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The Application of Polymer Crystal Growth Theory to the Kinetics of Formation of the *B*-Amylose Polymorph in a 50% Wheat-Starch Gel

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ABSTRACT

Gelatinized wheat-starch gels containing 50% water (w/w) were prepared by extrusion and submitted to storage at varying temperatures between 2 and 37°C. The development of crystallinity was followed by X-ray diffraction over a period of three weeks by which time all perceptible post-gelatinization changes were complete. The results were analysed by fitting to the Avrami equation (optimum fit occuring where the Avrami exponent $n = 1$). The derived rate of crystallization at the different temperatures was then analysed in terms of the Lauritzen–Hoffman theory of growth of polymer crystals. Although not all parameters had experimental values, it proved possible to evaluate a series of trial values of two parameters until the best fit to the growth rate data was obtained as judged by the correlation coefficient. All parameters so determined were deemed satisfactory in terms of comparable figures obtained with synthetic polymers. The theoretical T_g for the above 50% aqueous wheat-starch gel was calculated to be approximately 200 K which accorded well with a value calculated by free-volume theory. The practical implications with regard to retrogradation of starch gels at different temperatures and different water contents are discussed.

1 INTRODUCTION

The Avrami equation has been widely used to model the crystal growth kinetics of starch gels (Cornford *et al.*, 1964; Colwell *et al.*, 1969; Kim &

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D'Appolonia 1977*a*, *b*; Longton & LeGrys, 1981; Fearn & Russell, 1982; Russell, 1983*a*, *b*, *c*). The original development by Avrami (1939, 1940, 1941) was later simplified by Evans (1945) who expressed the change in crystallinity of a system by the equation

$$\theta = \exp(-kt^n) \tag{1}$$

where θ represents the non-crystalline fraction at time t, k is a rate constant and n the Avrami exponent. The exponent can take values between 1 and 4 which are characteristic of the mode of crystal growth.

However, the theory gives no indication as to the temperature dependence of the rate of crystallization. Many theories have been developed over the past forty years to explain the thermodynamics of polymer crystallization, both from the melt and from solution. The subject has been extensively reviewed by Mandelkern (1964), Sharples (1966), Sanchez (1974) and Hannay (1976).

All of the theories are essentially an extension of classical nucleation theory (CNT). Crystallization is thereby considered to be a process of secondary nucleation on a pre-existing substrate, or the growth of a primary nucleus which has greater than critical dimensions. Under such circumstances, the primary nucleus is of a size such that random thermal motions will not cause it to melt back into solution or the surrounding molten liquid.

According to CNT, the nucleation rate for a phase transformation in a condensed phase (liquid–solid or liquid–liquid) is given by

$$s^* = s_0 \exp(-\Delta G/kT)\exp(-\phi^*/kT) \tag{2}$$

where ϕ^* is the free energy required to build a nucleus of critical size, ΔG is the free energy barrier opposing transport of material across the interface and s_0 is a nearly temperature-independent constant. At temperatures near the melting point of the system, the nucleation term is dominant and inversely proportional to the undercooling $(T_m - T_c)$, where T_m and T_c are the melting and crystallization temperatures respectively. Hence, near the melting point, the nucleation rate decreases as the critical size of the nucleus increases. The nucleation rate therefore shows a negative temperature coefficient as the size of the critical nucleus decreases with decreasing temperature.

At temperatures near to the glass transition temperature, the transport term is dominant and the nucleation rate depends upon the microscopic viscosity of the system. Thus, as the microscopic viscosity increases the nucleation rate decreases.

As the temperature is reduced from the melting point (no nucleation), the driving force for nucleation increases until a maximum rate is observed and thereafter at lower temperatures the rate of nucleation decreases, due to an increase in the viscosity of the system. This causes a reduction in the rate of transport of material to the growth point, thus reducing the nucleation rate.

The positive and negative temperature coefficients for the growth of polymer crystals which have been widely reported can therefore be explained by considering the twin processes of nucleation and material transport through a viscous medium. More detailed analyses have been developed among which that of Lauritzen & Hoffman (1973) has been widely used and in this paper is applied to the growth of B-crystals in starch gels.

