

# Thermodynamic and structural properties of starches extracted from potatoes grown at different environmental temperatures

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## Abstract

Potato starches grown at different temperatures were investigated using high sensitivity differential scanning microcalorimetry (HSDSC) and Fourier transform infrared spectroscopy (FTIR). By applying physico-chemical approaches, the thickness of crystalline lamellae and the thermodynamic and structural characteristics (such as gelatinisation) of cooperative units and their surfaces were determined. It was established that a difference of growth temperature experienced by tubers during development does not lead to changes in the thickness of amylopectin crystalline lamellae and hence the constituent double helical length. However, the positive correlation established between growth temperature and gelatinisation temperatures was confirmed as being due to optimisation of crystallite structural organisation (at higher temperatures). © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Potato starch; Crystallinity; Growth temperature; Gelatinisation

## 1. Introduction

It is well known (Biliaderis, 1992; Gallant, Bouchet, Buleon & Perez, 1992; Jenkins & Donald, 1995; Manners, 1989; Matveev, Elankin, Kalistratova, Danilenko, Niemann & Yuryev, 1998; Yuryev, Wasserman, Andreev & Tolstoguzov, 2001; Zobel, 1988) that native starch granules consist of crystalline lamellae (composed of amylopectin short-chains as double helices in registered arrays), amorphous lamellae (amylopectin branch points with possibly some amylose) as well as amorphous background material composed of amylopectin and amylose in a disordered conformation. Amylopectin and amylose macromolecules may directly and indirectly form structural defects in amylopectin crystalline lamellae due to (a) suboptimum registration of amylopectin double helices in crystallites and (b) disorganised presence/orientation of amylose and amylopectin chains (with density and rigidity effects) and associated effects on the glass transition temperature ( $T_g$ ), within

amorphous regions (Andreev, Kalistratova, Wasserman & Yuryev, 1999; Kozhevnikov, Protserov, Pavlovskaya, Golischkin, Milyaev & Yuryev, 2001; Matveev, van Soest, Niemann, Wasserman, Protserov, Ezernitskaja et al., 2001; Protserov, Karpov, Kozhevnikov, Wasserman & Yuryev, 2000; Tester, Debon, Davies & Gidley, 1999; Yuryev et al., 2001). Native waxy and normal cereal starches contain A-type crystalline packing (polymorphs) of macromolecular (amylopectin) chains while the crystalline lamellae of potato starches consist of B-type polymorphic structures. Although the semi-crystalline model of starch structure is well established, it does not take into account lipid-complexed amylose in most cereal starches, which occurs as single helices in an ordered conformation, probably within amorphous regions interspersing crystalline lamellates (Tester, Debon & Sommerville, 2000).

Heating of aqueous dispersions of native starches is accompanied by dissociation of double helices and disruption of crystalline lamellae. In starch physical chemistry, this process is referred to as gelatinisation. However, taking into consideration that starch is a typical semi-crystalline substance and from the point of view of modern physical and physical chemistry approaches, the disruption of starch

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crystalline lamellae during heating in water can be modelled as a true melting process. This allows the use of polymeric approaches for the gelatinisation (melting) of starch granules.

It is thought that the melting (gelatinisation) temperature of native starches depends on a number of factors such as glass transitions of amorphous regions, amylose/amylopectin ratio, the type of crystalline unit, the length of amylopectin double helices and the surface entropy of starch crystalline lamellae (Gerard, Planchot, Colonna & Bertoft, 2000; Matveev et al., 2001; Safford, Jobling, Sidebottom, Westcott, Cooke, Tober et al., 1998; Tester et al., 1999; Wang, Bogracheva & Hedley, 1998; Whittam, Noel & Ring, 1991; Yuryev et al., 2001). Recently, it has been shown that, for the transition from low to high amylose, the increase in starch melting temperatures may be attributed to an increase in the magnitude of the melting of 'cooperative units' from  $13.7 \pm 1.7$  to  $30.6 \pm 5.0$  anhydroglucose residues and correspondingly, to an increase in lamellar thickness of starch crystals (Matveev et al., 2001). Working on developing wrinkled pea starches, other authors (Kozhevnikov et al., 2001) have drawn similar conclusions with respect to lamellae thickness regulating melting temperatures. In contrast with these studies, a decrease in the gelatinisation temperature of potato starches at maturation, as determined by an increase in the surface entropy of starch crystalline lamellae, has been reported to be due to an increase in the presence/orientation of defects such as  $\alpha$ -glucan 'long loops', 'torsional tie chains' and presence of 'long ends' of macromolecules arranged in amorphous lamellae (Protserov et al., 2000). These features potentially facilitate the hydration of amorphous lamellae (with associated decrease in glass transition temperatures) and associated destabilisation and melting of the crystalline regions.

