

# Starch Gelatinization: An X-ray Diffraction Study<sup>1</sup>

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## ABSTRACT

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Starch gelatinization was defined as the melting of starch crystallites, as determined by X-ray diffraction, in which the complete destruction of crystallite integrity was observed as a function of moisture content and temperature. Melting occurred over a range of temperatures, and melting temperatures increased as starch moisture content decreased. For moisture contents of 30% and higher, endothermic transitions determined by calorimetry were confirmed as reflecting loss of starch crystalline structure. The wide range of melting temperatures was attributed to different degrees of crystallite perfection within the granule and to their respective interaction with granule moisture content. For normal maize starch, heating caused formation of crystalline V-type complexes of amylose with

granule fatty acids. Formation of these complexes partly explains differences reported for heat of gelatinization values of amylose/lipid-bearing starches because of competing melting and crystallizing effects. X-ray analysis failed to confirm differential scanning calorimetry evidence of starch melting in samples at moisture contents lower than about 30% and heated to temperatures as high as 175°C. A glass transition was postulated to account for reports of apparent differential scanning calorimetry endotherms in such low-moisture starches. In the absence of an intermediate amorphous melt, the B to A or C structure changes observed in heat and moisture treated potato starches were interpreted as solid-state transitions.

There is widespread interest in the process of starch gelatinization, in which the organized granule structure is disrupted, often the first step in starch applications (Zobel 1984). Although the phenomena of gelatinization are readily apparent, the various ways (optical, rheological, calorimetric) used to determine gelatinization have made it difficult to formulate a precise and common definition. In addition, gelatinization thermograms obtained by differential scanning calorimetry (DSC) have been interpreted differently (Donovan 1979, Eberstein et al 1980, Biliaderis et al 1980, Evans and Haisman 1982, Zobel 1984, Maurice et al 1985, Hoseney et al 1986). On the other hand, the observed first-order endotherms are generally interpreted to mean that gelatinization is a melting process. Identification of the (DSC) transitions by X-ray diffraction, however, is critical to a comprehensive understanding of starch thermograms. Kugimiya et al (1980), for example, used complementary X-ray data to show that their 110–120°C endotherms were caused by the melting of crystalline V-type amylose-lipid complexes.

Application of the term "melting" to starch gelatinization is based on X-ray and synthetic polymer technologies. Thus, from diffraction studies, crystalline specimens yield reflections from crystal planes. After melting, these reflections disappear and a broad halo appears, indicating a change from a crystalline to an amorphous (molten) state. Accordingly, the material is no longer a rigid solid but rather exhibits the properties of a liquid. In this state, polymeric materials may show low fluidity, and as such, fit into the classic definition of a melt. High molecular weight materials, however, impart high viscosity or rubberlike qualities to the molten-liquid state (Mandelkern 1964).

In this report, X-ray diffraction was used to characterize transitions that produce endothermic DSC peaks when starches are heated after having been equilibrated to different moisture contents (Donovan 1979, Eberstein et al 1980, Eliasson 1980). Potato starch was used to illustrate typical starch-water interactions because of available DSC data and its purity with respect to granule lipids. Some of the data reported here are unique in that the X-ray diffraction patterns were recorded as the starch was maintained at its gelatinization (melt) temperature. This differs from past studies in which samples were gelatinized and then cooled before X-ray analysis. As a consequence of the cooling process, moist gels could display crystalline artifacts. In this study, samples that were first heated, cooled, and then subjected to X-ray analysis were in sealed tubes and were limited to 20% or less moisture to avoid recrystallization.

Maize (corn), potato, and waxy maize starches were investigated to cover granules with a range of crystal structure, amylose/amylopectin ratio, and lipid content. Maize has an A-type structure, 27% amylose, and polar lipids that can complex with the amylose fraction to form V crystals. These V structures are formed from collapsed amylose helices in which chemical adjuncts are trapped inside. Complex formation has been established by X-ray studies and investigated by DSC; the effect on thermograms of starch, however, has been subjected to speculation (Hellman et al 1954, Kugimiya et al 1980, Stute and Konieczny-Janda 1983, Zobel 1984, Biliaderis et al 1985). Waxy maize also has an A structure and lipids similar to those in maize, but amylose is absent for complex formation. Potato starch has a B structure and 22% amylose but lacks a lipid fraction for complex formation. The C form is native to certain root and tuber starches. From the standpoint of this study, C is formed when potato starch is heat and moisture treated (Sair 1967). X-ray patterns of starch structures are diagrammed in Figure 1 (Zobel 1964, 1988a).

