flash analysis
20 technique (LFA) allow thermal diffusivity to be measured as a function of
21 temperature to detect the glass transition process, and with time to detect the
22 development of crystallinity in PLA. Analysis of the thermal diffusivity in the
23 region of the glass to liquid transition shows close correlation with the response
24 of the material as detected by differential scanning calorimetry (DSC). Analysis of
25 the variation of diffusivity with time in terms of common models for the
26 crystallisation process in polymers i.e. Avrami and Hoffman-Lauritzen shows that
27 the LFA technique yields kinetic data that is comparable to that which originated
28 from DSC. Of particular note is the increased sensitivity of the technique to the
29 secondary crystallisation process (at least in comparison to DSC) such that the
30 secondary process can be readily resolved and analysed in terms of a root-time
31 dependence. In addition, the increased sensitivity of LFA to the secondary process
32 is likely to reduce the uncertainty in the estimation of the end of the primary
33 process and thereby increase the applicability of the Avrami analysis: over the
34 range of crystallisation temperatures studied, n values of 2.0 ± 0.1 were obtained

1 (Avrami analysis of crystallization data derived from DSC often yields non-integer
2 n values). Secondary crystallisation rate constants (k_s) increased with
3 crystallisation temperature and yielded an activation energy for the process of 40
4 kJ/mol. The LFA technique is particularly applicable to the characterisation of
5 microstructural development in PLA (but because the crystallisation behaviour
6 and kinetics vary with D-isomer content, the kinetic results presented in this work
7 are not applicable to all grades of PLA). The presence of a small proportion of D
8 isomer in an otherwise L isomer polymer, hinders crystallisation such that the
9 process takes place over a prolonged time-scale that is suitable for analysis using
10 this technique. However, there are limitations in that the diffusivity
11 measurements necessitate a laser pulse that causes an instantaneous (but
12 relatively small) increase in temperature followed by a decay such that the overall
13 temperature profile over time approximates to a reverse sawtooth wave. In effect,
14 the sample is subjected to a thermal analysis experiment that is comparable to a
15 quasi-isothermal experiment that may be carried out using modulated
16 temperature DSC and further work could aim to correlate LFA with this technique.

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1 **Figure Captions**

2

3 Fig. 1a and b: A schematic diagram showing the location of the sample
4 thermocouple.

5

6 Fig. 1c: Variation of the sample temperature with time showing a near
7 instantaneous increase in temperature following the application of the laser
8 pulse followed by a subsequent decay over 200 seconds.

9

10 Fig. 2: The thermal response of PLA2002D at cooling rates ranging from 50 to
11 0.2 °C/min showing crystallisation occurring at rates less than 1 °C/min. The
12 reheat at 10 °C/min confirms that crystallisation in this grade of PLA can be
13 prevented.

14

15 Fig. 3: The glass transition in PLA as detected by the change in diffusivity (open
16 triangle symbols) and heat flow (continuous curves).

17

18 Fig. 4: The variation of diffusivity with time during an isothermal crystallization
19 (98.5°C). Primary and secondary crystallization processes are apparent
20 indicating that LFA is sufficiently sensitive to characterize secondary
21 crystallization.

22

23 Fig. 5: The variation of relative crystallinity (as defined by diffusivity
24 measurements) with time showing that the timescale of the crystallization
25 process increases with increasing crystallization temperature.