The effects of environmental conditions on the composition, structure and properties of starches have progressively received more attention in recent years (Asaoka, Okuno, Hara, Oba & Fuwa, 1989; Cottrell, Duffus, Paterson & Mackay, 1995; Debon, Tester, Millam & Davies, 1998; Fergason & Zuber, 1962; Hizukuri, 1969; Shi, Seib & Bernardin, 1994; Tester, 1997; Tester, Morrison, Ellis, Piggott, Batts, Wheeler et al., 1995; Tester et al., 1999). At present, it has been established that an increase in the growth temperature of cereal and potato starches, irrespective of amylose content, leads to an increase in melting temperatures (Cottrell et al., 1995; Hizukuri, 1969; Shi et al., 1994; Tester, 1997; Tester et al., 1995, 1999). It is thought that such behaviour (with parallels to annealing mechanisms in vitro) may be caused by changes in double helix lengths, registration optimisation within crystalline laminates and/or amorphous region rigidity (Tester, 1997; Tester et al., 1999, 2000). The first supposition has been in part confirmed by work (Moates, Noel, Parker & Ring, 1997), where it was shown that the increase in the degree of polymerisation of amylose in spherulitic crystals leads to

an increase in their dissociation temperature. In addition, it has been hypothesised that elevated growth temperatures directly enhance *in vivo* 'annealing' and this is comparable to annealing *in vitro* (Debon et al., 1998; Tester, 1997; Tester et al., 1999, 2000). Firm evidence to support these hypotheses are lacking although this problem can be solved by means of different physical theories usually used for the description of melting (thermodynamic parameters) of semi-crystalline synthetic polymers and biopolymers (Bershtein & Egorov, 1994; Privalov & Khechinashvili, 1974; Wunderlich, 1976, 1980). Some of these approaches have also been used for the characterisation of structural features in different starches (Andreev et al., 1999; Danilenko, Shtykova & Yuryev, 1994; Kozhevnikov et al., 2001; Matveev et al., 2001; Protserov et al., 2000; Yuryev et al., 2001).

A detailed analysis of different melting theories (Bershtein & Egorov, 1994; Wunderlich 1976, 1980) shows that the changes in the melting temperatures of semi-crystalline synthetic polymers can have two major causes:

1. a decrease of crystalline lamellae thickness and,
2. an increase of surface free energy for faces of crystalline lamellae due to an increase of structural defects (as previously discussed).

The second point is very relevant because it is believed that the dissociation of polymer crystals begins from their defects (Bershtein & Egorov, 1994; Sharples, 1966; Wunderlich, 1976, 1980). According to a number of authors (Andreev et al., 1999; Danilenko et al., 1994; Kozhevnikov et al., 2001; Matveev et al., 2001; Protserov et al., 2000; Yuryev et al., 2001), the crystalline lamellae thickness in low amylose starches may be calculated by means of the 'two-state' model used for the description of the gelatinisation process of starches in quasi-equilibrium conditions, i.e. at low heating rate ( $0.5\text{--}2\text{ K min}^{-1}$ ) and low concentrations of dispersed starch (0.5–2% dry matter). In addition, the surface free energy, enthalpy and entropy for faces of crystalline lamellae may be calculated using the Thompson–Gibbs' equation and some additional well-known thermodynamic correlations (Bershtein & Egorov, 1994; Protserov et al., 2000; Wunderlich, 1976, 1980).

To provide a better understanding of the variations in the gelatinisation temperatures of potato starches grown at different temperatures, we have studied the thermodynamic and structural properties of some potato starches and have described these properties using different physical models. These data are presented below.

