Crystallization Kinetics of Lactose and Sucrose Based On Isothermal Differential Scanning Calorimetry

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ABSTRACT

Isothermal Differential Scanning Calorimetry (DSC) was used to study the crystallization kinetics of freeze-dried samples of lactose and sucrose at several temperatures between Tg and Tm. The sample was rapidly heated to the required temperature. 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 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. This could be explained by simple changes in Tg and Tm which could be accounted for by differences in moisture content.

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

INTRODUCTION

THE CRYSTALLIZATION OF SUGARS IS IMportant in the food industry as evidenced by the many processes where the degree of crystallinity of sugars is critical to acceptance of the final product. For example, crystallization of lactose in ice-cream, condensed milk and milk powders is considered undesirable, while in products such as milk chocolate lactose crystallization is desirable (Lai and Schmidt, 1990; Martinez et al, 1990; Nickerson and Patel, 1972; Nickerson, 1960; Whitaker, 1933). Likewise sucrose crystallization evidenced by graining in boiled sweets is considered to be a defect whereas the fine crystals present in fondant icing are desirable because they help enable the icing to retain its shape in confectionery products (Hartel and Shastry, 1991). The control of lactose and sucrose crystallization during processing is important for a wide variety of products and there is a need for a suitable method to determine the degree of crystallization which would occur under specific processing conditions.

There are various methods of studying the crystallization of amorphous sugars. Crystallization kinetics can be determined by humidifying samples and monitoring weight changes as the samples crystallize (Elamin et al., 1995; Saleki-Gerhardt and Zografi, 1994; Jouppila and Roos, 1994; Lai and Schmidt, 1990; 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 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.

There is much interest in the crystallization of amorphous sugars at low moisture (below 5%) and high temperatures (100 to 200°C). The rate constants are sufficiently high that crystallinity may go to completion during heating at e.g. 5°C/min in conventional non-isothermal scanning DSC. Isothermal DSC can be used to study crystallization when it occurs typically over short periods of seconds to minutes.

Isothermal DSC has been used extensively to study crystallization of polymers such as poly(ethylene terephthalate) (PET) (Chan and Isayev, 1994; Chan et al., 1995), poly(phenylene sulphide) (Auer et al., 1994) and copoly (ethylene terephthalate/imide)s (Park and Lee, 1995). The technique has been used less frequently in the study of low molecular weight compounds such as disaccharides (Elamin et al., 1995; Roos and Karel, 1990). We applied the approach reported for the study of the crystallization of PET (Chan and Isayev, 1994) for the study of the crystallization of lactose and sucrose.

Much isothermal DSC work with polymers includes the study of isotherms produced by 'melt-crystallization'. This involves heating the material to the molten state, to erase any previous thermal history, and then cooling rapidly to the chosen crystallization temperature where it is held for the desired time. However, in the study of sugars, subjecting the material to high temperatures results in thermal degradation. It is therefore necessary to study sugars based on the fact that cold-crystallization has been observed on heating the material. A sample of amorphous sugar, initially in the glassy state, is heated rapidly to the chosen crystallization temperature and held for the desired time period. It is important to start with completely amorphous samples as any residual crystals would affect crystallization kinetics. This can be achieved by freeze-drying and subsequently checking the amorphous nature of the samples by x-ray diffraction.

Our objective was to study the crystallization behavior of such freeze-dried lactose and sucrose samples using isothermal DSC and to describe the kinetics by standard published methods.

MATERIALS & METHODS

Preparation of amorphous sugars

Amorphous samples of sucrose and lactose were prepared by freeze-drying. Aqueous solutions (10%) of the sugars (Sigma-Aldrich, Poole, Dorset, UK) were prepared and each solution was divided into separate aluminum trays to produce a thin layer of material. Each tray was then placed in liquid nitrogen until the material was frozen and the trays were immediately transferred to an Edwards Super Modulyo freeze-dryer (Edwards High Vacuum, Crawley, Sussex, UK). Typically the temperature in the chamber was −55°C. The ultimate reduced pressure which could be achieved by the pump was 3×10^{-2} mB. The dried samples were stored over P_2O_5 (Merck, Poole, Dorset, UK) at room temperature in evacuated desiccators for at least 2 wk before characterization and for no longer than 6 mo.