## MATERIALS AND METHODS

X-ray patterns were taken primarily with a Guinier-Simon (G-S) circular cassette camera in which sample temperatures were

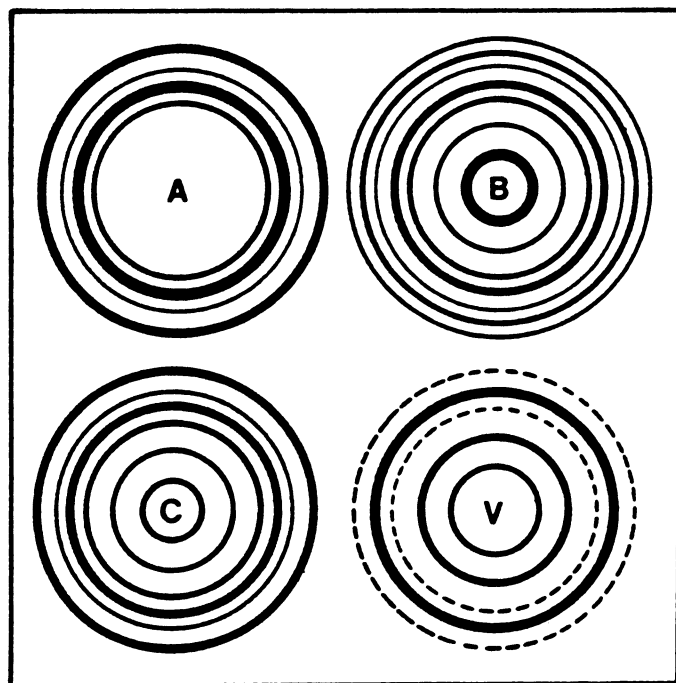


Fig. 1. Starch X-ray pattern designations.

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controlled during exposure; it is manufactured by Enraf-Nonius. Multiple exposure diffraction patterns were made on 13 × 16 cm pieces of Kodak OMAT film Type X-AR backed with an intensifying screen. The G-S camera was supplied with monochromatic copper radiation from a tube operating at 35 kV and 20 mA. At each moisture content, patterns were taken sequentially beginning at 25°C and continuing to temperatures beyond the sample's anticipated melting point. After 15 min equilibration at each temperature, sample X-ray exposures were made for 1 hr. Each exposure was a narrow strip corresponding to a radial slice through the type patterns shown in Figure 1. Pattern intensities were estimated visually. Judgments were based on the

**TABLE I**  
Effect of Heating on the Crystalline Structure  
of Granular Potato Starch Containing 69–22% Moisture

Moisture (% wt)	Intensity <sup>a</sup> of X-ray Diffraction Pattern						
	25°C	61°C	73°C	86°C	93°C	102°C	126°C 148°C
69	10	1	0				
59	10	3	1	0			
52	10	8	3	0			
38	10	9	6	1	0		
30	10	10	7	4	2	0	
22	10	10	10	9	9	7	* * <sup>b</sup>

<sup>a</sup> Intensities were estimated visually. Range: 10 at 25°C to 0 at the temperature of complete pattern loss.

<sup>b</sup> Residual pattern remains.

strongest line in the B pattern (5.2 Å) being given a value of 10 at 25°C and 0 at the temperature of complete pattern loss.