1.1 The Lauritzen–Hoffman theory of polymer crystallization

The theory of polymer crystallization developed by Lauritzen & Hoffman (1973) considers the growth of chain-folded polymer crystals by the deposition of polymer chains on an already-existing crystal substrate. It is assumed that the chains are deposited at adjacent positions on the crystal growth face by the polymer chain emerging from the crystal and then folding back on itself, as shown in Fig. 1. This situation is probably not strictly applicable in the case of starch, if amylopectin is the main component responsible for crystallization, because the side chains in the amylopectin molecule are not long enough to allow chain folding, although there is some evidence of chain folding from infrared studies of amylopectin solutions (Vasko & Koenig, 1972). If the work of chain folding is associated with an end-surface free energy of the crystal, then

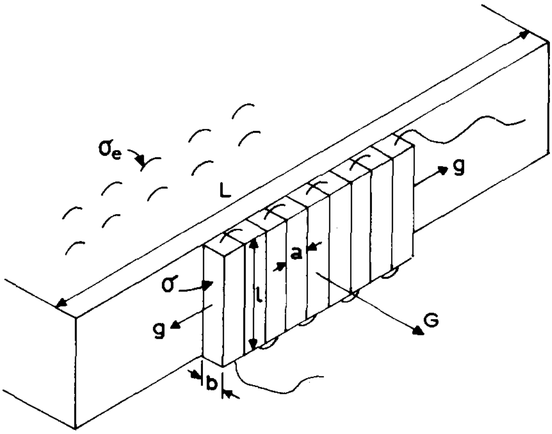

Fig. 1. Model for surface nucleation and growth of a chain-folded crystal.

the theory can be usefully applied as an approximation to the true situation. The rate of crystal growth is calculated by finding the steady-state net nucleation flux over the barrier to nucleation and then integrating over all possible values of crystal thickness to obtain the total flux, S_T. The nucleation term has the form shown in eqn (3).

$$S_T \propto \exp(-K_g/T\Delta Tf) \qquad (3)$$

where K_g is a constant, ΔT is the undercooling and $f = 2T/[T_m + T]$. This term dominates the growth rate at small undercoolings.

The term governing the growth rate at large undercoolings ($\simeq 100$ K) is deduced by considering the jump rate of local motions at temperature T. This is commonly expressed (Hoffman, 1964) as

$$\beta = (kT/h)J_i \quad \exp[-U^*/R(T-T_\infty)] \qquad (4)$$

where β = a factor that accounts for retardation to molecular motion resulting from the fact that polymer molecules or segments thereof must be transported to the site of the crystallization act;
h = Planck's constant;
R = gas constant;
J_i = a pre-exponential factor

This term is usually interpreted as representing the segmental jump motion of a polymer chain. The temperature T_∞ is a hypothetical temperature at which viscous flow ceases and is related to the glass transition temperature T_g. In practice, T_∞ has been found to be approximately 30 K below T_g (Suzuki & Kovacs, 1970). U^* is the activation energy for steady-state reptation, i.e. 'reeling in' the polymer chain. The form of eqn (3) is closely related to the theory of Williams, Landel & Ferry (WLF) (1955) which describes the variation of the viscosity or diffusion constant with temperature for glass-forming liquids. The WLF equation, which is a semi-empirical relationship, has been tested for many substances and appears to hold in the temperature range $T_g < T < T_g + 120$ K. The fluidity of molten polymers is known (Hoffman, 1964; Ferry, 1970) to vary with temperature according to a factor similar to eqn (4) between T_g and $T_g + 100$ K. If the WLF constants C_1 and C_2 are known for the polymer in question, then a similar equation can be used, involving the full WLF equation, and can be substituted in place of eqn (4) (Palys & Philips, 1970).

The form of β is empirical in character, which is not surprising, in view of the fact that no completely satisfactory molecular theory of fluidity of polymers near the glass transition has yet been devised.

Now that the forms of the nucleation and transport terms have been discussed, the growth rate G can be deduced by considering the surface nucleation rate and gathering together all the nearly temperature-independent terms into a constant factor G_0. This yields the expression

$$G = G_0\exp[-U^*/R(T-T_\infty)]\exp(-K_g/T\Delta Tf) \tag{5}$$

The form of this equation predicts zero growth rate of T_m and T_g, and a maximum in the rate at some intermediate temperature. The results obtained by Magill (1977) for poly(tetramethylphenylene) are shown in Fig. 2.

This clearly demonstrates that a negative temperature coefficient is predicted for the growth of crystals at higher temperatures and a positive temperature coefficient for crystals grown at temperatures far removed from the melting point.