26

27 Fig. 6: Avrami plots of the data shown in fig. 5, mechanistic 'n' values of 2.0 ± 0.1
28 were obtained.

29

30 Fig. 7: The variation of crystallization half-time and rate constant with
31 temperature.

32

33 Fig. 8: A Hoffman-Lauritzen plot yielding a nucleation constant (K_g) of 6.58×10^{-5}
34 K^2 .

35

36 Fig. 9: The variation of secondary crystallization with root-time.

37

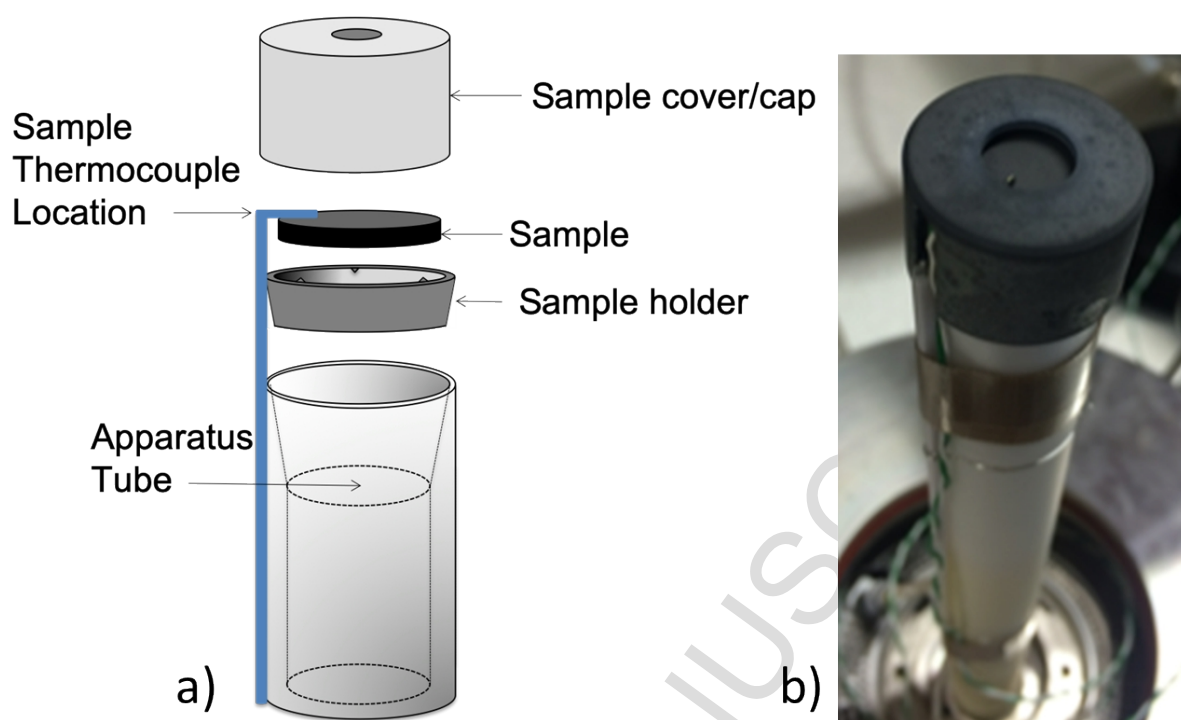


Figure 1a, b

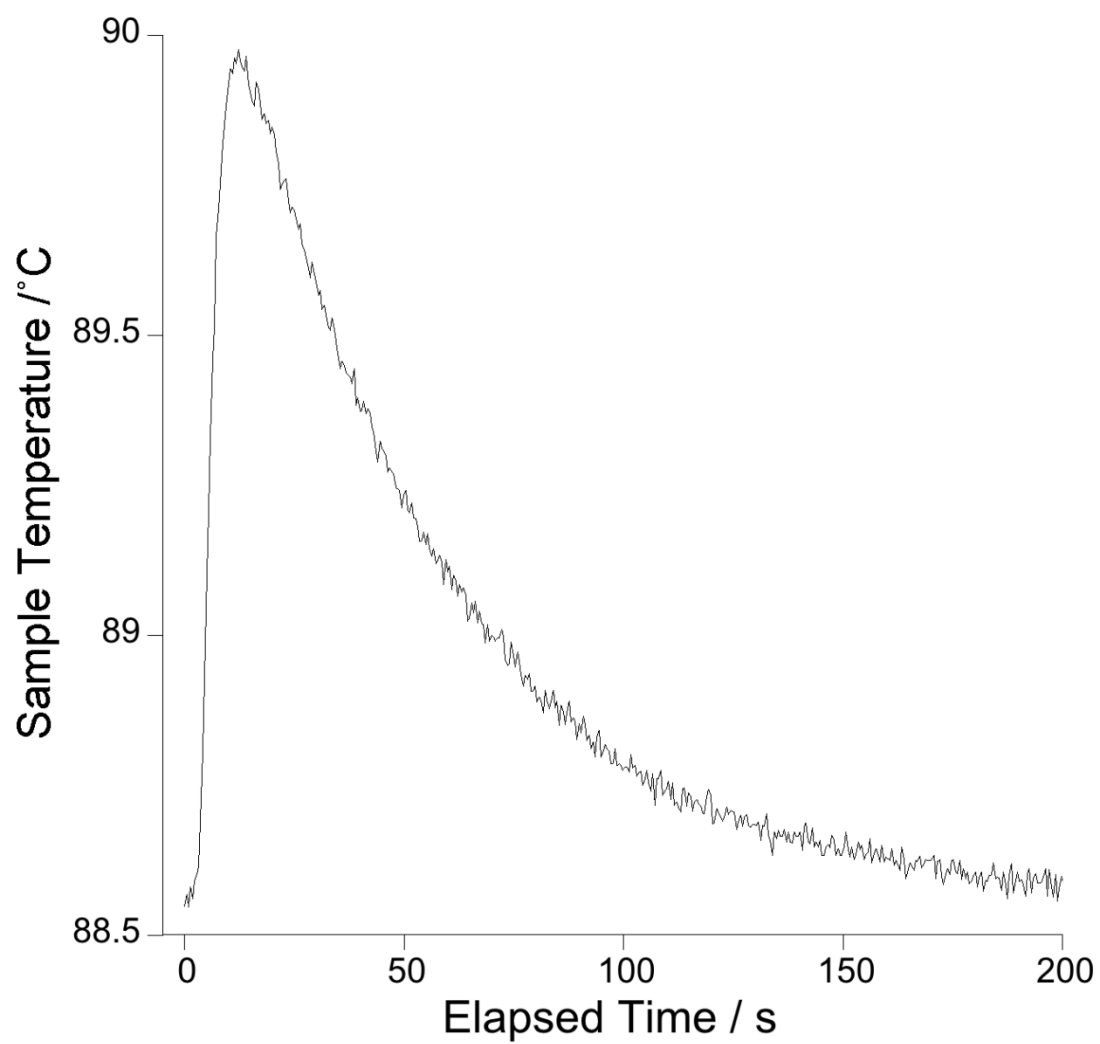


Figure 1c

ACCEPTED

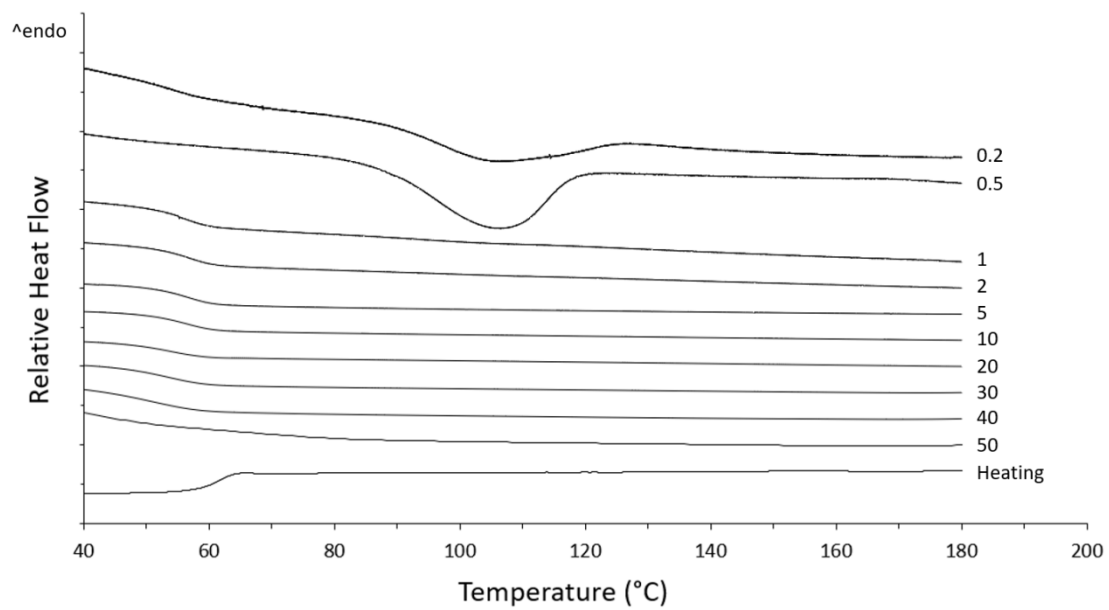


Figure 2

ACCEPTED MANUSCRIPT

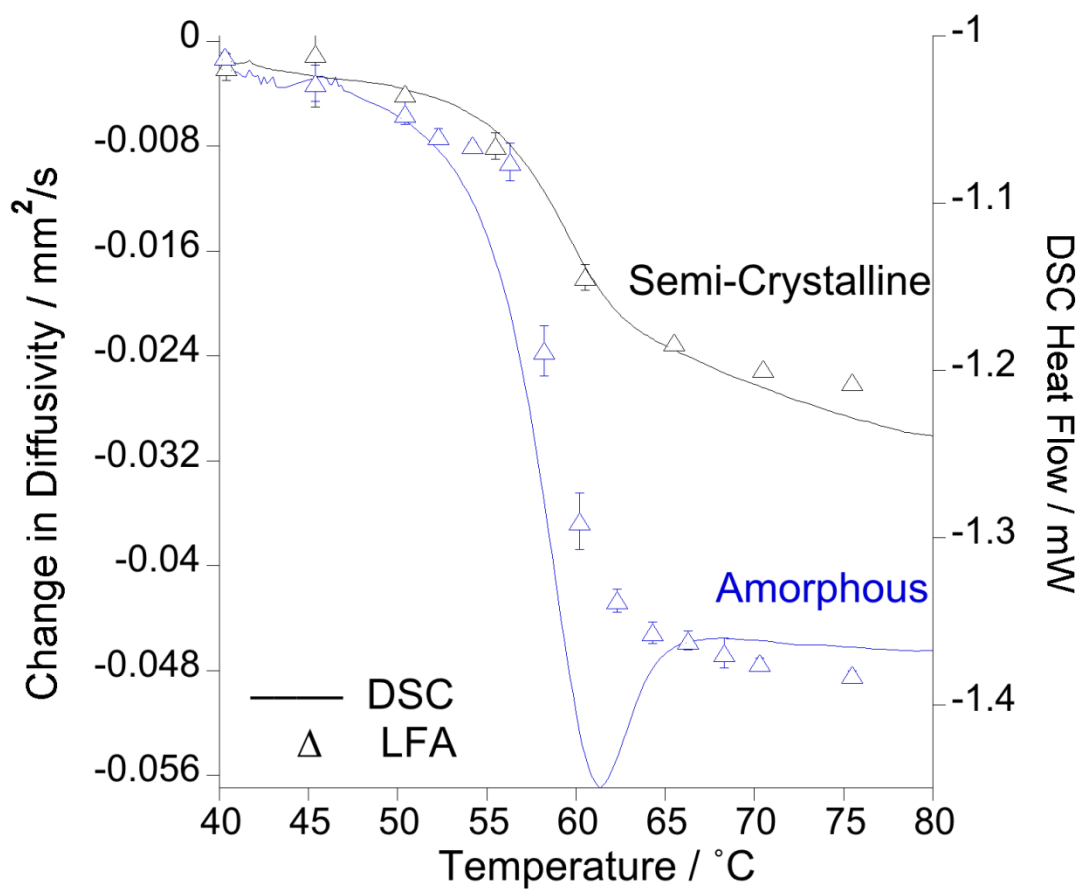


Figure 3

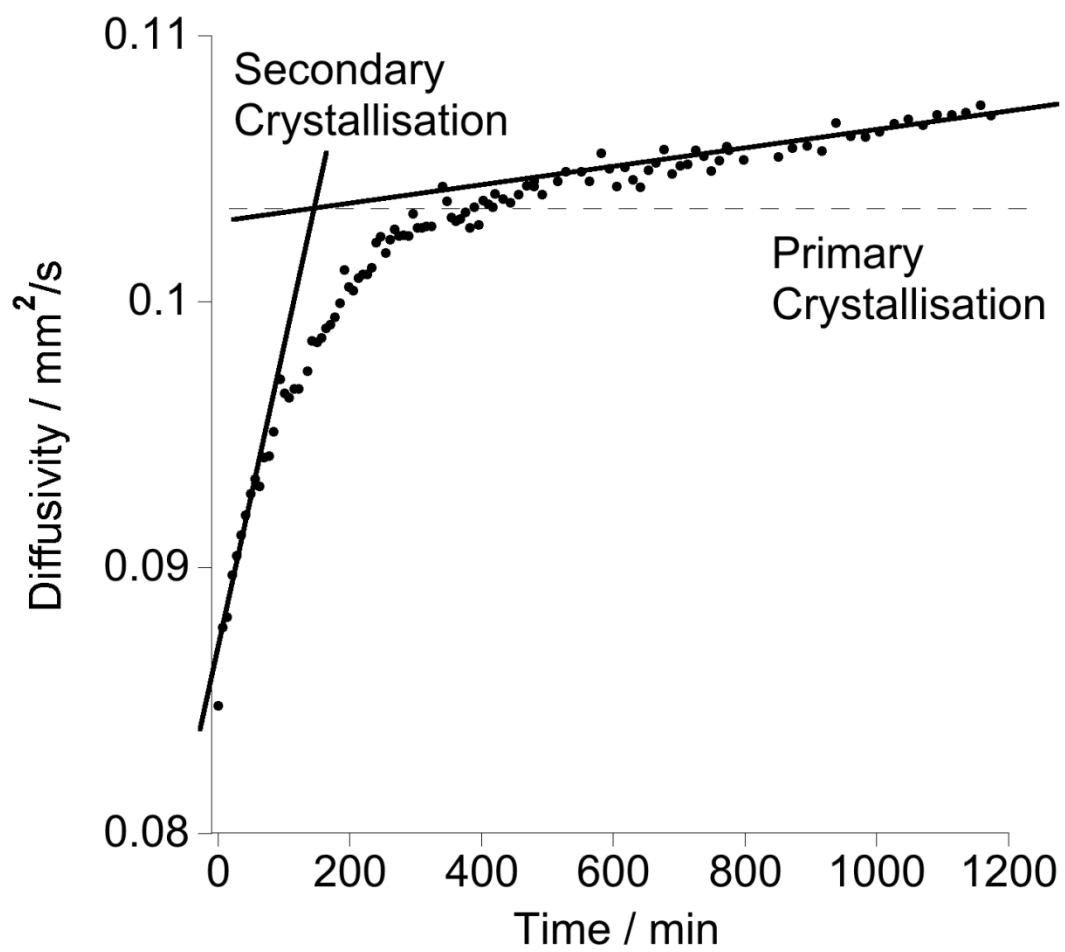


