Crystallization Kinetics of Amorphous Lactose as a Function of Moisture Content Using Isothermal Differential Scanning Calorimetry

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ABSTRACT: Isothermal differential scanning calorimetry (DSC) was used to study the crystallization kinetics of amorphous lactose at 3 moisture contents. Each sample was heated to several temperatures between Tg and Tm. After subtraction of an induction time, the Avrami equation was used to model the data and a Lauritzen-Hoffman like expression used to fit the crystallization rates between Tg and Tm. The highest Tm/Tg ratio and crystallization rate were observed for the sample containing the most moisture. Conversely the lowest Tm/Tg ratio and crystallization rate were observed for the sample containing the least moisture. Evidence for multiple transitions was seen. The Avrami equation may not be the best way to model such data.

Key Words: DSC, lactose, crystallization, Avrami, Lauritzen-Hoffman

Introduction

THE STUDY OF SUGAR CRYSTALLIZATION IS IMPORTANT IN A variety of foods. In some dairy products, the degree of crystallinity of lactose may affect properties, such as texture, flavor, and general acceptability. For example, crystallization of lactose in milk powders results in lumping and caking of the powder and a reduction in reconstitution properties (Lai and Schmidt 1990). Crystallization of lactose is also considered undesirable in ice-cream and condensed milk as it results in a sandy texture that can be detected by the tongue (Martinez and others 1990; Nickerson and Patel 1972; Whitaker 1933). In milk chocolate containing high levels of crystalline lactose, flavors such as caramel, chocolate, and milk have been found to be significantly higher than for chocolate containing less crystalline lactose (Aguilar and others 1994).

There are several methods for studying the crystallization of amorphous sugars. Crystallization kinetics can be determined by humidifying samples and monitoring weight changes as the samples crystallize (Elamin and others 1995; Saleki-Gerhardt and Zografi 1994; Jouppila and Roos 1994; Lai and Schmidt 1990 and Iglesias and Chirife 1978). This method is used most successfully at ambient temperatures where crystallization occurs at a rate slow enough to be measured by sampling over days or weeks. X-ray powder diffraction and Cross Polarization Magic Angle Spinning (CPMAS) NMR have been used in our laboratory to study the crystallization kinetics of amorphous sugars. Again the crystallization rate had to be slow enough to obtain a reliable set of data points.

Using a method similar to that of Chan and Isayev (1994) in the study of polyethylene terephthalate (PET), isothermal DSC has been successful in the study of the crystallization of amorphous sugars at low moisture (below 5%) and high temperatures (365 to 460 K) where crystallization occurs over short periods of seconds to minutes (Kedward and others 1998). Isothermal DSC was used to study the crystallization kinetics of freeze-dried samples of lactose and sucrose (with moisture contents of about 3% and about 1%, respectively) at several temperatures between Tg and Tm. A Lauritzen-Hoffman like expression was used to fit derived rates of crystallization over the temperature range $Tg < T < Tm$. For both sugars the maximum rate of crystallization occurred at a temperature slightly higher than the midpoint of Tg and Tm. Crystallization rates were higher for lactose than sucrose. It was hypothesized that these differences in rates could be explained by simple changes in Tg and Tm that could be accounted for by differences in moisture content.

The objective of this study was to test this hypothesis by investigating the crystallization kinetics of lactose at various moisture contents.

Results and Discussion

Sample Characterization

The results from the moisture analysis (wet weight) of the freeze-dried lactose gave a mean of 1.24% and a standard deviation of 0.71%.