2 MATERIALS AND METHODS

2.1 Materials

Wheat starch was supplied by ABR Chemicals Ltd. The moisture content of the starch (by drying in a vacuum oven at 70°C overnight) was 11% by weight. The starch granules exhibited a characteristic Maltese

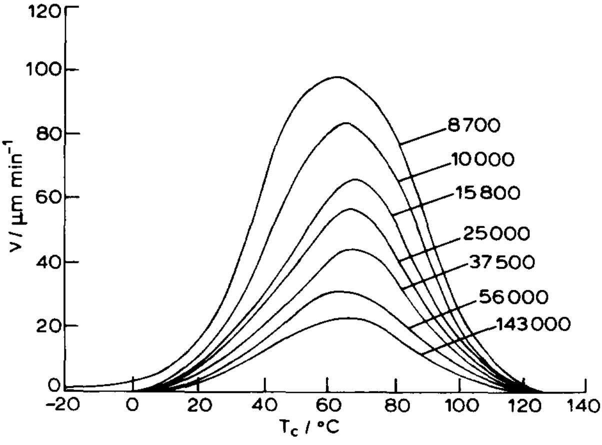

Fig. 2. Dependence of crystal growth rate v on crystallization temperature T_c for different fractions of poly(tetramethyl-*p*-phenylene)siloxane (molar mass given in g mol^{-1}). (After Magill, 1977).

cross pattern when viewed through cross polarizers in the optical microscope and had an A-type X-ray diffraction pattern.

2.2 Sample preparation

Attention in this paper is concentrated on the behaviour of 50% starch gels, i.e. 50 g water and 50 g totally dry state. Preliminary studies showed that satisfactorily-gelatinized samples of wheat starch could be prepared by first heating the mixture, contained in a plastic bag, in a microwave oven to produce an inhomogeneous, semi-gelatinized intermediate product. This 'pre-gel' was allowed to cool for approximately 30 min to prevent moisture loss when introduced into the feed hopper of the extruder, and then kneaded to produce a more homogeneous solid. The solid material was then extruded using a Brabender, laboratory scale, single screw extruder (model DN driven by a Docorder drive unit, model number 330, with a 1:1 screw and open discharge; length to diameter ratio of the ground barrel, 20:1; die piece diameter, 8 mm). The extruder was operated at a speed of 150 RPM with a temperature gradient of 110°C to 50°C from the feed hopper to the die piece. This temperature gradient technique was found to produce the best results, because it allowed full gelatinization of the sample but also prevented excessive 'flash-off' of moisture as the 'rope' of hot starch gel emerged from the die piece. In practice, a minimum retention time of approximately 45 s was found necessary to produce a fully-gelatinized sample. This timescale allowed sufficient time for heating and hydration of the sample within the barrel.

The 1:1 screw selected to transport the premix down the barrel permitted a gentle mixing of the sample without the application of large shear forces and pressures. This method allowed for full solvation of the material but without an attendant rupturing of the granule. The latter was confirmed microscopically.

2.2.1 Sample moisture content

Due to the 'flash-off' of water as the gel emerged from the extruder die piece, the precise water content of any gel could only be determined after the sample had been prepared. The moisture content was determined by drying a finely-divided sample of the 'fresh' gel in a vacuum oven at 70°C overnight.

2.2.2 Sample storage

The warm extrudate was allowed to cool to room temperature for approximately 30 min before being cut into 80 mm lengths for storage in aluminium-backed plastic pouches. A sachet of 'ageless' oxygen absorbing material, supplied by Croxton and Garry Ltd, was enclosed with the samples to minimize mould growth during storage.

2.3 X-ray diffraction

The X-ray diffractometer system used in this study was a Philips APD 15 system, modified by the addition of a BBC/Torch microcomputer for the analysis and storage of data. The goniometer, which was used in the symmetrical reflection mode, was equipped with a Panmure Instruments curved graphite crystal monochromator set to pass copper K_α radiation of wavelength 0·154178 nm. A Philips PW1964/60 scintillation counter was used as the detector and the divergence and scatter slits were 1° and 0·5° respectively. A specimen of a single quartz crystal was used to calibrate the goniometer using the reflection at 26·664° 2θ as the calibration angle. Throughout the programme of experiments the goniometer did not drift from calibration by more than 0·05° 2θ — which was the size of one step used in the data collection procedure.