Sugar crystallinity by x-ray powder diffraction

The prepared amorphous sugars 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 4–78° (2θ) using a Philips APD15 x-ray system and a BBC microcomputer to collect results. Nitrogen gas was flushed over the sample during all x-ray experiments to prevent water sorption.

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Moisture analysis

Samples (0.5g) of each amorphous sugar were transferred to 5 mL vials, as quickly as possible to avoid water sorption, and left in 2mL of formamide (Fisher, Loughborough, Leicestershire, UK) for 2 days to extract any water present. Each sample was analyzed for moisture content using a Mitsubishi CA-05 Moisture Meter (Anachem, Luton, Bedfordshire, UK) and a formamide blank. Experiments were performed in quadruplicate.

Glass transition temperature (Tg) by differential scanning calorimetry (DSC)

The Tg values of the amorphous samples were obtained using DSC. A Perkin-Elmer DSC-2 (Perkin-Elmer, Beaconsfield, Buckinghamshire, UK) equipped with an intracooler was used for all measurements with a sealed empty pan as the reference material, with N_2 as a flushing agent over the head. The instrument was calibrated with indium and cyclohexane. A baseline run was recorded after the intracooler had been switched on for several hours, before measurements were made. This baseline, which was found to be very stable, was subtracted during each run. Samples of 3-5 mg were weighed into standard aluminum pans as quickly as possible to avoid water sorption. The pans were sealed and each sample was heated over the desired temperature range at 10°C/min. Measurements were made in triplicate. Results were analyzed using the Perkin-Elmer TADS software (Perkin-Elmer, Beaconsfield, Buckinghamshire, UK).

Isothermal crystallization by differential scanning calorimetry (DSC)

A Perkin-Elmer DSC-2 equipped with an intracooler was used for isothermal measurements. All experiments were carried out with a sealed empty pan as the reference material and with N_2 as a flushing agent over the head. Amorphous samples (3-5 mg) were weighed into standard aluminum pans as quickly as possible to avoid water sorption and the pans were sealed. Each sample was held at an initial temperature (low enough to ensure no crystallization) for 1 min. The sample was then ramped up at a maximum rate (320°C/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) which was subtracted from each isothermal trace. A range of final isothermal holding temperatures between Tg and Tm was used. Duplicate or triplicate measurements were made at each chosen temperature.

RESULTS & DISCUSSION

Sample characterization

The x-ray powder diffractograms of both the freeze-dried lactose and sucrose samples showed no evidence of crystallinity. The diffraction patterns showed broad and diffuse maxima indicating the random arrangement of constituent molecules in contrast to the sharp and defined diffraction patterns found for crystalline materials. The moisture measurements, in quadruplicate gave results (wet weight) for lactose of a mean 3.20%, standard deviation 0.31%. The results for sucrose gave a mean 0.94%, standard deviation 0.13%. Tg measurements in triplicate, for lactose gave a mean of 330K, standard deviation 4K. Results for sucrose gave a mean of 337K, standard deviation 3K.

Experimental difficulties using isothermal DSC

As sugars degrade when subjected to high temperatures, it was necessary to use a fresh sample for each DSC run. This affected the reproducibility of results due to non-ideal thermal contact between the powdered sample and the pan, which varied from sample to sample. To improve reproducibility, Bright and Muzzy (1975) suggested adding a small amount of heat transfer fluid to the sample holder to reduce heat resistance. Chan and Isayev (1994) reported the suggestion of Janeschitz-Kriegl to deliberately increase the heat resistance by making three dents in the flat bottom of the pan (so that it is supported only at the three points) as a way of improving reproducibility although heat transfer would be impeded. We did not consider this necessary since duplicate runs showed acceptable reproducibility.