The results from the periodic weighing of the samples equilibrated over the saturated salt solutions are shown in Fig. 1. By this method the moisture contents (wet weight) were found to be 6.60%, 5.02%, and 4.44% for the samples stored at 20 °C over relative humidities of 33.1% ($MgCl_2$), 22.5% (CH_3COOK), and 11.3% (LiCl) respectively. These values are different from those of Jouppila and Roos 1994, being system-

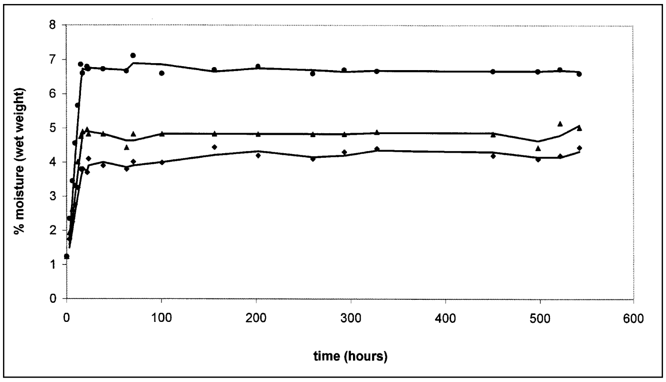

Fig. 1—The moisture content as a function of time for freeze-dried lactose equilibrated over saturated salt solutions of ◆ LiCl (RH = 11.3%), ▲ CH_3COOK (RH = 22.5%), and ● $MgCl_2$ (RH = 33.1%).

atically higher by between 1% to 2%. The reason for this is unclear but may be due to uncertainty in the initial moisture content. In any case, the objective was to obtain samples with different moisture contents rather than accurate equilibration.

The x-ray powder diffractograms of each humidified lactose sample showed no evidence of crystallinity. The diffraction patterns showed broad and diffuse maxima indicating a random arrangement of constituent molecules in contrast to the sharp and defined diffraction patterns found for crystalline materials.

The mean values of Tg and Tc for the humidified lactose samples, obtained from DSC, are shown in Table 1. Moisture contents were also calculated from the Tg values using the ten-Brinke modification of the Couchman-Karasz equation shown in Eq. 1 (ten-Brinke and others 1983).

$$T_g = (w_1\Delta C_{p1}T_{g1} + w_2\Delta C_{p2}T_{g2})/(w_1\Delta C_{p1} + w_2\Delta C_{p2}) \qquad (1)$$

w_1 is the weight fraction of the sugar and w_2 is the weight fraction of the water. ΔC_{p1} is the change in heat capacity at the glass transition of the pure sugar (0.52 J/g/K for lactose) and T_{g1} is the glass transition temperature of the pure sugar (374.4K for lactose) (Arvanitoyannis and Blanshard 1994). ΔC_{p2} is the change in heat capacity at the glass transition of pure water (1.94 J/g/K) and T_{g2} is the glass transition temperature of pure water (134K) (Sugisaki, Suga, and Seki 1968). The calculated moisture values were found to be in good agreement with the experimentally determined values (Table 1). This gave us some confidence that the moisture contents of the samples did not change appreciably during transportation to the DSC pans.

Table 1—Glass transition temperature (T_g) and crystallization temperature (T_c) values for freeze-dried lactose obtained by DSC at 10 K/min. Percentage (%) moisture determined experimentally[a] and calculated from the T_g value, using the ten-Brinke modification of the Couchman Karasz equation[b]

Sample	% Moisture content[a]	T_g (K)	T_c (K)	% Moisture content[b]
Lactose after humidification over LiCl (RH = 11.3%)	4.44	338	399	4.6
Lactose after humidification over CH_3COOK (RH = 22.5%)	5.02	335	390	5.1
Lactose after humidification over $MgCl_2$ (RH = 33.1%)	6.60	324	381	6.7

The crystallization peaks obtained by DSC of the humidified lactose samples are shown in Fig. 2. The width of the crystallization peak was found to depend on the moisture content of the sample. Sharper peaks were found for samples with greater moisture contents, probably due to higher rates of crystallization.