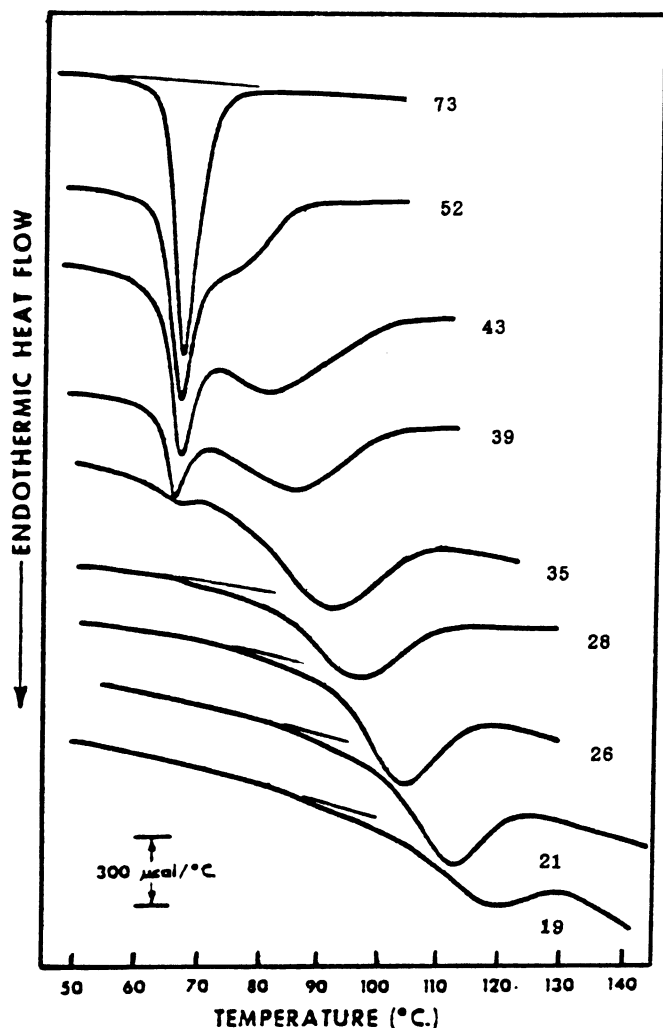
Samples for X-ray diffraction were prepared from commercial starches that were placed into thin-walled (0.01 mm) glass capillary tubes (2.0 mm diam). The capillary tubes, of German manufacture (Mark-Rohrchen), were obtained from Blake Industries, Inc., Scotch Plains, NY. After loading the capillary, it was sealed using a flame or a heat-resistant silicone adhesive; sealing was done in a manner that minimized free air space into which moisture could transfer during heating. Samples of high (69%) and intermediate (59–30%) water contents were prepared by weighing the starch, and then the water, directly into a capillary. After sealing, the capillary tube was generally held for 24 hr for moisture equilibration. Specimens with 22% or less water were prepared in a dry desiccator by desorption from starch saturated with water. Selection of the low-moisture conditions was determined from DSC investigations that report first-order endotherms on similar samples (Donovan 1979, Eliasson 1980, Burt and Russell 1983, Maurice et al 1985, Biliaderis et al 1986). Dry specimens were analyzed not only in the G-S camera but also after they were heated for an hour in an air oven and then X-rayed. A flat cassette camera attached to an auxiliary port on the X-ray generator was used for these samples; recorded patterns were of the type shown in Figure 1. A metal block machined to fit over the end of the X-ray collimator held the capillary in place for irradiation. Adjustable jaws, fitted to the block, aligned the capillary with the X-ray beam. The block permitted quick transfer of samples from oven to the X-ray machine, and its high heat capacity slowed sample cooling. Exposure times were 0.5 hr, with the sample 5.0 cm from the X-ray film. All G-S and flat-cassette specimens were reweighed after heating to ensure their initial moisture content.

The flat cassette camera also was used to verify the presence of, and to determine the identity of, lower levels of crystallinity that occurred in some of the samples. This technique was helpful in part because of the higher flux of X-radiation that was available to give better pattern definition. In other instances, patterns were taken with this camera immediately after breaking a sealed capillary tube and hydrating the crystal structure by adding water to the sample. This procedure enhances existing crystallinity but avoids any recrystallization by not allowing the sample to age.