When analyzing 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
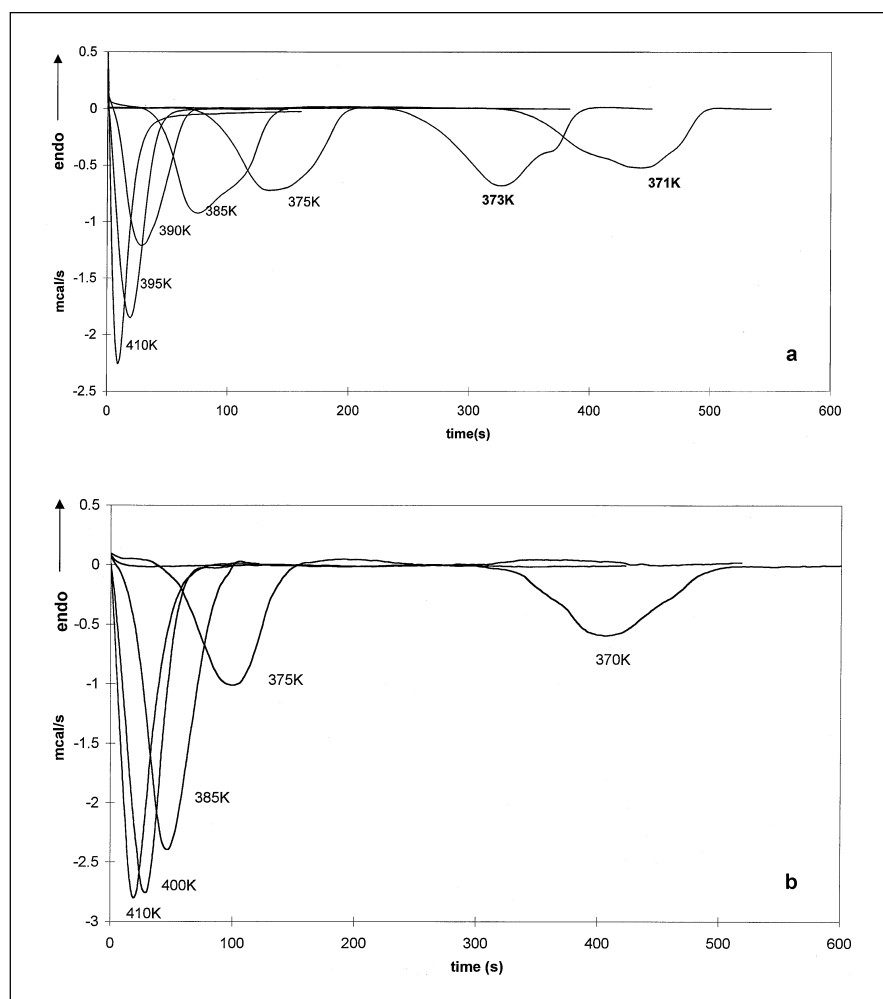

Fig. 1—(a) Isothermal DSC traces for lactose; (b) Isothermal DSC traces for sucrose.

time to reach equilibrium was typically around 30 sec — 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.

Interpretation of isothermal data

Typical isothermal traces of lactose and sucrose are shown (Fig. 1a, b). The induction times for each temperature studied are listed (Table 1). 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. Due to the time required to reach equi-

librium, 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

Table 1—Induction times for lactose and sucrose

Temp (K)	Induction times (s)	
	Lactose	Sucrose
365	—	410
370	—	280
371	384 ± 52	—
373	245 ± 8	—
375	71 ±15	44
380	13 ± 10	8
385	40 ± 18	—

point at which a stable crystal nucleus starts to grow. The induction time was found to be longer at lower temperatures (Table 1). At high temperatures, above 385K for lactose and 380K for sucrose, the induction time could not be established experimentally.

Taking the end of the induction period as time zero, the peaks were integrated with respect to time. The degree of crystallinity [$\theta(t)$] was plotted against time for each peak (Fig. 2a,b). $\theta(t) = 0$ 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 calculated heat of crystallization values showed no direct relationship to temperature. Using a reference temperature (371K for lactose and 390K for sucrose) all integrated curves were fitted to one 'master' curve (Chan et al., 1995). This involved multiplying the time axis of each original curve by a shift factor which placed the new curve onto the master curve. Shift factors were calculated by determining the value on the time axis at 10 different points on the $\theta(t)$ axis at intervals of $\theta(t) = 0.1$, for both a reference temperature curve and the curve of interest. The ratio of the time values at $\theta(t)$ was obtained (e.g. time at T when $\theta(t) = 0.5$/time at T_{ref} when $\theta(t) = 0.5$). An average of the 10 values was taken as the shift factor $a_T(T)$ (Table 2). The curves were fitted to the one master curve (Fig. 3a,b). The curves obtained at higher temperatures (above 400K for lactose and above 410K for sucrose) did not overlay the master curve. This was probably partly due to the missing data points because of short induction times.