The melting temperature (Tm) was more difficult to obtain using DSC due to degradation occurring at high temperatures, but it appeared to be less sensitive to changes in moisture content. If the samples were scanned to high enough temperatures, often two melting peaks were observed: 1 at about 493 K and 1 at about 503 K, perhaps indicating the presence of both α-lactose and β-lactose crystals (Elamin and others 1995).

Isothermal DSC data

The same experimental difficulties were found in this work as were found in our previous paper (Kedward and others 1998). A fresh sample was required for each run due to the degradation of lactose at high temperatures. This affected the reproducibility of results because of non-ideal thermal contact between the powdered sample and the pan, which varied from sample to sample. Each point on Fig. 6 is the average of two loadings. The duplicates were reproducible and the points on this figure are the results of completely independent experiments.

When analyzing the isothermal DSC results, it was necessary to consider the transient response of the system. The final isothermal holding temperature required considerable time to reach equilibrium when it was ramped from the initial temperature at a maximum rate. This time period — response time or time lag — is different from the induction period of the sample. For the instrument we used, the time to reach equilibrium was typically around 30 s, depending on the difference between initial and final temperatures. At high temperatures, crystallization occurred very quickly and the induction period could be so short that crystallization might have started before thermal equilibrium was reached, resulting in inaccuracy in the initial data points.

Typical isothermal traces of lactose are shown in Fig. 3. Average induction times for each lactose sample at some of the different temperatures studied are listed in Table 2. The induction time was taken to be the point at which the trace left the baseline. There was a large error associated with induction time for the low temperature traces as the crystallization peak was quite flat. Because of the time required to reach equilibrium, all values were corrected by rejecting the first few seconds of data. The corrected response period depended on the difference between the initial and final temperatures. The induction time is normally defined as the most probable time from the beginning of isothermal crystallization to the point at which a stable crystal nucleus starts to grow. The induction time was found to be longer at lower temperatures. At high temperatures the induction time could not be established experimentally due to the rapid crystallization rate.

Taking the end of the induction period as time zero, the peaks

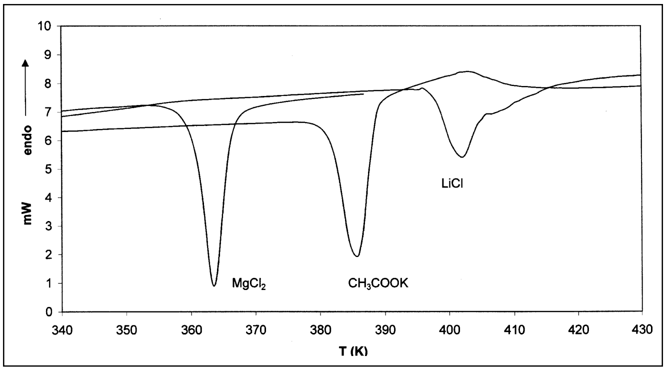

Fig. 2—Crystallization peaks, obtained by DSC at 10 K/min, for lactose samples after humidification over LiCl (RH = 11.3%), CH_3COOK (RH = 22.5%), and $MgCl_2$ (RH = 33.1%). The crystallization temperature (Tc) is taken as the temperature at the peak.

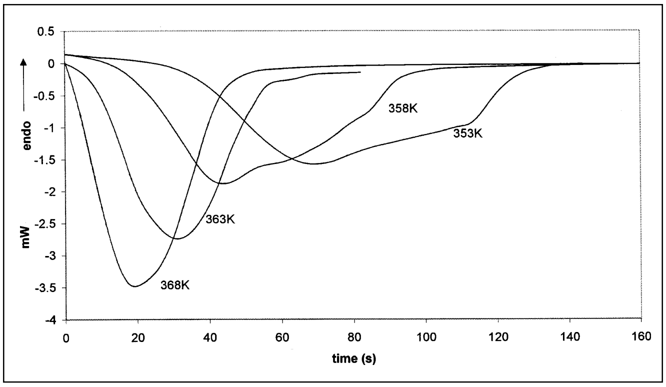

Fig. 3—Isothermal DSC traces for lactose (6.7% moisture).