2.3.1 Specimen preparation for X-ray analysis

Samples of gel were cut into slabs of dimensions 10 × 20 × 5 mm and placed into an aluminium sample holder so that the largest surface was flush with the face of the sample holder. This procedure was necessary because the *para*-focussing geometry of the goniometer relies on the specimen presenting a flat surface which is tangential to the focussing circle of the incident X-ray beam.

2.3.2 Experimental conditions

Monochromatic copper K_α radiation of wavelength 0·154178 nm was used to irradiate the sample. Data was collected over an angular range from 4° 2θ to 32° 2θ in 0·05° 2θ steps. This angular range encompassed all the diffraction peaks of starch crystals. The time of data collection per step was 2 s. Data was passed in blocks of 200 points from the Philips minicomputer to a BBC/Torch microcomputer and stored on floppy disc for subsequent processing.

2.3.3 Sample examination

To follow the development of crystallinity with time, the samples were examined periodically for times up to three weeks post-gelatinization, by which time all the perceptible changes, as determined by X-ray diffraction, were complete.

2.4 Data analysis

The collected X-ray data were graphically displayed on the BBC/Torch microcomputer and the absolute crystallinity determined by the method of Hermans & Weidinger (1948) as described by Nara & Komiya (1983).

2.4.1 Kinetic analysis of crystallinity data

The raw crystallinity, as derived from the analysis of X-ray diffractograms, was used to determine the rate, mode and extent of crystallization in starch gel systems, in order to gain an insight into the kinetics of crystallization in model starch gels. Data were fitted to the Avrami equation using a non-linear least-squares fitting algorithm. The parameters to be determined from the data were the final crystallinity, the rate constant for crystallization and the Avrami exponent, n, which gives information concerning the mode of crystallization.

The data were treated in two ways. Firstly, all the parameters in the equation were allowed to vary simultaneously, so that the best fit to the data was outlined. Secondly, the Avrami exponent was fixed at physically reasonable values and the remaining parameters calculated. The Avrami exponent was constrained to the values 1, 1·5, 2, 2·5, and 3, which represent distinct modes of crystallization, all of which can be explained theoretically (Mandelkern, 1964). A measure of the goodness-of-fit to a particular model was given by the sum of squared deviations.

The program to fit the crystallinity data to the Avrami equation used FORTRAN subroutine number E04FDF supplied by the Numerical Analysis Group, Oxford. The program was written in FORTRAN and ran interactively on a VAX 11/780 minicomputer. The program used an iterative procedure to minimize the sum of squared deviations (SSD) between the fitted function and the data. The routine supplied useful information on the goodness-of-fit in terms of a numerical parameter which indicated the reliability of the final fit in accordance with a table supplied with the routine document. This table is reproduced in Table 1.

3 RESULTS

The actual moisture content determined post-extrusion was 50·8% w/w (i.e. 50·8 g water per 100 g extrudate).

Figure 3 displays the limiting crystallinities attained on storage at different temperatures, while Table 2 and Fig. 4 record the kinetic data. It is evident from Fig. 3 that the *extent* of crystallization of this 50% w/w starch gel has a negative temperature dependence, while Fig. 4 exhibits

TABLE 1
The Reliability and Significance of Calculated Results as Represented Numerically by the IFAIL Parameter over a Linear Range (1–8)

IFAIL	*Significance*
0	Results good fit to data.
1	Parameter outside expected range.
2	400 × N calls to LSFUN1 — no convergence.
3	Final point does not satisfy the conditions for acceptance as minimum, but no lower point can be found.
4	Auxiliary unable to complete singular value decomposition in reasonable number of iterations.
5	Some doubt if X is a real minimum. Degree of confidence
6	decreases as IFAIL increases. IFAIL = 5 probable that
7	X gives good estimate of minimum.
8	IFAIL = 8 unlikely to be good fit.

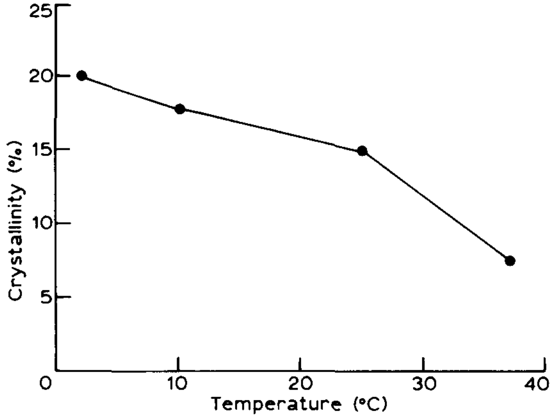

Fig. 3. Limiting absolute X-ray crystallinity versus temperature for a 50% wheat-starch gel.

the well-known fact that a 50% starch gel recrystallizes in the B-form more rapidly at 2°C than at 37°C (i.e. displays a negative temperature gradient).