The results were also analyzed using the Avrami equation (Avrami, 1939)

$$\theta(t) = X(t)/X_\infty = 1 - \exp(-kt^n) \quad (1)$$

where $\theta(t)$ is the relative crystallinity at time t, $X(t)$ is the absolute crystallinity at time t, X_∞ 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 equation (1) gives:

$$\log_{10}k + n\log_{10}t = \log_{10}\{-\ln[1 - \theta(t)]\} \quad (2)$$

$\log_{10}\{-\ln[1-\theta(t)]\}$ was plotted against $\log_{10}t$ for each curve (Fig. 4) and k and n values extracted from the linear portion relating to relative crystallinity values between 30 and 70% (Table 3). The Avrami index n, which has an effect on the shape of the integrated crystallinity curves such as those shown (Fig. 2a, b), was found to decrease with temperature. This could also account for the poor fit of the high temperature data to the master curve and may indicate a differ-
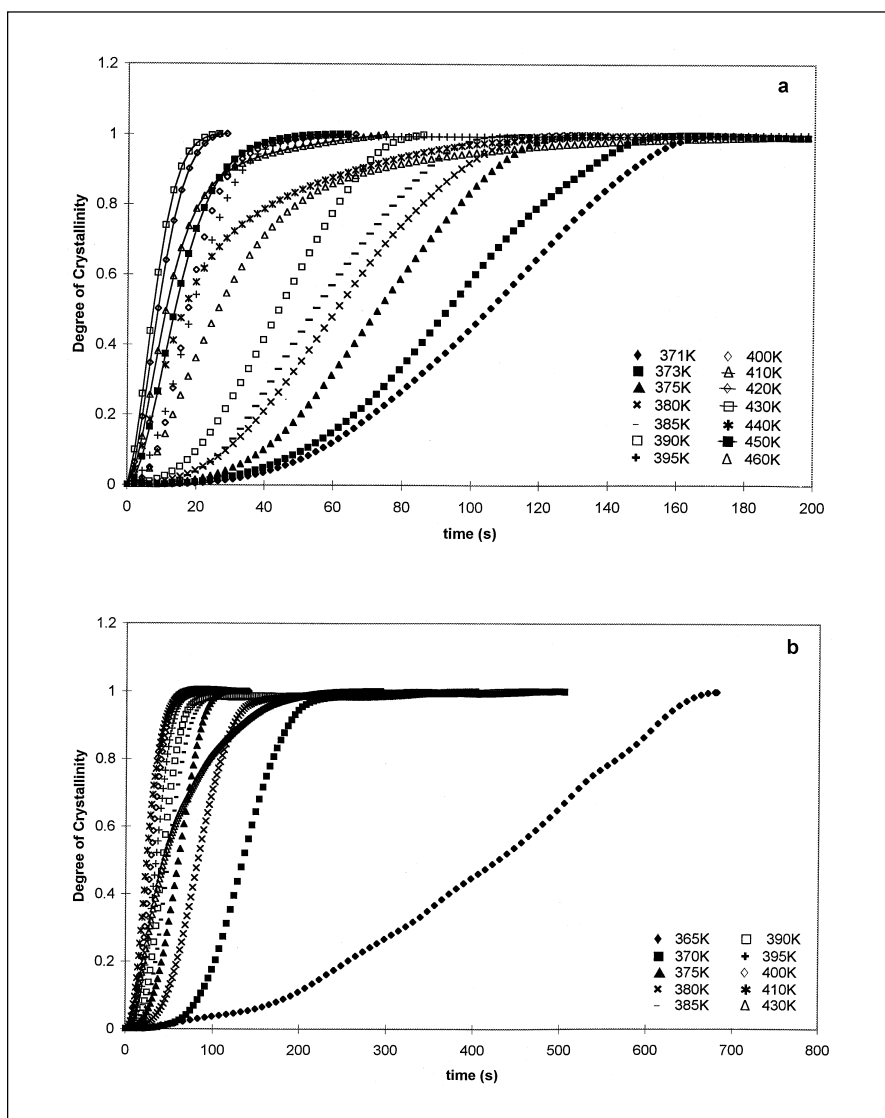

Fig. 2—(a) Integrated isothermal DSC traces for lactose; (b) Integrated isothermal DSC traces for sucrose.

ent crystallization mechanism at higher temperatures.