Table 2—Induction times for lactose at 3 moisture contents (4.6%, 5.1%, and 6.7% wet weight).

T (K)	Time (s)		
	4.6%	5.1%	6.7%
353	–	–	18
363	–	56	3
368	–	17	–
373	–	12	–
378	–	5	–
388	7	–	–
393	6	–	–

were integrated with respect to time. The degree of crystallinity ($\Theta(t)$) was plotted against time for each peak (for example Fig. 4). $\Theta(t) = 0$ was the end of the induction time and $\Theta(t) = 1$ was the end of the exotherm, when the trace had returned to the baseline and crystallization was complete. The results were then analyzed using the Avrami equation (Eq. 2) (Avrami 1939).

$$\Theta(t) = X(t)/X_\propto = 1 - \exp(-kt^n) \qquad (2)$$

where $\Theta(t)$ is the relative crystallinity at time t, X(t) is the absolute crystallinity at time t, $X_\propto$ is the ultimate absolute crystallinity, k is the isothermal crystallization rate constant containing the nucleation and growth rates and n is the Avrami index. Time t was taken to be the time of the experiment minus the induction time. Rearrangement of Eq. 2 gives:

$$\log_{10}k + n\log_{10}t = \log_{10}[-\ln(1 - \Theta(t))] \qquad (3)$$

$\log_{10}[-\ln(1-\Theta(t))]$ was plotted against $\log_{10}t$ for each curve and k and n values extracted from the linear portion relating to relative crystallinity values between 30 and 70% (see Fig. 5).

Reciprocal crystallization half-time values were calculated using the equation

$$k = \ln 2/(t_{1/2})^n \qquad (4)$$

$1/t_{1/2}$ was then plotted against T (Fig. 6) where T was the isothermal holding temperature. A Lauritzen-Hoffman (1973) like expression was used to describe the overall rate of crystallization as a function of temperature:

$$(1/t_{1/2}) = (1/t_{1/2})_o\exp(-U^*/R(T - T_\propto)\exp(-K/T.\Delta T.f) \qquad (5)$$

where T is the crystallization temperature, R is the universal gas constant, $\Delta T = Tm^o - T$ is the supercooling, $f = 2T/(T + Tm^\circ)$ is a correction factor accounting for the reduction in the latent heat of fusion as the temperature is decreased and Tm^o is the equilibrium melting point. $(1/t_{1/2})_o$ is a pre-exponential factor that includes all terms independent of temperature, U* is the activation energy for the transport of crystallizing units across the phase boundary, $T_\propto$ is the temperature below which such transport ceases, and K is a nucleation term. In the Lauritzen-Hoffman equation $T_\propto$ is usually taken to be Tg - 30K. The characteristic bell shaped curve for crystallization rate as a function of temperature is the result of the interplay between the rate of nucleation and the rate of crystal growth. At high levels of supercooling, close to the glass transition temperature, the rate of nucleation is high but the rate of diffusion is low. At low levels of supercooling, close to the melting temperature, the rate of diffusion is high but the rate of nucleation is low. A curve having a maximum in the crystallization rate is produced when these 2 effects are combined.

A Lauritzen-Hoffman like fit to each data set was obtained using a nonlinear least squares fitting routine (Fig. 6). The unknown parameters U*, K, and $(1/t_{1/2})_o$ were fixed to values of 5000 J/mol., 80000 K^2 and 220 s^{-1} respectively for each data set. These are values which have previously resulted in good fits to crystallization data of this kind (Kedward and others 1998). Only the upward side of the bell-shaped curve was observed experimentally, as it was impossible to reach high temperatures without severe distortions on the thermograms and grossly incorrect analysis. In polymer studies, the downward side of the Lauritzen Hoffman curve is measured by crystallization from the melt. This is not possible for most food materials where degradation at high temperatures is the norm.