By examining the parameter IFAIL (Table 2), it can be seen that the most likely value for the Avrami exponent, *n*, is unity. This value is uniquely associated with the instantaneous growth of crystals in one dimension and agrees with the conclusions reached by previous workers. The value of *n* would imply that the crystal nuclei were not completely destroyed during the gelatinization process, which is not surprising since

TABLE 2
Results of an Avrami Analysis of Absolute X-Ray Crystallinity for a 50% Moisture Wheat-Starch Gel

Temperature (°C)	*n*					
	1	*1·5*	*2*	*2·5*	*3*	*Variable (nv)*
2 nv[a]						0·2
Cl%	19·9	19·8	—	—	—	20·6
$k \times 10^{-3}\ h^{-n}$[b]	82·3	13·9	—	—	—	2605·0
SSD	19·8	20·0	—	—	—	17·4
IFAIL	0	5	—	—	—	2
10 nv						0·83
Cl%	17·8	18·2	—	—	—	18·2
$k \times 10^{-3}\ h^{-n}$	28·3	4·5	—	—	—	51·3
SSD	19·5	4·3	—	—	—	18·4
IFAIL	0	8	—	—	—	0
25 nv						1·59
Cl%	14·9	14·5	—	—	—	14·5
$k \times 10^{-3}\ h^{-n}$	18·6	2·4	—	—	—	1·7
SSD	2·7	3·9	—	—	—	2·7
IFAIL	0	3	—	—	—	3
37 nv						0·42
Cl%	7·4	7·5	7·4	7·4	—	7·4
$k \times 10^{-3}\ h^{-n}$	15·4	5·3	3·5	2·3	—	19·8
SSD	5·3	6·5	5·3	5·3	—	10·9
IFAIL	0	2	7	5	—	2

[a] nv — variable n
[b] *k* — rate constant
Cl% — limiting percentage crystallinity

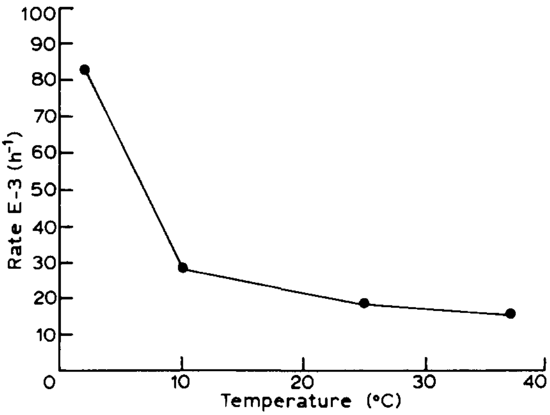

Fig. 4. Rate of crystallization versus temperature for a 50% wheat-starch gel.

the gels were prepared so as not to excessively damage the granules. This would have left sufficient intragranular material (amylopectin) intact for spontaneous crystallization to occur.

In general, as the Avrami exponent was allowed to take on higher values (corresponding to multidimensional growth or the production of fresh nuclei with increasing time post-gelatinization), SSD increased, and IFAIL indicated that the results were becoming more unreliable. Alternatively, the program simply failed, which indicated that no fit to the data could be found by using that particular model of crystallization.

The activation energy for the transformation from the disordered to the ordered state was calculated by applying the Arrhenius equation to the rate data for the B-crystals derived from the Avrami equation with n equal to unity.

The form of the Arrhenius equation is:

$$k = A \exp(-E_a/RT) \tag{6}$$

where k is the rate of crystallization, A a constant, E_a the activation energy, R the universal gas constant, and T the absolute temperature of crystallization. Values of $\ln(k)$ were plotted against $1/RT$ to find E_a. For B-crystals the activation energy was $-30{\cdot}9$ KJmol^{-1}. This value is in the range associated with hydrogen bonding and probably reflects the nature of interchain interactions in starch crystals.