Reciprocal crystallization halftime values were calculated using the equation

$$k = \ln2/(t_{1/2})^n \qquad (3)$$

$1/t_{1/2}$ was then plotted against T (Fig. 5) where T was the isothermal holding temperature. The $1/t_{1/2}$ values are means of values calculated from the Avrami analysis of each individual replicate. The coefficient of variation for this method was 22%. A Lauritzen-Hoffman (1973) like expression was used to describe the overall rate of crystallization as a function of temperature:

$$(1/t_{1/2}) = (1/t_{1/2})_o\exp(-U^*/R(T - T_\infty)$$
$$\exp(-K/T \cdot \Delta T \cdot f) \qquad (4)$$

where T is the crystallization temperature, R is the universal gas constant, $\Delta T = Tm° - T$ is the supercooling, $f = 2T/(T + Tm°)$ is a correction factor accounting for the reduction in the latent heat of fusion as the temperature is decreased and $Tm°$ 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_∞ is the temperature below which such transport ceases, and K is a nucleation term. In the Lauritzen-Hoffman equation T_∞ is usually taken to be $Tg - 30K$.

In the original Lauritzen-Hoffman equation the nucleation term was directly related to surface energies of the folded polymer. This is inappropriate for small molecular materials. However, we hypothesized that a similar equation containing surface energy and heat of fusion terms would apply here although the exact relationship to K is unknown.

In Eq. (4) there are 4 unknowns: U^*, T_∞, K and $(1/t_{1/2})_o$ which cannot be found directly by substituting in observed $(1/t_{1/2})$ values. Using the method of Marsh and Blanshard (1988), the number of unknowns could be reduced by assuming values of some of the parameters and then varying the others to obtain the best correlation between experimentally observed $1/t_{1/2}$ values. This could be done by linear regression analysis. Equation (4) was rearranged in logarithmic form to give:

$$\ln(1/t_{1/2}) + U^*/R(T - T_\infty) =$$
$$\ln(1/t_{1/2})_o - K/(T \cdot \Delta T \cdot f) \qquad (5)$$