The Tg and Tm values were optimized by computer to provide the best fit. The Tg and Tm values in each case are shown in Table 3. The Tg values are not identical to the values obtained using conventional DSC, but they follow the trend of the lower the moisture content, the higher the Tg value.

Roos (1993) reported that polymers and sugars with a high Tm/Tg ratio tend to crystallize rapidly. The results from this work are in agreement with this observation as the lactose sample with the highest moisture content has the highest Tm/Tg ratio (Table 3) and has the highest maximum crystallization rate. Conversely, the lowest moisture sample has the lowest Tm/Tg ratio and has the lowest maximum crystallization rate.

The fit for the data obtained from the lactose sample containing the lowest amount of moisture (4.6%) is not as good as for the other data sets. This is believed to be due to significant crystallization into different lactose polymorphs and is more noticeable at lower moisture contents. On the scanning DSC thermograms, (Fig. 2), the pronounced shoulder on the crystallization peak of the lowest moisture lactose sample (after storage over LiCl), is

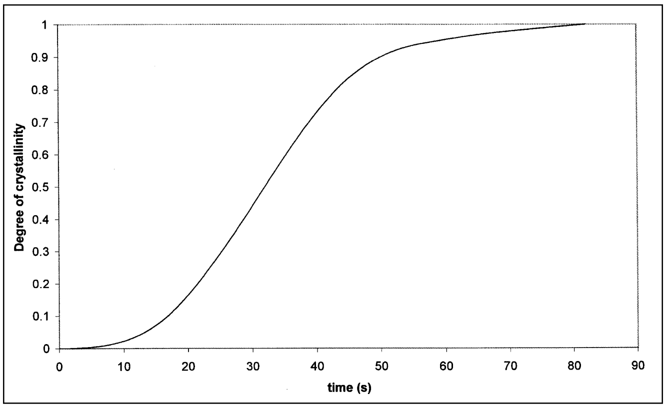

Fig. 4—Integrated isothermal DSC trace for lactose (6.7% moisture) at 363 K.

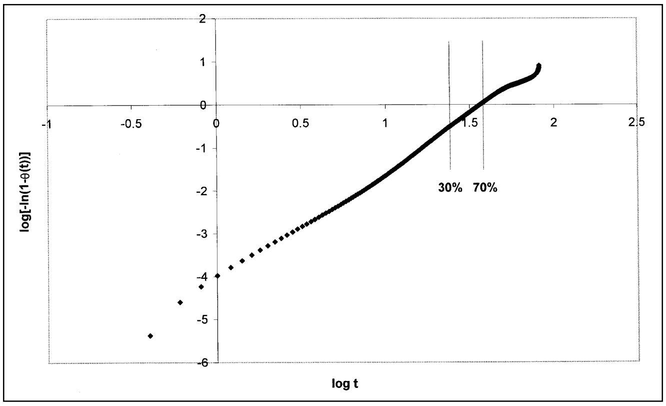

Fig. 5—An Avrami plot of the data in Fig. 4 showing the linearized portion of crystallization between 30% and 70%.

Table 3—The optimal glass transition temperature (Tg) and melting temperature (Tm) values obtained by computer for the Lauritzen-Hoffman-like fits to the crystallization rates for amorphous lactose. (Moisture content taken from Table 1). Also shown are the experimental Tg values

	Measured		Computer generated		
Sample	% Moisture	Tg (K)	Tg (K)	Tm (K)	Tm/Tg
Lactose after humidification over LiCl (RH = 11.3%)	4.44	338	344	492	1.43
Lactose after humidification over CH_3COOK (RH = 22.5%)	5.02	335	319	483	1.51
Lactose after humidification over $MgCl_2$ (RH = 33.1%)	6.60	324	305	485	1.59