4 DISCUSSION

Experience with synthetic polymers would suggest that both positive and negative temperature coefficients of the crystal growth process can be observed if the appropriate temperature regimes can be realized. Therefore, although only a negative temperature coefficient of growth of the polymorph has been reported here, nevertheless it should be possible to see whether the Lauritzen–Hoffman theory of polymer crystal growth can be applied in a way which is consistent with the experimentally determined or predicted properties of the system.

5.1 Application of Lauritzen–Hoffman crystallization theory to B-type starch crystals

5.1.1 Calculation of U^*, T_∞, K_g and G_0

Equation (5) governing the crystal growth rate of polymeric systems contains a number of unknown parameters which cannot be found directly by substituting in observed growth rates. To make the problem more tractable, it is usual to reduce the number of unknowns by assuming values of some of the parameters and then to vary the others to obtain the best correlation between the experimentally-observed growth rates and those predicted by the theory. The simplest way to do this is to perform a linear regression analysis.

Thus, rewriting eqn (5) in logarithmic form:

$$\ln(G)=\ln(G_0)-\frac{K_g}{T\Delta Tf}-\frac{U^*}{R(T-T_\infty)} \tag{7}$$

and rearranging

$$\ln(G)+\frac{U^*}{R(T-T_\infty)}=\ln(G_0)-\frac{K_g}{T\Delta Tf} \tag{8}$$

Plotting the right hand side of eqn (8) with estimated values for U^* and T_∞ against $1/T\Delta Tf$ should yield a straight line of slope $-K_g$ and intercept $\ln(G)$.

A series of trial values of U^* and T_∞ were substituted into eqn (8) until the best fit to the growth rate data (produced by the Avrami equation with n equal to unity) was obtained, as judged by the correlation coefficient. The results are tabulated in Table 3, from which it can be seen that the value of K_g was dependent upon the choice of U^* and T_∞. The results for K_g are in approximate agreement with those for synthetic polymers obtained by previous workers, as can be seen from Table 4, which is taken from Hannay (1976).

From Table 3 it can be seen that the values of U^* of approximately 15 kJmol^{-1} and T_∞ of 170 K give a good fit to the data, with the value of U^* probably being the most reliable, because the correlation coefficient tended to increase with U^*, irrespective of the value T_∞. This value for U^* does fit in with that found for other polymers, as can be seen from Table 4.

As $T_\infty \simeq T_g - 30$ (Hannay, 1976), the glass transition temperature (T_g) for a 50% starch-and-water gel is predicted to be approximately 200 K.

5.2 Comparison of predictions of T_g from the results of the Lauritzen–Hoffman theory with those from the free volume theory

It is interesting to compare this prediction of T_g for a 50% starch gel with that obtained by considering the free volume theory of the glass transition. This theory treats the glassy state as an iso-free volume state in which 1/40 of the volume of a liquid is free volume at the glass transition temperature.

TABLE 3

Results of Linear Regression Analysis of the Lauritzen–Hoffman Equation to Determine the Optimum Values of U^* and T_∞

Input parameters		*Output parameters*		
T_∞ *(K)*	U^* *(J mol^{-1})*	G_0 *(s^{-1})*	$K_g \times 10^5$ *(K)*	*Correlation coefficient*
213	3000	734	1·49	−0·916
213	7500	2·63E7	2·83	−0·939
218	7000	2·57E7	2·98	−0·938
223	6000	2·36E7	2·96	−0·935
233	5000	1·95E8	3·33	−0·931
233	7500	7·16E12	4·12	−0·899
238	6500	2·45E14	4·87	−0·932
248	3000	3·38E8	3·70	−0·915
248	7500	3·37E26	8·33	−0·923
213	10000	1·15E11	3·56	−0·944
213	15000	2·19E18	5·04	−0·949
233	10000	1·22E20	6·04	−0·939
233	15000	7·56E31	8·76	−0·942
200	10000	9·46E7	2·78	−0·943
200	15000	5·27E13	3·86	−0·949
170	7500	142	1·53	−0·949
170	10000	1·09E4	1·84	−0·953
170	15000	6·43E7	2·45	−0·955
150	7500	11·4	1·29	−0·917
150	10000	372·6	1·51	−0·927
150	15000	4·06E5	1·96	−0·941
200	20000	2·86E19	4·94	−0·943
170	20000	3·79E11	3·06	−0·951
150	20000	4·42E8	2·41	−0·947

Thus

$$V_f = 1/40 + \alpha(T - T_g) \tag{9}$$

where V_f is the free volume at temperature T, and α is the volume expansion coefficient of the liquid minus the volume expansion coefficient of the glass. If free volumes are assumed to be additive, the effect of a diluent on the glass transition temperature of a polymer–diluent system is to reduce T_g according to eqn (10) (Bueche, 1979):

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d(1 - V_p)\, T_{gd}}{\alpha_p V_p + \alpha_d(1 - V_p)} \tag{10}$$

where the subscripts *p* and *d* refer to polymer and diluent respectively.