Plotting the left hand side of Eq. (5) with estimated values for U^* and T_∞ against $1/T \cdot \Delta T \cdot f$ should yield a straight line of slope $-K$ and intercept $\ln(1/t_{1/2})_o$. A series of values of U^* and T_∞ were substituted into Eq. (5) until the best fit to the experimental data was obtained. The values which gave the best correlation coefficient for lactose were $U^* = 5000$ J/mol and $T_\infty = 300K$, leading to values of $K = 81144$ K^2 and $(1/t_{1/2})_o = 221.40$ s^{-1} (using $Tg = 330K$ and $Tm = 495K$). The values which gave the best correlation coefficient for sucrose were $U^* = 4500$ J/mol and $T_\infty = 307K$, leading to values of $K = 79047$ K^2 and $(1/t_{1/2})_o = 371.07$ s^{-1} (using Tg
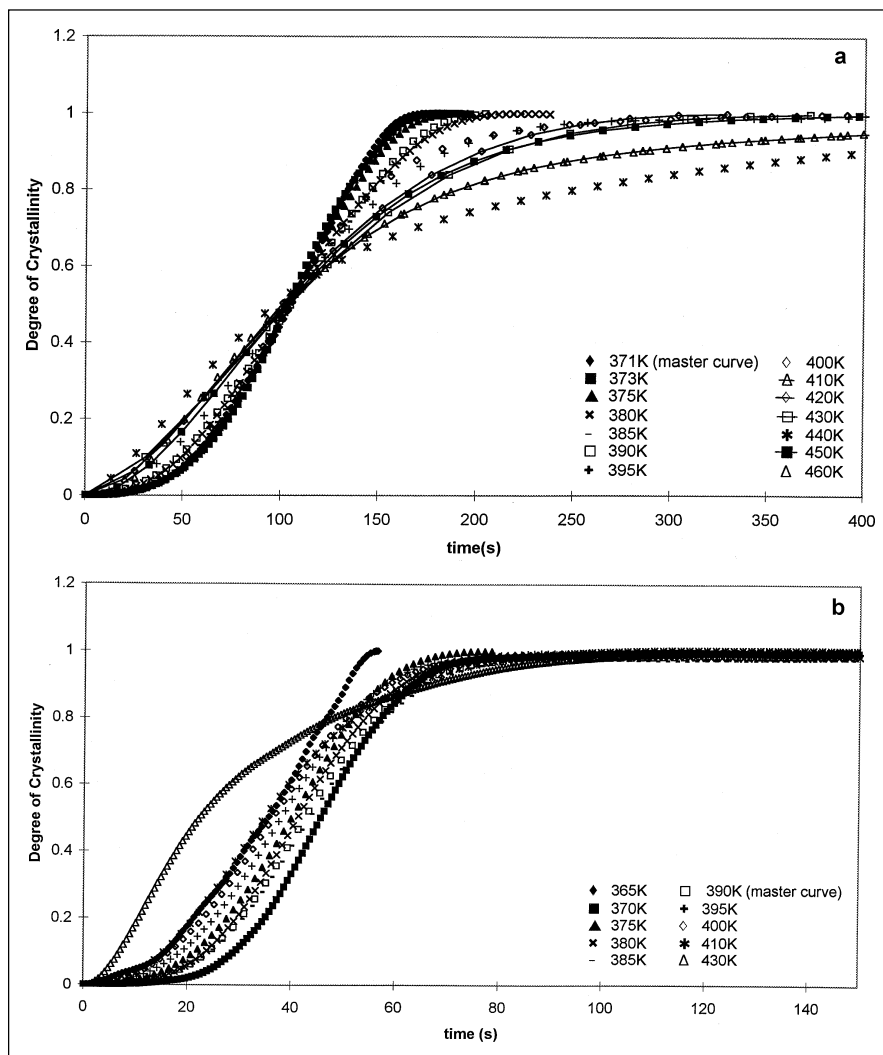
Table 2—Shift factors for lactose and sucrose

| | Shift factors | |
Temp (K)	Lactose	Sucrose
365	—	0.083
370	—	0.34
371	1	—
373	1.116	—
375	1.429	0.666
380	1.712	0.5
385	1.905	0.92
390	2.381	1
395	5.556	1.101
400	5.917	1.26
410	9.259	1.46
420	11.494	—
430	14.085	0.5065
440	5.952	—
450	7.519	—
460	3.861	—

Table 3—k and n values for lactose and sucrose

| | Lactose | | Sucrose | |
Temp (K)	logk	n	logk	n
365	—	—	−6.63	2.5
370	—	—	−8.68	4.0
371	−7.53	3.5	—	—
373	−6.73	3.4	—	—
375	−6.33	3.2	−5.73	3.1
380	−5.49	3.0	−6.42	3.3
385	−7.04	3.5	−5.36	3.1
390	−3.66	2.3	−5.44	3.2
395	−4.27	2.9	−4.53	2.8
400	−3.44	2.6	−3.92	2.6
410	−2.35	1.9	−3.24	2.2
420	−2.20	1.9	—	—
430	−1.69	1.6	−2.22	1.3
440	−1.52	0.9	—	—
450	−2.03	1.6	—	—
460	−1.93	1.2	—	—