Figure 4

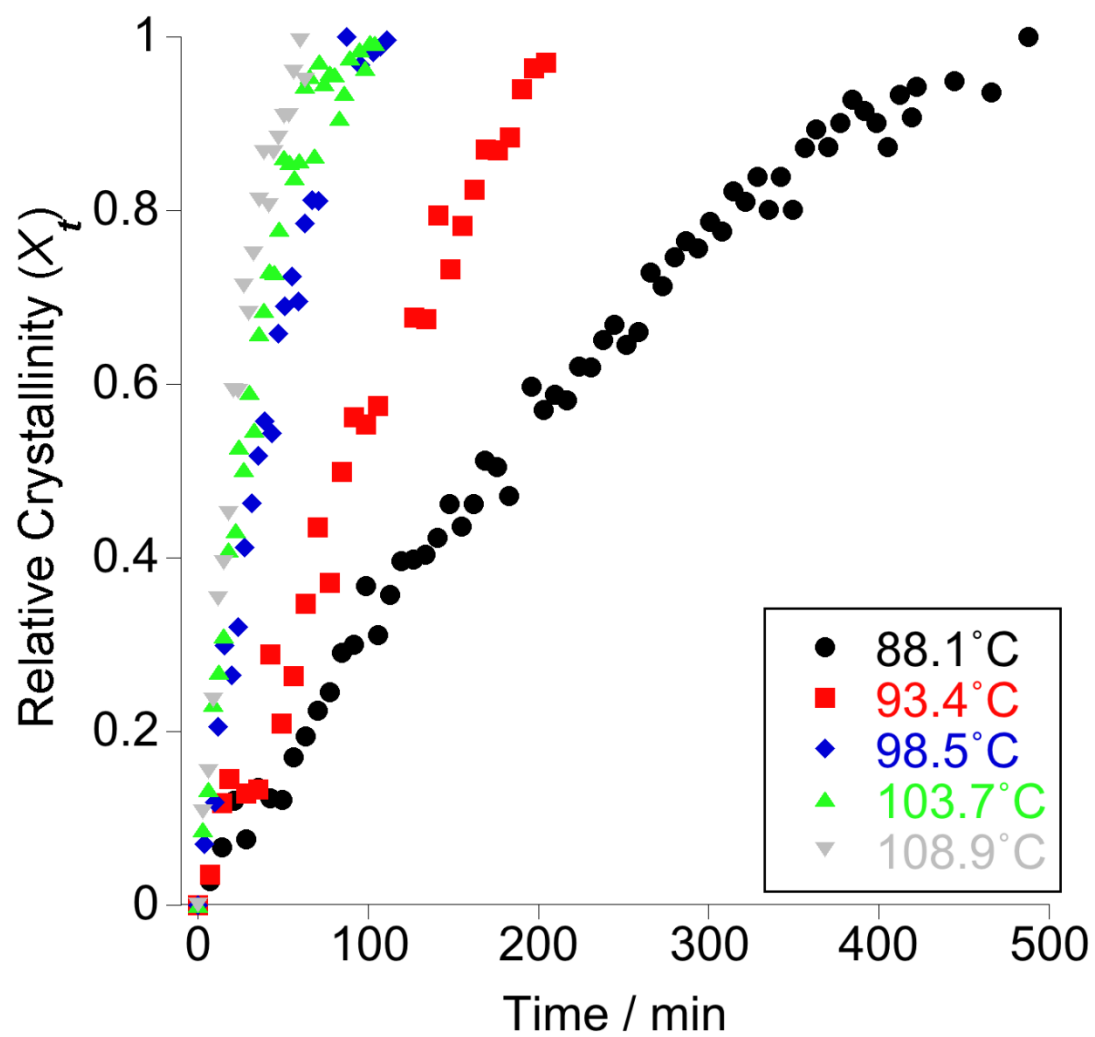


Figure 5

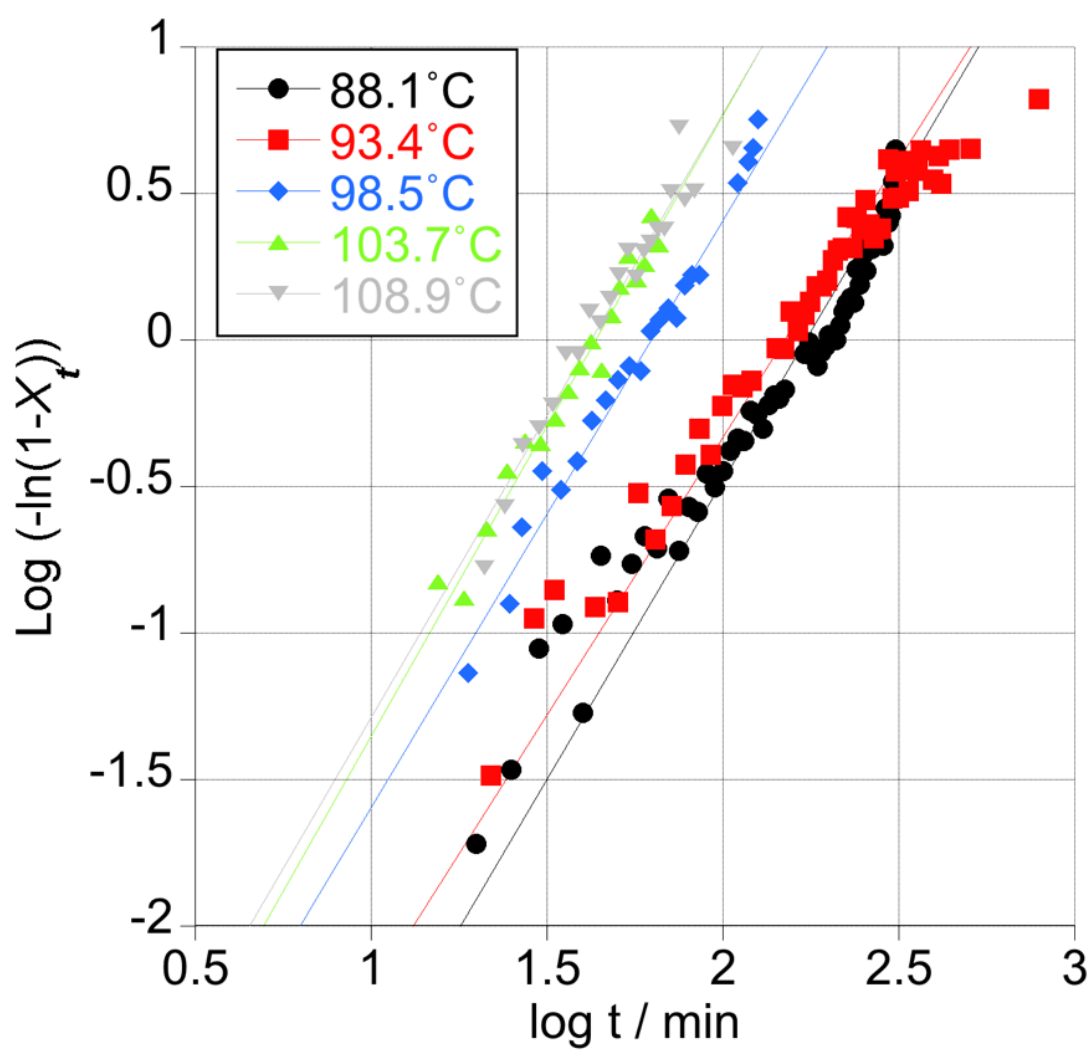


Figure 6

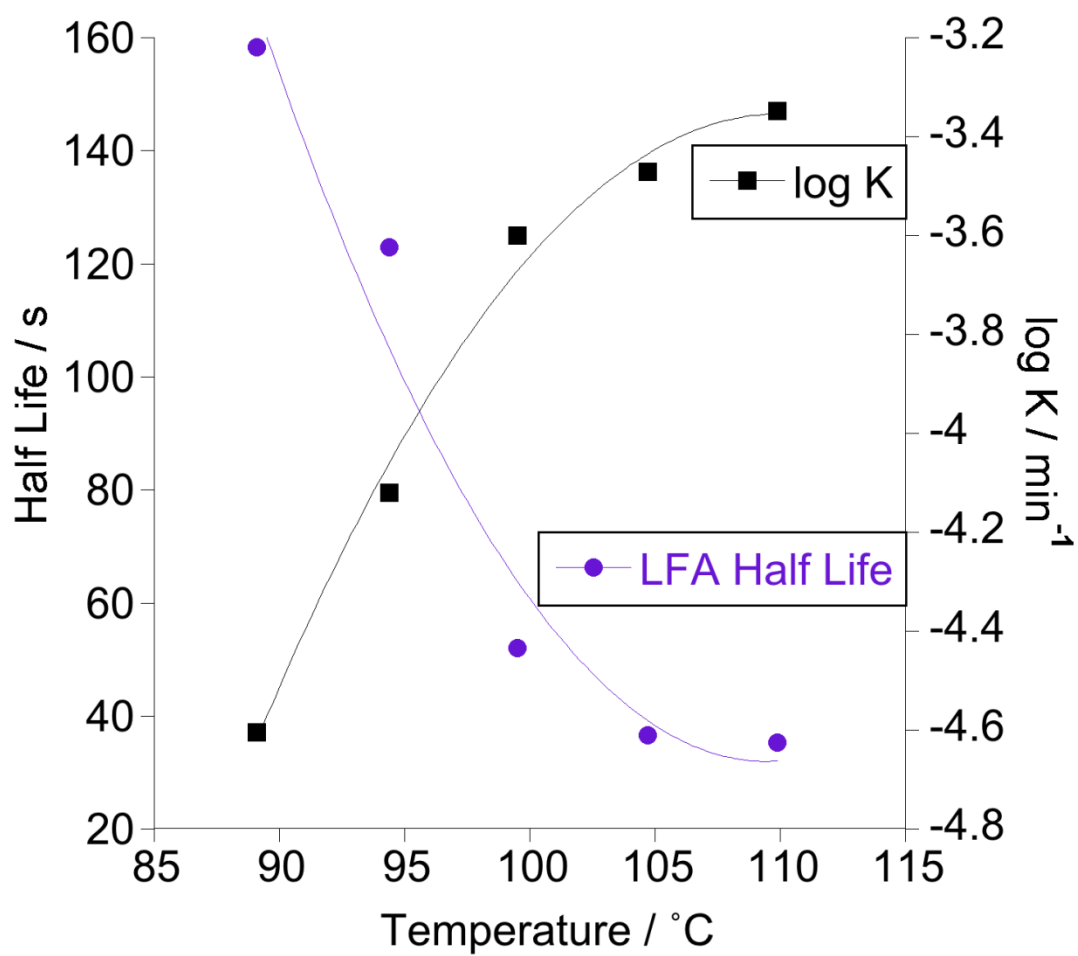


Figure 7

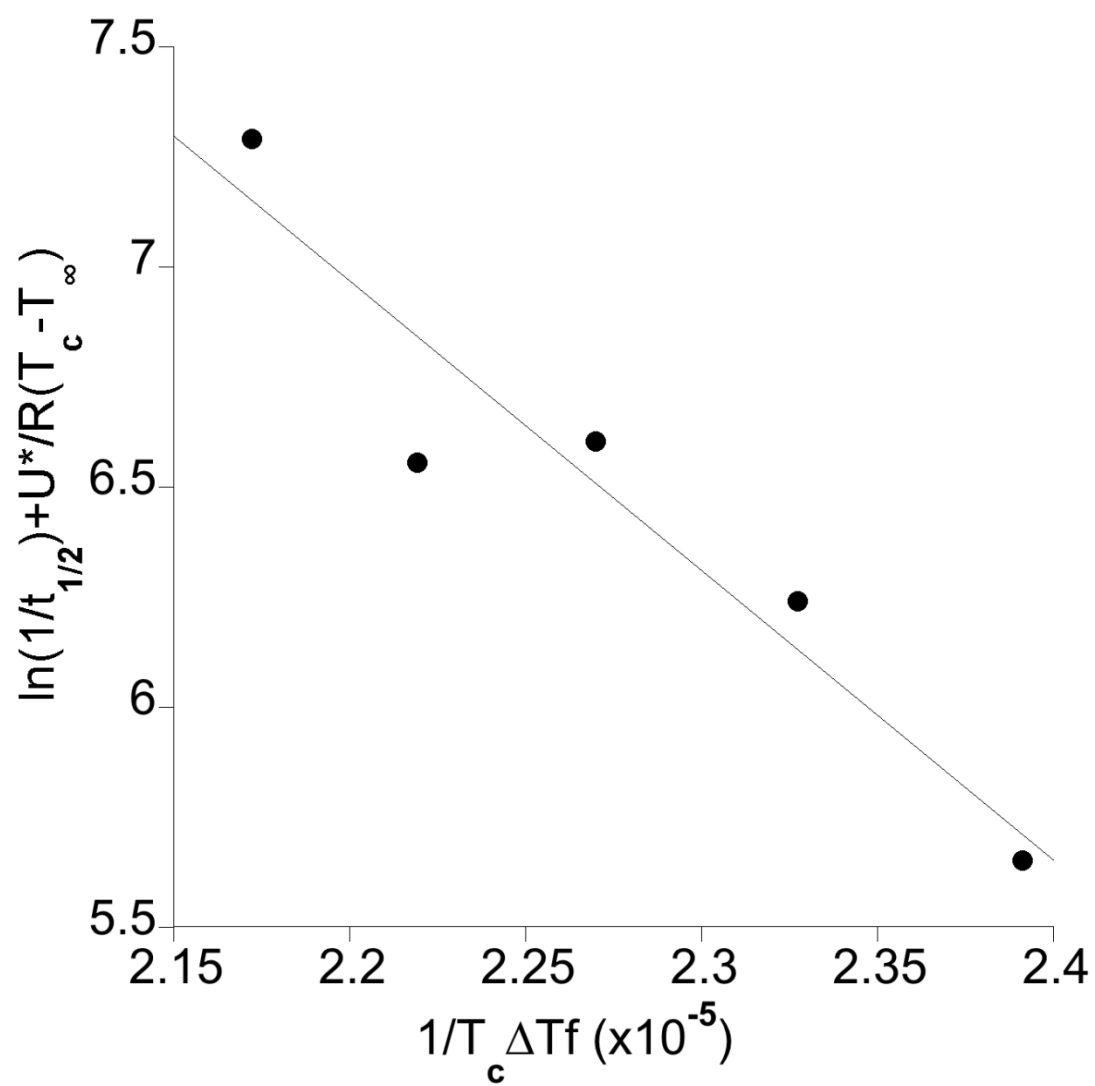


Figure 8

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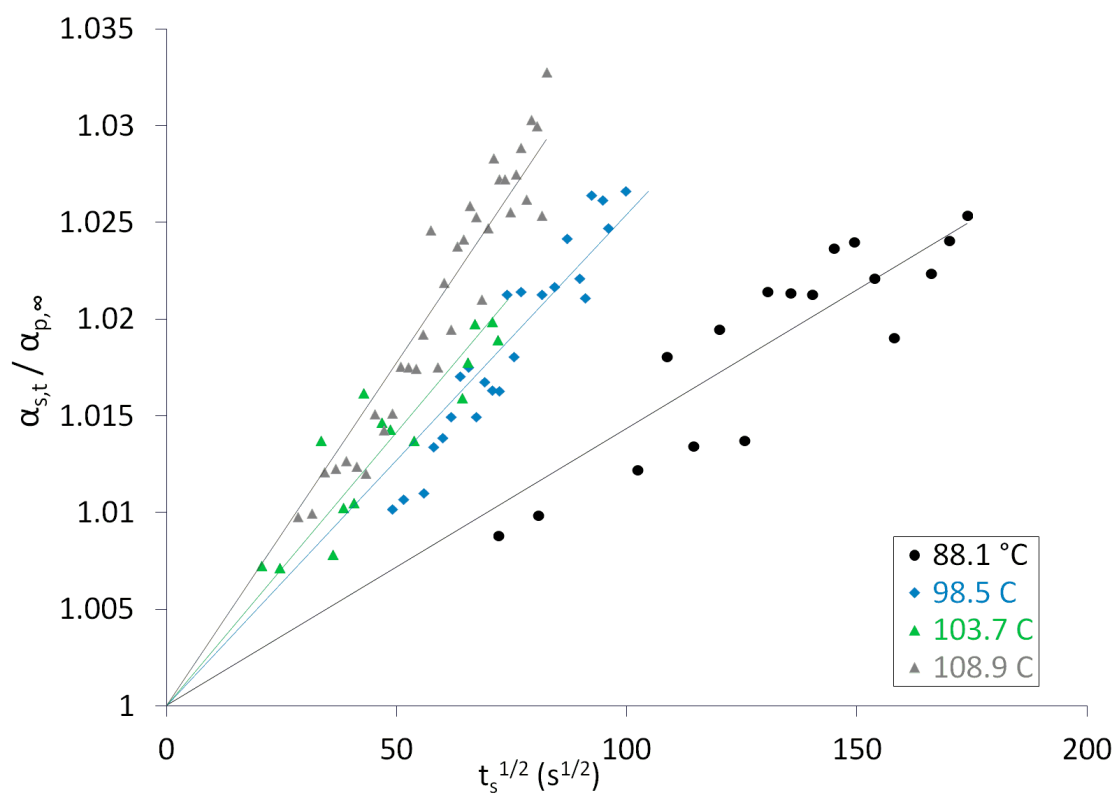


Figure 9