## 2. Materials and methods

### 2.1. Materials

Native starches carefully extracted from a single potato cultivar (cv. Maris Piper) were used for this study. Potato

Table 1

Amylose content, peak melting (gelatinisation) temperature ( $T_{\text{merl}}$ ) and enthalpy ( $\Delta H_{\text{merl}}$ ) by DSC, calculated van't Hoff's enthalpy ( $\Delta H^{\text{vH}}$ ), differences in heat capacity between the molten and native states ( $\Delta C_p$ ), gelatinisation of cooperative unit ( $\nu$ ) and thickness of crystalline lamellae ( $L_{\text{crl}}$ ) for potato starches grown at 10, 16, 20 or 25°C

Growth temperature (°C)	Amylose content (%)	$T_{\text{merl}}$ (K)	$\Delta H_{\text{crl}}$ (kJ mol $^{-1}$ )	$\Delta H^{\text{vH}}$ (kJ mol $^{-1}$ )	$\Delta C_p$ kJ mol $^{-1}$ K $^{-1}$	$\nu$ anhydro glucose residues	$L_{\text{crl}}$ N m
10	32.2	333.4	2.5	39.8	0.021	15.7	5.5
16	29.7	336.0	3.4	47.8	0.007	14.1	4.9
20	29.4	338.6	3.1	43.8	0.032	14.1	4.9
25	31.0	343.4	4.4	51.1	0.043	11.6	4.1
Average						13.8 ± 1.7	4.8 ± 0.6

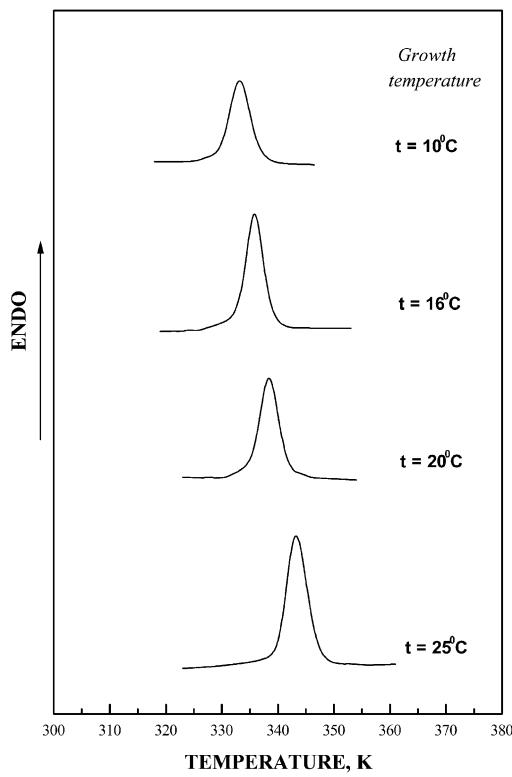


Fig. 1. DSC-traces of 0.3% dispersions of potato starches grown at different temperatures.

tubers were grown at the Scottish Crop Research Institute (SCRI, Dundee) in constant — environment chambers (equilibrated air and soil temperature) at 10, 16, 20 or 25°C with 12 h days, 50% relative humidity and a light intensity of 500 micromol photons  $m^{-2} s^{-1}$ . Plants were grown from tubers in 30 cm diameter pots filled with compost. The tubers were harvested, at maturity whereupon starch was extracted (Tester et al., 1999). Some characteristics of the native starches (Table 1), have been reported previously (Tester et al., 1999).

## 2.2. Methods

Calorimetric investigations of starch dispersions in water (0.3% dry matter, sample volume  $0.5 \text{ cm}^3$  in gold units) were performed using a high sensitivity differential scanning microcalorimeter DASM-4 (Moscow, Russia) from 10–130°C with a heating rate of  $2 \text{ K min}^{-1}$  under excess pressure. Deionised water was used as a reference material. The heat capacity scale was calibrated using the Joule–Lenz effect for each run. Corrections for dynamic temperature lag and residence time of the samples in the calorimetric cell were not necessary under these conditions (Andreev et al., 1999; Danilenko et al., 1994).

The average values of the thermodynamic parameters were determined as described elsewhere (Andreev et al., 1999; Danilenko et al., 1994; Matveev et al., 1998), using five measurements at 95% significance level and converted

to a dimension per mole anhydroglucose unit ( $162 \text{ g mol}^{-1}$ ). Values for van't Hoff enthalpy ( $\Delta H^{\text{vH}}$ ) were determined according to others (Andreev et al., 1999; Danilenko et al., 1994; Kozhevnikov, et al., 2001; Matveev, et al., 2001; Prosterov et al., 2000; Yuryev et al., 2001).