TABLE 4

Estimates of U^*, T_∞, K_g and G_0 for Three Synthetic Polymers: Isotactic Polystyrene, Nylon 6 and TMPS Polymer M (After Hannay, 1976)

T_∞ (K)	U^* (cal mol^{-1})	G_0 (s^{-1})	K_g E5 (K)	CC
Isotactic polystyrene				
333·5 = $T_g - 30$	1560	2·7E−2	1·2	−0·998
333·5 = $T_g - 30$	4000	2·0E10	5·3	−0·777
311·9 = $T_g - 51{\cdot}6$	4120	1·5E5	3·0	−0·905
0	21000	6·9E3	0·21	−0·12
Nylon 6				
273 = $T_g - 30$	1430	6·5	1·74	−0·997
273 = $T_g - 30$	4000	2·7E8	4·1	−0·894
251·4 = $T_g - 51{\cdot}6$	4120	2·4E6	3·24	−0·943
0	13000	2·2E5	1·68	−0·979
TMPS polymer (M. W. = 56000)				
219·2 = $T_g - 30$	990	2·16E−1	1·14	−0·995
219·2 = $T_g - 30$	4000	9·78E6	2·05	−0·896
197·6 = $T_g - 51{\cdot}6$	4120	1·84E5	1·75	−0·945
0	13000	2·12E6	1·39	−0·990

This expression has been tested for a number of polymer–diluent systems and has been found to be a reasonably accurate predictor of T_g (Kelley & Bueche, 1961).

In the case of starch and water, the glass transition temperature of pure starch according to Van den Berg (1981) is 424 K and that of water is 135 K. The value of α_d is difficult to estimate, but reasonable agreement between theory and experiment can be obtained by setting it to 10^{-3} K^{-1}, and for most polymers α_p is approximately $4{\cdot}8 \times 10^{-4}$ K^{-1} (Bueche, 1979). Table 5 shows the results of substituting these values into eqn (10) as a plot of T_g against volume fraction of starch. At a volume fraction of starch of 0·4, which corresponds to 50% starch by weight, the predicted glass transition temperature is approximately 200 K. This is the same as that predicted when using the Lauritzen–Hoffman theory of crystallization to model the growth of B-type starch crystals in a gel of the same composition. This would indicate that the results obtained for U^* and T_∞ are reasonable estimates of the true values.

If Table 5, which shows the variation of T_g with volume fraction of starch is examined, then it is interesting to observe that no crystallization of starch–water systems which contain less than 15% water is predicted to occur when they are stored at temperatures less than 40°C. For gels containing 20% moisture, no crystallization should occur at storage

TABLE 5
Values of T_g versus Volume Fraction of Starch[a]