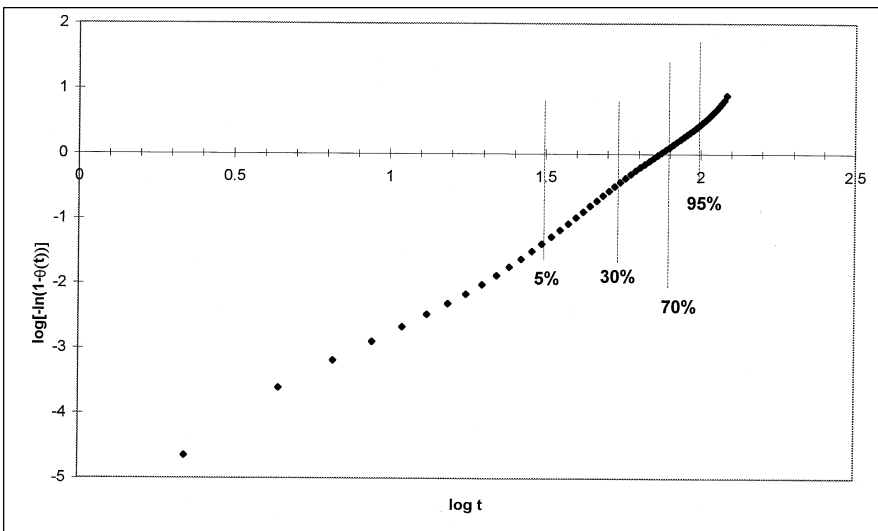Fig. 3—(a) Master Curve fitting for lactose; (b) Master Curve fitting for sucrose.

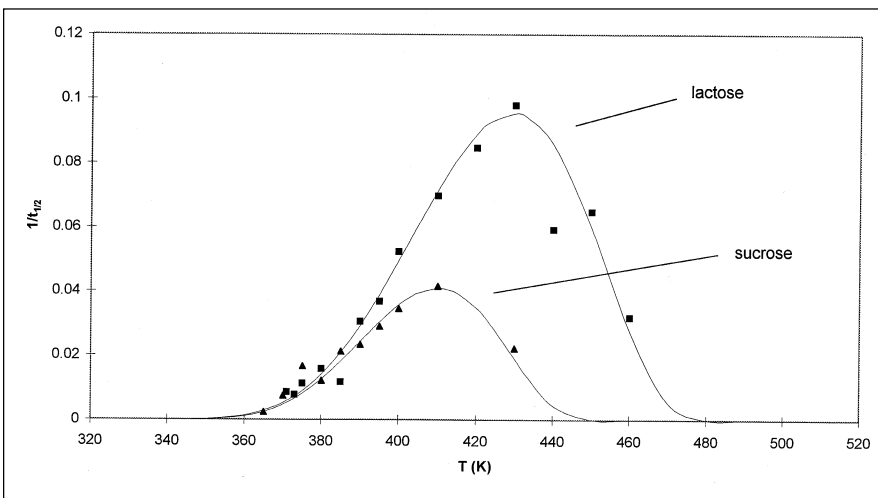**Fig. 4—Avrami plot for lactose.**

Fig. 5—Lauritzen-Hoffman fit for lactose and sucrose as a function of temperature.

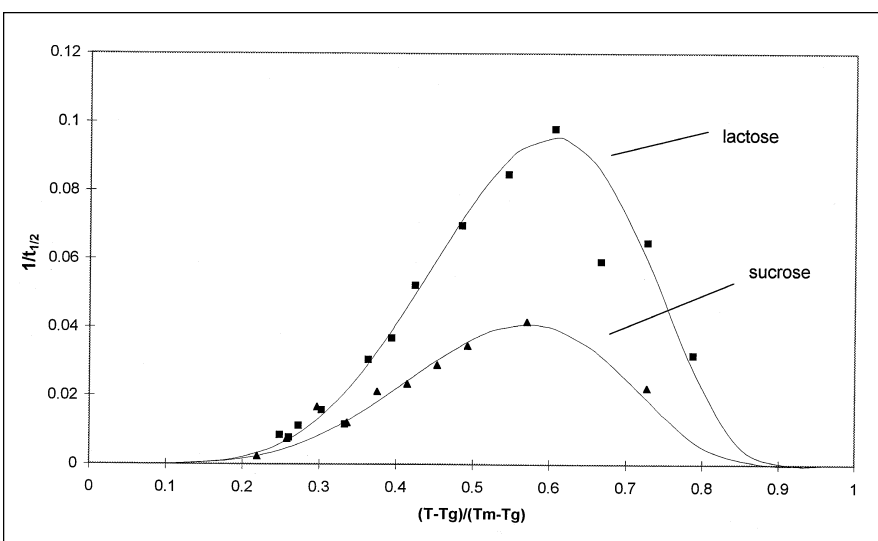**Fig. 6—Lauritzen-Hoffman fit for lactose and sucrose as a function of Tg and Tm.**

= 337K and Tm = 465K).