Values for the melting cooperative unit ( $\nu$ ) and the thickness of crystalline lamellae ( $L_{\text{crl}}$ ) for starches were calculated according to others (Andreev et al., 1999; Danilenko et al., 1994; Kozhevnikov, et al., 2001; Matveev, et al., 2001; Prosterov et al., 2000; Yuryev et al., 2001), and are represented in Eqs. (1) and (2) as follows

$$\nu = \Delta H^{\text{vH}} / \Delta H_m \quad (1)$$

$$\text{where } \Delta H_m \text{ is the experimental melting enthalpy of starches} \\ L_{\text{crl}} = 0.35 \nu \quad (2)$$

Hence

$$L_{\text{crl}} = 0.35(\Delta H^{\text{vH}} / \Delta H_m) \quad (3)$$

where, according to Gernat, Radosta, Anger and Damaschun (1993), there is the pitch height of  $0.35 \text{ nm}$  per anhydroglucose residue in a double helix.

Fourier transform infrared spectra (FTIR) in the range of  $1200$ – $800 \text{ cm}^{-1}$  for powder samples were recorded on a Nicolet Magna 750 spectrometer at  $2 \text{ cm}^{-1}$  resolution. A Specac ATR cell with a KRS-5 crystal at an angle of incidence of  $45^\circ$  was used to receive ATR spectra. Starch powders were pressed on the KRS-5 crystal and 128 interferograms were co-added before Fourier transformation analysis. A spectrum of the empty cell was used as a background. The spectra in the range of  $1200$ – $800 \text{ cm}^{-1}$  were divided into components using the Curve Fit procedure included in a standard GRAMS Research program. The contours were assumed Gaussian. The spectra were baseline-corrected and then deconvoluted. The height of the absorbance bands were used as a measure of band intensities ( $I$ ).

## 3. Results and discussion

Original thermograms obtained for gelatinisation of the aqueous potato starch dispersions are presented in Fig. 1. Analysis of DSC thermograms for all the starches investigated indicate that the calorimetric peaks are typical for native potato starch in a quasi-equilibrium condition (Andreev et al., 1999; Donovan, 1979; Matveev et al., 1998; Yuryev, Kalistratova, van Soest & Niemann, 1998), i.e. the asymmetry of the calorimetric peaks is not great. The gelatinisation/thermodynamic parameters of the native starches investigated are summarised in Table 1. Generally, the values of these parameters are in agreement with typical native starches (Andreev et al., 1999; Donovan, 1979; Matveev, et al., 1998; Protserov et al., 2000; Tester, 1997; Tester et al., 1999; Yuryev et al., 1998). As can be seen from Table 1, elevation of growth temperature leads to an

Table 2

Free surface energy ( $\gamma_i$ ), enthalpy ( $q_i$ ) and entropy ( $s_i$ ) of sides of crystalline lamellae of potato starches grown at different temperatures

Growth temperature (°C)	$\gamma_i$ (J cm <sup>-2</sup> )10 <sup>7</sup>	$q_i$ (J cm <sup>-2</sup> )10 <sup>7</sup>	$s_i$ (J cm <sup>-2</sup> K <sup>-1</sup> )10 <sup>7</sup>
10	4.6	53.9	0.147
16	3.7	39.0	0.105
20	2.8	44.0	0.121
25	1.2	22.4	0.062

increase in the thermodynamic melting parameters, i.e. gelatinisation temperature of crystalline lamellae in these starches as well as tendency for gelatinisation enthalpy to increase. This is consistent with the earlier works on potato tuber and microtuber starches (Cottrell et al., 1995; Debon et al., 1998; Hizukuri, 1969; Tester, 1997; Tester et al., 1999) and may be caused by an improvement of crystallite double helix registration and/or increase in double helical lengths (Tester, 1997; Tester et al., 1999).