## RESULTS AND DISCUSSION

G-S camera data obtained from potato starch at 69, 52, 38, 30, and 22% moisture content are summarized in Table I. Thus, at 69%, the initially strong B pattern had largely disappeared at 61°C and was absent at 73°C. At 59% moisture, the main loss of pattern shifted to 73°C and total loss to 86°C. The 52, 38, and 30% samples exhibited complete loss of starch crystallinity at 86, 93, and 102°C, respectively. The 22% moisture sample, however, showed anomalous behavior with a major but incomplete loss of pattern at 126°C (Table I). Raising the temperature to 148°C did not melt an apparent structure that was identified as A rather than the starting B. Identification was aided by the hydration technique cited earlier. In contrast with the behavior of the 22% moisture sample, other samples in Table I showed complete loss of pattern (crystallinity) at specific temperatures.

The X-ray experiments on potato starch (Table I) were designed to cover the melt temperature and moisture content ranges shown in Figure 2, which is reproduced from the DSC investigation of potato starch by Donovan (1979). Moisture contents are shown as percent by weight rather than published volume fractions to facilitate comparisons with present X-ray data. Three areas of moisture content were covered: high (69%), intermediate (59 to 30%), and low (22%). Thus, in the high and intermediate moisture regions, loss of X-ray crystallinity (Table I) generally agrees with DSC melt temperature and endotherm data acquired on starch samples at comparable moisture contents. With the exception of the 22% moisture sample, Table I indicates a steady loss of starch crystallinity throughout the temperature range of melting. In effect, the data reflect the melting of a variety of starch crystallites. These observations, DSC melt temperature agreement and steady



**Fig. 2.** Differential scanning calorimetry thermograms of potato starch labeled with weight percent water in each sample. Reprinted with permission from Donovan (1979), © John Wiley & Sons, Inc.

crystallinity loss, along with a lack of narrowing in diffraction line widths, indicate that recrystallization or annealing were not factors in our G-S camera experiments on potato starch.

X-ray analysis of the 59, 52, and 38% moisture content potato starches was of interest because two endotherms are recorded by DSC analysis of these samples; one at about 70°C and another at around 80–100°C (Fig. 2). Both of these endotherms are defined by these X-ray experiments as indicating starch melting. We conclude that the two endotherms describe thermal events that are alike. On the other hand, differing events are suggested when the terminology of gelatinization (G) and melting (M) is used to describe these respective endotherms. The outcome of the X-ray and DSC data is that it provides two aspects of starch melting: the loss of crystalline order within the granule and the energy required to cause that loss. Both the X-ray and DSC data are congruous with the view that starch gelatinization and general granule disruption in water is dependent upon starch crystallites with varied degrees of perfection (or internal order) that become disordered at temperatures that are contingent upon the amount of water available for melting. Hence at 30% or higher moisture contents, starches are analogous to other natural and synthetic polymers where the degree of crystalline order and polymer-solvent/plasticizer interactions are major factors in determining their melt behavior and other properties (Flory 1953, Mandelkern 1964, Meares 1965, Zobel 1984).

G-S camera experiments (data not shown) on normal maize starch with limited water content (45–50%) indicate crystallite melting at higher temperatures than the 66–73°C range in excess water (Biliaderis et al 1980, Eberstein et al 1980, Zobel 1984). Substantial loss of A-type crystallinity occurs at 92°C and complete loss by 103°C. In addition, as shown by a strong 4.4 Å X-ray spacing, a V-type structure begins to appear prior to melting of the A structure. The "V" is due to complex formation between granule fatty acids and the amylose fraction, which is generally considered as being in the amorphous phase of granular maize starch (French 1984). Unlike high-amylose maize starches (Zobel 1988a), the presence of V in normal maize starches cannot be determined with certainty because of an overlap of diffraction lines. Hence, the appearance of a V structure under the conditions cited suggests its presence as crystal nuclei that then mainly require favorable heat and moisture conditions for development (Zobel 1988a). The V structure is not only retained through the 103°C exposure but also exhibits further development during two additional 1 hr exposures at 120 and 142°C. After being held for 18 hr at room temperature, the sample showed a well-formed V structure as well as B. The B structure is due to crystallization of an amorphous starch melt, which presumably is mainly amylopectin owing to complexing of the amylose with granule fatty acids. Thus, heating amylose-bearing starches that contain fatty acids can cause simultaneous crystallizing and melting effects to occur. These findings can account for part of the wide differences between authors in heat of gelatinization calculations for high-amylose and regular maize starches (Zobel 1984).