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3rd June 2019

Dear Editors,

We have re-submitted a research article manuscript entitled “Thermal diffusivity and secondary crystallisation in poly(lactic acid)”, for your consideration for publication as an article in **Polymer**.

The highlights of this work documented by the manuscript include:

- A characterisation of iso-thermal crystallisation in poly(lactic acid) using LFA
- By thermal diffusivity measurement, LFA is sensitive to secondary crystallisation
- LFA diffusivity datasets can be analysed using a modified Avrami model
- This model predicts activation energies comparable to those from FTIR datasets

On behalf of the authors,

Yours sincerely,

Dr Mike Jenkins & Dr Richard Turner

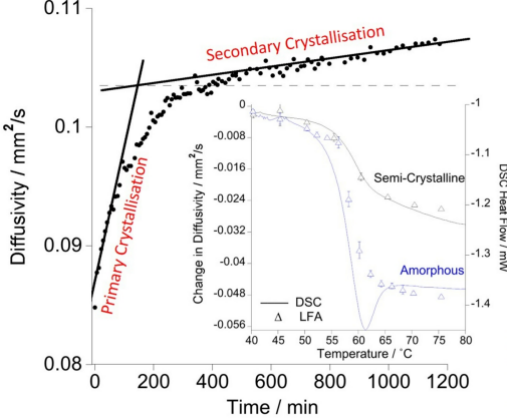


Table 1 – Mechanistic constants for the primary process obtained from the Avrami analysis

Temperature / °C	n	Log K / min ⁻¹	t _½ / min
88.1	2.0	-4.6038	158.28
93.4	1.9	-4.1193	123.01
98.5	2.0	-3.6000	52.08
103.7	2.1	-3.4705	36.60
108.9	2.1	-3.3480	35.34

Table 2: Modified Secondary Crystallisation equation and fitting parameters

Temperature (C)	Temperature (K)	k _s (s ^{-0.5})	ln (k _s)	R ² fit
88.1	361.25	0.000143	-8.85267	0.792
93.4	366.55	0.00016	-8.74034	0.418
98.5	371.65	0.000254	-8.27818	0.87
103.7	376.85	0.000283	-8.17006	0.774
108.9	382.05	0.000355	-7.94339	0.902