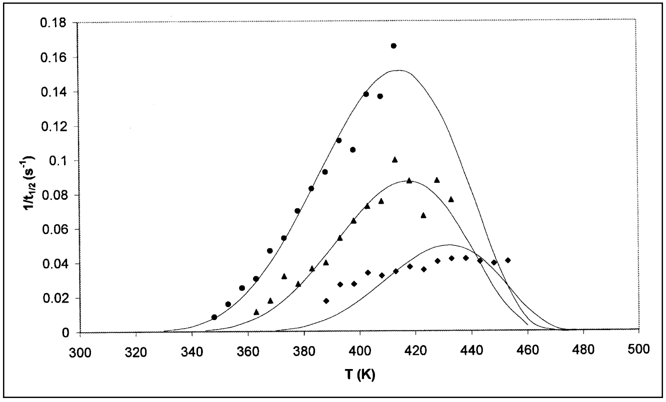

Fig. 6—$1/t_{1/2}$ in contrast to T and Lauritzen-Hoffman like fits for the crystallization of amorphous lactose at 3 moisture contents. ◆ moisture = 4.6%. ▲ moisture = 5.1%. ● moisture = 6.7%.

also likely to caused by crystallization into more than one crystalline form. The lactose may crystallize initially as α-lactose monohydrate until all the moisture is used up and then the remaining amorphous material may crystallize into an anhydrous crystalline form of lactose for example, β-lactose. No measurements were made to determine the crystal form. However, CPMAS experiments would address this problem. Multiple crystallization will inevitably lead to errors in the Avrami analysis and could explain deviations from the Lauritzen-Hoffman-like fit. A better fit to the low moisture data (Fig. 6) may be composed of several Lauritzen-Hoffman-like curves, each representing the crystallization of amorphous lactose to a different form. The different Tm values for each would lead to a shift of each Lauritzen-Hoffman curve and so flatten the bell shaped curve.

The shoulders observed on the isothermal peaks obtained from the higher moisture sample (Fig. 3) suggest that crystallization into multiple lactose forms also occurs at higher moisture contents. It has been pointed out (Roos and Karel 1990) that crystallization to a form containing a different water content from the amorphous material can lead to changes in the concentration of water in the remaining amorphous sugar. This will inevitably lead to differences in the rate of crystallization if diffusion is sufficient to redistribute the water. For this additional reason, the Avrami analysis can only be regarded as approximate.

We intend to investigate these transitions by using CPMAS (cross polarization magic angle spinning) NMR. This will be done both after crystallization has taken place (final forms) and also during crystallization (transitions between forms). The identification of lactose crystalline forms using this method is well established (Earl and Parrish 1983). Previous work in our laboratory has shown evidence of transitions between forms of lactose crystallizing from a biopolymer lactose mixture at room temperature and high moisture contents (MacNaughtan 1995).

One other important point concerns the apparent inconsistency between the Tc values (380–400K) obtained from the conventional DSC traces (Table 1) and the estimated maxima (410 to 430 K) for the isothermal data (Fig. 6). This arises because the scanning rate used in the conventional DSC is comparatively slow (10 K/min) compared with the time for crystallization observed isothermally (1 to 2 min, Fig. 3). This means that the crystallization event is essentially over at a comparatively low temperature in the scanning experiment before it reaches a temperature region that has a higher true rate. We will discuss the marrying of isothermal and non-isothermal data in a further publication.

Conclusion

THIS INVESTIGATION FURTHER SUGGESTS THAT THE DIFFERENCES in the maximum crystallization rate of freeze-dried amorphous sugars can be explained by changes in Tg and Tm which in turn are explained by differences in moisture content. The Avrami analysis may not be the most appropriate analysis when there is evidence of multiple crystalline transitions.