Alternatively a Lauritzen-Hoffman like fit to the data could be obtained directly using a nonlinear least squares fitting routine to optimize the unknown parameters. This was also carried out and the parameter values obtained were essentially identical with those obtained using linear regression.

Using DSC it was difficult to experimentally obtain melting temperatures for the lactose and sucrose samples as decomposition occurred at high temperatures. Published Tm values vary, presumably due to such difficulties. Elamin et al. (1995) reported that α-lactose monohydrate melted at 493K and that β-lactose melted at 503K. Saleki-Gerhardt and Zografi (1994) reported that α-lactose monohydrate melted at 486K. The crystalline material produced from the amorphous lactose sample in our study may be a mixture of crystalline forms including α-lactose monohydrate, β-lactose, anhydrous α-lactose and mixed crystals with α:β ratios of 5:3 and 4:1 which have been reported (Earl and Parrish, 1983). The double peaks observed in the isothermal traces at certain temperatures (Fig. 1a) may be due to transformations between the crystalline forms. CPMAS NMR spectroscopy could be used to identify the crystal type. The Tm value used for the Lauritzen-Hoffman type of fit was taken to be 495K, an intermediate value of those reported for α-lactose monohydrate and β-lactose. For dry samples of amorphous sucrose, Saleki-Gerhardt and Zografi (1994) reported a Tm of 461K whereas Elamin et al. (1995) reported a Tm of 465K. We used the value 465K for the fit although there is evidence this may be a few degrees lower due to the 1% moisture (Saleki-Gerhardt and Zografi, 1994). A small change in Tm chosen for the fitting procedure would not notably affect the parameters or the maximum crystallization rates obtained.

The Lauritzen-Hoffman plot describes the overall crystallization rate which depends on the relative rates of nucleation and growth. At low temperatures, close to Tg, nucleation is dominant and at high temperatures, close to Tm, growth is dominant. The optimum crystallization rate would occur somewhere between Tg and Tm.

A Lauritzen-Hoffman like fit was found for the lactose and sucrose data as a function of temperature (Fig. 5). If the moisture contents of the two samples were the same, the Tg for sucrose would be lower than that for lactose and the crystallization of sucrose would be expected to begin at a lower temperature than that of lactose. However, due to differences in moisture contents, the Tg of the two samples were found to be similar (330K for lactose and 337K for sucrose). At lower temperatures, close to Tg, both lactose and sucrose crystallized at the same rate but the maximum crystallization rate of sucrose

was lower and occurred at a lower temperature than for lactose.

The fitted data were replotted so that Tg and Tm for both samples were overlaid (Fig. 6). For both samples the maximum crystallization rate occurred just over half way between Tg and Tm. If the parameters U^*, T_∞, Kg and $(1/t_{1/2})_o$ for both lactose and sucrose were held at similar levels then the results (i.e. differences in maximum crystallization rate) could be explained by simple changes in Tg and Tm which in turn could be explained by differences in moisture content.

The profound effect of small amounts of moisture on the crystallization of amorphous sugars was observed in the work by Saleki-Gerhardt and Zografi (1994). Freeze-dried sucrose was subjected to humidities to produce a range of moisture contents up to 3.13%. Analysis by non-isothermal DSC showed that as moisture level increased, Tg, Tc (crystallization temperature) and Tm all decreased. The Tc values obtained experimentally agreed well with predicted values calculated from the midpoint of Tg and Tm. From their results and others (e.g. Roos and Karel, 1991) it is expected that small increases in moisture content would affect crystallization kinetics by lowering the temperature at which the maximum crystallization rate occurs. In addition, Roos reported (1993) that polymers and sugars with a high Tm/Tg ratio tend to crystallize rapidly. In our results the lactose had a higher Tm/Tg than sucrose due to the higher moisture content of the lactose sample. The crystallization kinetics of lactose and sucrose at various moisture contents should be investigated to test the idea that the results in our study may be explained by changes in Tm and Tg.

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