With reference to work of other authors (Andreev et al., 1999; Danilenko et al., 1994; Kozhevnikov et al., 2001; Matveev et al., 2001; Protserov et al., 2000; Yuryev et al., 2001), the values for the melting cooperative units, corresponding to the degree of polymerisation of amylopectin short-chains as well as the thickness of the crystalline lamellae, can be determined (using Eqs. (1) and (2)). The results of calculations based on these data are shown in Table 1. The values for these melting cooperative units and the thickness of the crystalline lamellae are almost constant in magnitude, irrespective of starch origin and amylose content of the starches. The calculated values of  $\nu$  are in agreement with published values for different starches grown in field conditions (Andreev et al., 1999; Danilenko et al., 1994; Kozhevnikov et al., 2001; Matveev et al., 2001; Protserov et al., 2000; Yuryev et al., 2001). In addition, the calculated values of  $L_{\text{crl}}$  are practically equal to the length of starch crystalline lamellae (5.0 to 6.0 nm), according to the early amylopectin structural model proposed by Robin, Mercier, Charbonniere and Guilbot (1974) and the more recent Oostergetel and van Bruggen (1993) model. Overall then, the data show that the observed changes in the melting temperatures of starches grown at different temperatures are *not* caused by an increase of the double helix length and correspondingly, of the lamellar thickness in crystalline starch lamellae. The latter conclusion is in agreement with the result of work on maize and potato starches reported elsewhere (Protserov et al., 2000; Waigh, Kato, Donald, Gidley, Clarke & Riek, 2000). In these studies, it was shown that lamellar structure for the starches investigated remained invariant during growth of the plants, whereas changes were only seen in growth ring dimensions/distribution.

It has been established (Bershtain & Egorov, 1994; Wunderlich, 1976, 1980) that the melting temperature ( $T_m$ ) of semi crystalline synthetic polymers can be calculated by means of the Thompson–Gibbs' Eq. (4)

$$T_m = T_m^0 \left\{ 1 - 2\gamma_i / (\Delta H_m^0 \rho_{\text{crl}} L_{\text{crl}}) \right\} \quad (4)$$

where  $T_m^0$  and  $\Delta H_m^0$  are the melting temperature and the melting enthalpy of a hypothetical crystal with unlimited size (a perfect crystal),  $\gamma_i$  is the free surface energy of faces of crystalline lamellae,  $\rho_{\text{crl}}$  and  $L_{\text{crl}}$  are respectively the density and the thickness of the crystal.

Taking into consideration that the thickness of crystalline lamellae in the starches investigated is, practically the same (Table 1), analysis of Eq. (4) shows that an increase in  $T_m$  for starches at increasing growth temperature (Table 1) can be due to the change in the free surface energy of the faces of crystalline lamellae.

Melting of polymer crystals may begin with melting of crystalline defects arranged in amorphous lamellae (Bershtain & Egorov, 1994; Sharples, 1966; Wunderlich, 1976, 1980). In case of starches, such defects may be due to (i) amylopectin long chains extending from and associated with amorphous lamellae and (ii) amylose ‘tie chains’, which are anchored in the amorphous lamellae. Both these defects have been defined and discussed elsewhere (Matveev et al., 1998; Protserov et al., 2000; Yuryev et al., 2001). In addition, there may be (iii) sub-optimal registration of amylopectin double helices in crystallites (Tester & Debon, 2000; Tester, Debon & Karkalas, 1998; Tester et al., 1999, 2000) and (iv) sub-optimal double helix lengths (Moates et al., 1997; Safford et al., 1998). A decrease of the temperature difference  $T_m - T_{\text{cr}}$ , (melting temperature of polymer crystals minus crystallisation temperature), leads to a decrease in the amount of such defects, i.e. to the formation of more perfect crystals and to an increase in the melting temperature of crystals (Bershtain & Egorov, 1994; Wunderlich, 1976, 1980). Since the biosynthesis of starches and the process of crystallisation of amylopectin chains in granules occur at temperatures close to growth temperature, at a first approximation it can be assumed that the growth temperature of starches is equal to the temperature of crystallisation of starch crystals. In this case, the conclusion drawn by other authors (Bershtain & Egorov, 1994; Wunderlich, 1976, 1980) is in agreement with the data obtained here (Table 1). Moreover, the study of model starches has shown that an increase in crystallisation temperature leads to the formation of spherulitic crystals with higher melting temperature (Yuryev et al., 2001). If our assumptions are valid, we should observe a decrease in the surface entropy ( $s_i$ ) of starch crystalline lamellae at increasing growth temperature of starch granules.