Materials and Methods

Freeze-drying of lactose

Amorphous lactose was obtained by freeze-drying. A 10% aqueous solution of lactose (Sigma-Aldrich, Poole, Dorset, U.K.) was prepared and poured into aluminium trays producing a thin layer of material (at most, a few millimeters thick). Each tray was floated in liquid nitrogen until the solution was frozen and the trays were immediately transferred to an Edwards Super Modulyo freeze-dryer (Edwards High Vacuum, Crawley, Sussex, U.K.). Typically the condenser temperature was −55 °C and the pressure which could be achieved by the pump was 3Pa (3×10^{-2} mB). The dried sample was stored over P_2O_5 (Merck, Poole, Dorset, U.K.) at room temperature in an evacuated desiccator for at least 2 weeks before characterization.

Moisture analysis

Using a dry-box, four samples (0.5 g) of amorphous lactose were transferred to 5-mL vials and left in 2 mL of formamide (Fisher, Loughborough, Leicestershire, U.K.) for 2 d to extract any water present. Each sample was analyzed for moisture content using a Mitsubishi CA-05 Moisture Meter (Anachem, Luton, Bedfordshire, U.K.) and a formamide blank.

Humidification of amorphous lactose

Portions of the freeze-dried lactose were transferred, as quickly as possible to avoid moisture sorption, from the evacuated desiccator to 20-mL open vials to produce a thin layer of material in each vial. The vials were then weighed and placed in desiccators containing saturated salt solutions of lithium chloride (LiCl), potassium acetate (CH_3COOK) or magnesium chloride ($MgCl_2$) (Merck, Poole, Dorset, U.K.) and held at room temperature. Each vial was re-weighed at set times (see Fig. 1) on a 4-figure balance and the readings converted to percentage moisture content (wet weight). All vials were closed with lids during weighing to avoid uncontrolled evaporation or adsorption of water.

Sugar crystallinity by x-ray powder diffraction

After equilibration with the salt solutions, the lactose samples were checked for zero crystallinity using x-ray powder diffraction. Each sample was ground to a fine powder, as quickly as possible to avoid water sorption, and loaded into the sample holder. The surface was smoothed with a glass slide and then scanned from 4 to 78° (2Θ) using a Philips APD15 X-ray system. A BBC microcomputer was used to process data.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC-7 (Perkin-Elmer, Beaconsfield, Buckinghamshire, U.K.) equipped with an intracooler was used for all measurements with a sealed empty pan as the reference and nitrogen as a flushing gas over the head. The instrument was calibrated with indium and cyclohexane. The intracooler was switched on for several hours before the first measurement, normally a baseline run, was made. This baseline, which was found to be very stable, was subtracted during each subsequent scan. For each measurement, 3 to 5 mg of amorphous lactose was weighed into an aluminum pan (20 μL) as quickly as possible to avoid water sorption and the pan was hermetically sealed.

Determination of glass transition temperature (Tg) and crystallization temperature (Tc) using DSC

Each sample was heated over the desired temperature range at 10 K/min. Measurements were made in triplicate. Results were analyzed using the Perkin-Elmer Pyris software (Perkin-Elmer, Beaconsfield, Buckinghamshire, U.K.). The Tg value was taken to be the midpoint temperature and the Tc value was taken to be the peak temperature.

Isothermal DSC measurements

Each sample was held at an initial temperature of 293 K for 1 min. The sample was then ramped up at a rate of 320 K/min to the final isothermal holding temperature where it was held for 20 min, during which time crystallization was observed. A baseline was recorded immediately after each measurement (using the same two pans as during the measurement) and subtracted from each isothermal trace. A range of final isothermal holding temperatures between Tg and Tm (estimated using conventional DSC at 10 K/min) was used. Duplicate measurements were made at each chosen temperature. The Perkin Elmer DSC maintained the sample holders at the specified temperature during the ramping operation, however the sample was not necessarily at this temperature due to temperature lags throughout the system. The degree to which the sample was in equilibrium could only be estimated by the subsequent trace. In practice we recorded up to temperatures where the main crystallization event was just affected by temperature equilibration distortions on the trace.

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