The effect of heating starches having less than 30% water content also warranted investigation, because DSC literature is not clear on whether or not melting occurs at this or lower moisture contents (Donovan 1979, Wootton and Bamunuarachchi 1979, Eberstein et al 1980, Eliasson 1980, Burt and Russell 1983, Maurice et al 1985, Biliaderis et al 1986). Furthermore, the 22% sample (Table I) does not follow the melting path shown by the higher moisture content samples. Unfortunately, the G-S data (Table I) at 126 and 148°C give the impression that considerable melting had taken place in this sample. Table II shows work on other potato starch samples and the structure transitions that occur under the moisture contents and temperatures indicated. In these experiments, the heated samples showed some loss of intensity but not nearly what was indicated in the earlier experiment of Table I. Two reasons can be cited: the heating times were much shorter (1 hr vs. 6), and the X-ray source intensity was higher. Regardless, significant melting is not believed to have occurred in any of the potato starch samples. However, the observed changes in pattern quality are evidence of small, and or, imperfect crystals (French 1984). Such loss of

crystallite integrity is understandable from the B and A starch structure determinations of Sarko and Wu (1978). Their findings indicate that a B-to-A transformation requires reorientation in the packing of the double helical starch molecules and a redistribution of water within the crystallites—for example, a change from 36 water molecules per unit cell in the B structure to eight per cell in the A. And, lacking sufficient moisture for their reordering, transformed crystallites would give diffuse pattern reflections (Zobel 1964). Sair (1967) reports, for example, that a high moisture atmosphere (100% rh) during heat-treatment was "essential for permanent conversion of one X-ray pattern to another." Arguments against recrystallization as an explanation for the observed transitions in potato starch are as follows: 1) no amorphous melt peak was evident from the G-S camera negatives that were obtained on samples maintained at elevated temperatures; 2) the time intervals during the G-S experiments at 102, 126, and 148°C were too short for recrystallization to occur (Hellman et al 1954); and 3) the level of crystallinity in transformed and hydrated samples appeared more like that found in native starches than that in a potato starch gel. Thus, we conclude that a B-to-A or B-to-C structure change occurred in the solid state rather than through the process of melting and recrystallization.

Table II shows the effects on crystal structure of heating maize and waxy maize starches as well as potato under conditions that are cited. As stated earlier, the conditions were chosen to reflect as nearly as possible experimental conditions where DSC experiments appear to denote melting endotherms. By visual examination, none of the starches showed any physical damage due to heating. The transitions shown for potato starch not only have been discussed earlier, but also have been described in the literature on heat and moisture treatments of this starch (Sair 1967; Zobel 1988a,b). One possible consequence of our findings is that low-moisture, short-time, high-temperature conditions for heat and moisture treatment of potato starch could lead to commercial processes that are more feasible than those taking from 10 to 16 hr. Maize starch (Table II) at either 10 or 16% moisture that was heated for 1 hr at 175°C gave the same results as those observed under higher moisture conditions, i.e., formation of V with retention of A structure prior to gelatinization. Because the granules remained intact, conditions are provided for effecting formation of V structure in granular starch. The formation of V structures in gelled and in semidry extruded starches is discussed by Zobel (1984) and by Mercier and co-workers, respectively (Charbonniere et al 1973, Mercier et al 1979, Mercier et al 1980). A waxy maize starch (Table II), after equilibration to 12% moisture and heating to 175°C, showed no structural changes by X-ray diffraction and no loss of diffraction intensity. In contrast, Maurice et al (1985) indicate a DSC melting endotherm at about 175°C for a 9% moisture starch.