According to previously published values (Bershtain &

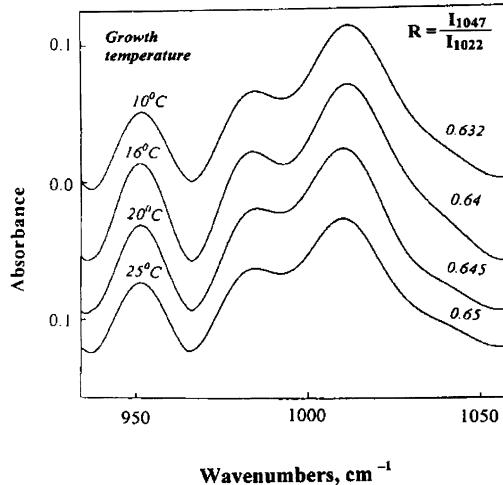


Fig. 2. Deconvoluted FTIR spectra of potato starches grown at different temperatures. The ratio ( $R$ ) of the bond intensities ( $I$ ) at 1047 and 1022  $\text{cm}^{-1}$ .

Egorov, 1994; Protserov et al., 2000),  $s_i$  can be estimated by from Eqs. (4)–(6) as follows

$$q_i = \left[ (\Delta H_m^0 - \Delta H_{\text{exp}}) / 2.5 \right] \quad (5)$$

$$\gamma_i = q_i - T_m s_i \quad (6)$$

where  $q_i$  is the surface enthalpy of crystalline lamellae.

Since the values of the melting temperature ( $T_m^0$ ) and the melting enthalpy ( $\Delta H_m^0$ ) for perfect crystals are not available, for calculations of the thermodynamic parameters the values of  $T_m^0$  (346.8 K) and  $\Delta H_m$  (35.5  $\text{J g}^{-1}$ ) for B-type spherulitic crystals (Protserov et al., 2000; Whittam et al., 1991) were used. In addition, values of  $\rho_{\text{crl}}$  for B-type structures ( $1.4 \text{ g cm}^{-3}$ ) (Protserov et al., 2000; Whittam et al., 1991) as well as  $L_{\text{crl}}$ ,  $\Delta H_m$  and  $T_m$  values for the starches investigated (Fig. 3, Table 1) were used. The calculated values of the  $\gamma_i$ ,  $q_i$  and  $s_i$  are shown in Table 2. It is important to note that the calculated values of the thermodynamic parameters for faces of starch crystalline lamellae are in agreement with the results published earlier for other potato starches (Protserov et al., 2000). However, these values are one order of magnitude less than corresponding values for synthetic polymer crystals of polyethylene (Bershtein & Egorov, 1994). The differences observed between our values of  $\gamma_i$ ,  $q_i$  and  $s_i$  and data for polyethylene crystals may be due to differences between the  $\Delta H_m^0$  and  $T_m^0$  values for perfect starch crystals and B-type spherulitic crystals, and to a less dense packing of starch macromolecules in crystalline lamellae compared with polyethylene macromolecules.

As can be seen from Table 2, an increase in the growth temperature of starch granules is accompanied by a decrease of the surface entropy of starch crystalline lamellae. This means that an increase in the growth temperature is accompanied by a decrease in the amount of defects arranged in