V_f *Starch*	T_g *(K)*	V_f *Starch*	T_g *(K)*	V_f *Starch*	T_g *(K)*
0·00	135·00	0·34	192·29	0·68	280·93
0·01	136·39	0·35	194·36	0·69	284·28
0·02	137·80	0·36	196·44	0·70	287·68
0·03	139·20	0·37	198·55	0·71	291·14
0·04	140·67	0·38	200·70	0·72	294·65
0·05	142·10	0·39	202·86	0·73	298·26
0·06	143·60	0·40	205·06	0·74	301·86
0·07	145·10	0·41	207·29	0·75	305·56
0·08	146·58	0·42	209·54	0·76	309·32
0·09	148·10	0·43	211·83	0·77	313·14
0·10	149·63	0·44	214·15	0·78	317·04
0·11	151·19	0·45	216·49	0·79	321·00
0·12	152·75	0·46	218·87	0·80	325·03
0·13	154·34	0·47	221·29	0·81	329·13
0·14	155·95	0·48	223·73	0·82	333·31
0·15	157·57	0·49	226·21	0·83	337·56
0·16	159·21	0·50	228·73	0·84	341·90
0·17	160·87	0·51	231·28	0·85	346·31
0·18	162·55	0·52	233·87	0·86	350·81
0·19	164·25	0·53	236·49	0·87	355·39
0·20	165·96	0·54	239·16	0·88	360·06
0·21	167·70	0·55	241·86	0·89	364·82
0·22	169·46	0·56	244·60	0·90	369·68
0·23	171·24	0·57	247·38	0·91	374·63
0·24	173·04	0·58	250·20	0·92	379·68
0·25	174·86	0·59	253·07	0·93	384·83
0·26	176·71	0·60	255·98	0·94	390·08
0·27	178·57	0·61	258·93	0·95	395·44
0·28	180·46	0·62	261·93	0·96	400·92
0·29	182·37	0·63	264·97	0·97	406·51
0·30	184·31	0·64	268·07	0·98	412·21
0·31	186·27	0·65	271·21	0·99	418·04
0·32	188·25	0·66	274·40	1·00	424·00
0·33	190·26	0·67	277·64		

[a] T_g values were calculated using the Bueche equation (Bueche, 1979).

temperatures below room temperature. Thus, as is found in practice, no crystallization of starch is predicted when low moisture content systems are stored below room temperature. The authors therefore have grounds for confidence in the results just derived.

Two further points should be made. Firstly, although the experimental work was conducted in the temperature range between 2 and 37°C, the parameters that were derived through application of the Lauritzen–Hoffman equation are applicable over the whole temperature range between T_g and T_m. The form of the crystallization rate with respect to temperature can then be calculated and this is shown in Fig. 5.

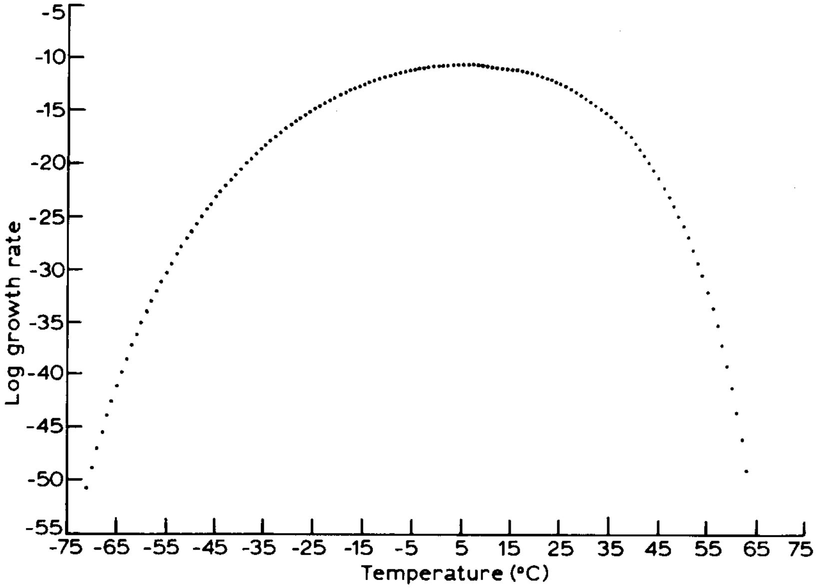

Fig. 5. Theoretical variation of crystallization rate of a 50% wheat-starch gel between T_g and T_m calculated using parameters determined through application of the Lauritzen–Hoffman theory to experimental results obtained between 2–37°C.

Secondly, a superficial comparison of the data in Table 5 might suggest that the calculated T_g is seriously at variance with the experimental results of Slade & Levine (1984). They used DSC to show that the T_g of a starch gel containing 55% water occurred at -7°C (actually a T'_g), i.e. some 65°C higher than that predicted by either of the above two theories. It will be obvious on reflection, however, that the T_g computed here is 'theoretical', in that it presumes that the solvent (water) does not freeze. In practice, of course, the water does freeze at -3 or -4°C and, in consequence, the effective concentration of the starch component in the starch gel is greatly enhanced. Indeed the actual percentage of unfrozen water in a frozen starch gel may be estimated from the value of T'_g given by Levine & Slade as -6 to 2°C as 28% (28 g H_2O per 72 g starch). This agrees well with the figure of 27% for W'_g (grammes unfrozen water per gramme solute) reported by Levine & Slade (1987).

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