Overall, our results do not confirm "apparent" DSC endotherms reported for starches at about 20% or less moisture content as being due to melting (Donovan 1979, Burt and Russell 1983, Maurice et al 1985, Biliaderis et al 1986). We postulate rather that

**TABLE II**  
Crystal Transitions Effected by Heating  
Low-Moisture Granular Starches

Starch	Conditions		X-ray Pattern	
	Water (%)	Temperature (°C)	Original	Final
Potato	15	126	B	C
Potato <sup>a</sup>	16	125	B	C
Potato	19	125	B	A
Potato <sup>a</sup>	22	126	B	A
Potato	22	148	B	A
Maize	10	175	A	A + V
Maize	16	175	A	A + V
Waxy maize	12	175	A	A

<sup>a</sup>X-ray simultaneous with heating; for others, heating was followed by X-ray analysis.

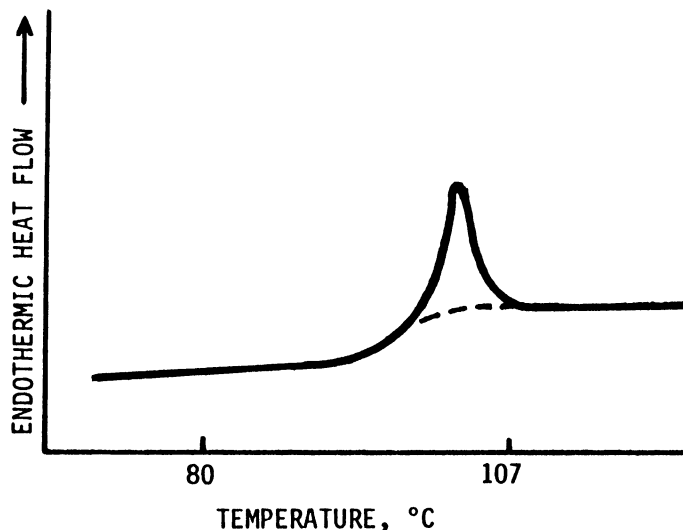


Fig. 3. Thermogram of glassy polystyrene showing an anomalous endotherm associated with a glass transition temperature at 100°C.

the respective DSC tracings depict a starch glass transition ( $T_g$ ) (Zobel 1988a). In support of this view, thermograms for the low-moisture potato starches in Figure 2 are cited as showing thermal baseline shifts that are characteristic of glass transitions. Likewise, shifts analogous to those in Figure 2 are reported in the references cited above for wheat, rice, and waxy maize starches. The proposed transition also is seen as providing the molecular mobility needed for the observed B-to-A or B-to-C transformations that occur in potato starch during heat and moisture treatments. Furthermore, a glass transition could account for the results of Burt and Russell (1983), who found retention of granular structure but loss of birefringence in low-moisture samples (26, 12, and 8%). In these instances, passage through a glass transition could result in a loss of birefringence by relaxing molecular orientation within amorphous parts of the granule.

As a rule, glass transitions are not thought of in terms of causing endotherms. Glassy polymers, however, often display apparent endotherms like that shown in Figure 3, which was adapted from Petrie (1972). Such polymers, which show no X-ray crystallinity, generally have been annealed by slow heating, causing more orderly arrangements between chain segments in amorphous regions. Upon heating through the glass transition, an endothermic event is displayed with the moving of polymer segments into an adjacent free volume. For starch, the process of granule formation and aging can be equated with slow annealing. In addition, the semicrystalline nature of starch (15–40%, Zobel 1988b) means that some degree of molecular order can be expected in amorphous regions next to crystallites (Meares 1965). An interaction between these phases in starch was confirmed by Zeleznak and Hoseney (1987) who found that the  $T_g$  of native wheat starch may be as much as 30°C higher than its pregelatinized counterpart. In addition, one of their published thermograms could be interpreted as showing a slight endotherm at the temperature of a  $T_g$ . One can foresee, therefore, the possibility of transitions of the type shown in Figure 3 for some of the amorphous regions in starch.

Further investigation is certainly warranted to develop information on the possibility of relatively high-temperature glass transitions in low-moisture starches. Because heat capacity changes are often slight and diffuse through the transition point, techniques other than DSC need to be investigated. For example, the utility of thermomechanical analysis (dilatometry) to identify these transitions has been demonstrated by Maurice et al (1985) and Maurice (1986). X-ray analysis, however, must remain the final arbiter as to whether or not a thermal event is melting.

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