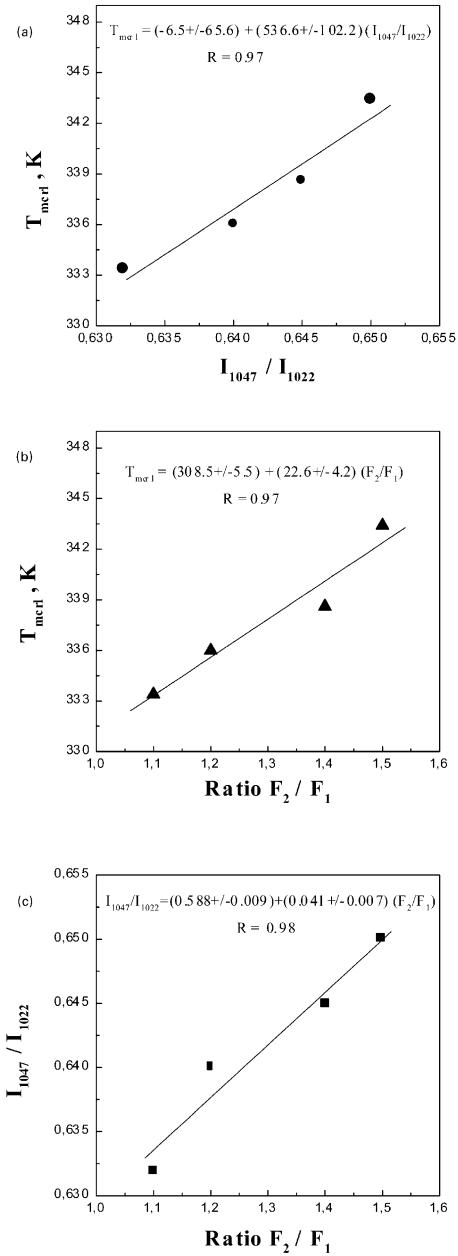


Fig. 3. Correlation dependence for: (a) the gelatinisation temperature of crystalline lamellae ( $T_{\text{mel}}$ ) as a function of  $R$  ( $R = I_{1047}/I_{1022}$ ); (b) the gelatinisation temperature of crystalline lamellae ( $T_{\text{mel}}$ ) as a function of amylopectin weight ratio ( $F_2/F_1$ ); and (c)  $R$  ( $R = I_{1047}/I_{1022}$ ) as a function of amylopectin weight ratio ( $F_2/F_1$ ).

crystalline (double helix registration) and amorphous (rigidity) lamellae. The improved orientation of amorphous regions will increase  $T_g$  (of these regions). Hence, there is an elevation of the gelatinisation 'trigger temperature' ( $T_g$ ), formation of more perfect starch crystals and an overall increase in the gelatinisation temperature.

Taking into consideration that: (i) the thickness of starch crystalline lamellae irrespective of starch origin does not change at different growth temperatures (Table 1), (ii) an increase in growth temperature is accompanied by a

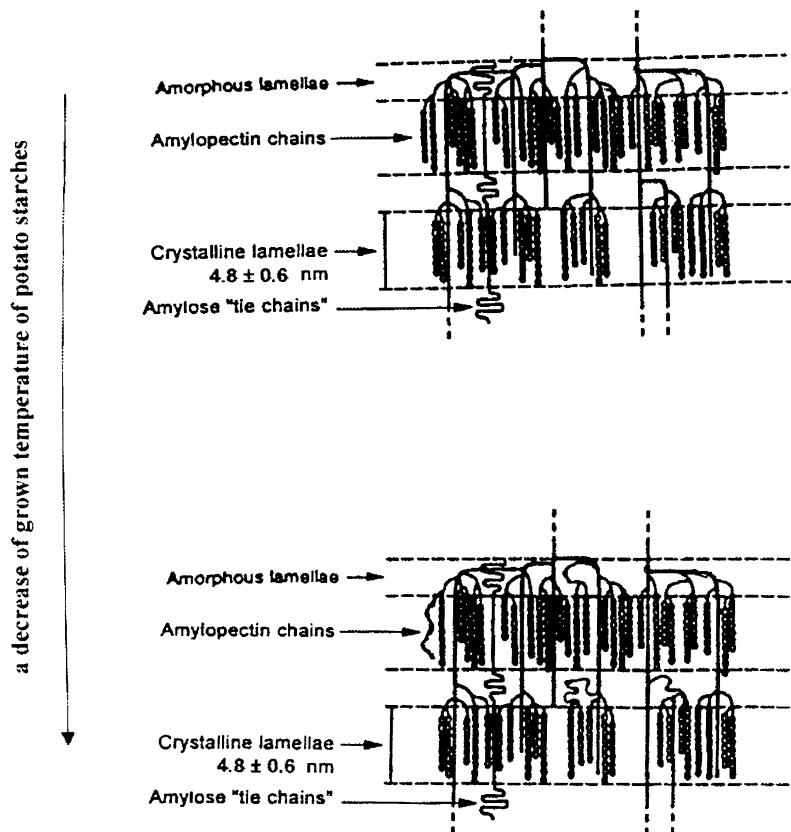


Fig. 4. Schematic presentation of the effects of growth temperature on the amorphous and crystalline regions of potato starches.

decrease of the surface entropy (Table 2) and that, (iii) an essential contribution to  $s_i$  is carried in defects, in both amorphous and crystalline lamellae (Protserov et al., 2000), it can be seen that an increase in the growth temperature reduces defects in starch crystallites due to *in vivo* type annealing.

As discussed above, and in earlier work (Matveev et al., 1998; Protserov et al., 2000; Yuryev et al., 2001), it may be considered that starch crystallite defects are in part due to the destabilising presence of amylose 'tie' chains anchored in amorphous regions (Matveev et al., 1998; Protserov et al., 2000; Yuryev et al., 2001). According to Protserov et al. (2000), an increase in the amylose content or the molecular weight of amylose in granules leads to an increase in the extent of such defects and correspondingly, to a decrease in the gelatinisation temperature of starches. However, the previously reported data for the starches used for this study (Tester et al., 1999) (Table 1) show that the amylose content in the investigated starches is practically constant. This means that the proposed defects in starch granules are not generated by the amount of the amylose fraction.

It might be imagined that the previously proposed (Matveev et al., 1998; Protserov et al., 2000; Yuryev et al., 2001) long loops, torsional tie chains and long ends of macromolecules form structures associated with specific amylopectin subfractions arranged in different starch lamellae. If this supposition is valid, we should observe a correlation

between the values of the melting temperature and the ratio ( $R$ ) of the band intensities at 1047 and 1022  $\text{cm}^{-1}$  ( $R = I_{1047}/I_{1022}$ ), since it is believed (van Soest, Tournois, de Wit & Vliegenthart, 1995) that  $R$  is determined by relative intensities of bands associated with different groups and bonds arranged in crystalline, amorphous lamellae and amorphous background. The deconvoluted FTIR spectra as well as the ratio ( $R$ ) of the band intensities at 1047 and 1022  $\text{cm}^{-1}$  in the investigated starches are shown in Fig. 2. Our calculations show (Fig. 3) that changes in the gelatinisation temperature of the starches correlate reasonably well, not only with the changes in the  $R$  values but also with the ratio (weight basis) of amylopectin subfractions  $F_2/F_1$  (Tester et al., 1999), for the starches investigated. Moreover, disregarding the value of  $s_i$  for the starch grown at 16°C, correlation functions as:  $T_m(I_{1047}/I_{1022}; F_2/F_1) = f(s_i)$  are evident. This means that these parameters ( $T_m$ ,  $I_{1047}/I_{1022}$ ,  $F_2/F_1$  and  $s_i$ ) are interconnected. At a first approximation, it may be viewed that in fact the defects in starch crystallinity can be due to both amylose tie chain destabilisation and  $F_2$  or  $F_1$  amylopectin subfraction disorganisation as arranged in crystalline and amorphous lamellae.

Thus, our study has shown that the changes leading to a decrease in melting temperatures at low growth temperatures are caused by changes in the number of structural defects within or associated with crystallites. Schematic presentation of the structural changes occurring at an

increasing growth temperature of starch granules are presented in Fig. 4. This figure compares starch sections grown at high (top of figure) and low (bottom of figure) temperatures. In the high temperature representation, more rigid or glassy amylopectin long chains are apparent in the amorphous regions, double helix registration is optimised and amylose tie chains are evident. The low temperature representation indicates a less ordered structure with sub-optimal registration of double helices in crystallites, less rigid (less glassy or more rubbery) amorphous regions and a more destabilising influence of amylose tie chains on granule order. These features will be discussed in more detail in following papers.

#### 4. Conclusions

The application of different physico-chemical approaches for the description of the melting process of starches, grown under various temperature conditions, has allowed us to estimate the thickness of crystalline lamellae and the thermodynamic parameters characterising the surface of starch crystalline lamellae. The results obtained permit us to make suppositions concerning the influence of growth temperature on the structure and the melting thermodynamic parameters of potato starches. In particular, it is apparent that a decrease in growth temperature leads to the formation of starch crystals with decreased gelatinisation temperatures whereas the thickness of crystalline lamellae is constant with respect to dimensions. Such behaviour can be explained by the accumulation of defects in crystalline and amorphous lamellae (registration and orientation respectively). This provides strength to the previously proposed hypothesis of these authors that increased environmental temperature effects on starch gelatinisation temperatures are due to enhanced registration of double helices within crystallites and optimised structural orientation within amorphous regions (which both contribute to an increase in the gelatinisation temperature) rather than enhanced crystallite length.

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