

STUDY OF SAGO STARCH (*METROXYLON SAGU*) GELATINIZATION BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Differential scanning calorimetry (DSC), at various heating rates (1-30C/min) and water:starch ratios (0.1:1-4:1), was used to study gelatinization phenomena of sago starch. The results showed that the gelatinization temperature and enthalpy (ΔH) of starches in excess water were 60-77C and 15.5-15.8 J/g, respectively. ΔH of gelatinization remained substantially the same at excess water contents, but decreased significantly beyond a water:starch ratio of 1.3:1. A single endothermic transition (G) that transformed into a double endotherm (G and M_1) and only M_1 occurred, respectively, at excess, intermediate and limited water contents. At 50% water content, evidence of the M_1 endotherm was observed, and 85C represented the effective conclusion temperature (T_m) at the end of melting for sago starch. The experimental data were treated thermodynamically by applying an equation describing phase transitions of semi-crystalline polymers. The calculated value for the melting point of the undiluted polymer (T_m^0) was 432 K ($R^2=0.96$).

INTRODUCTION

Sago starch (*Metroxylon sagu*), obtained from the pith of the sago palm, is a useful resource as a commercial raw material and is an important product in South Asia (Yatsugi 1986). Sago palm contains a large amount of starch in its trunk, and its starch productivity has been calculated to be four times that of paddy rice (Ishizuka *et al.* 1995).

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Starch gelatinization is an important phenomenon occurring in various food processing operations. Processes such as baking of bread and cakes, extrusion of cereal-based products, thickening and gelling of sauces, production of pregelatinized starch and pie fillings are all dependent on proper starch gelatinization. Each starch molecule forms a part of many crystallites in the periodically spaced, crystalline, shell-like layers of starch granules and extends through many layers of crystallites (Yamaguchi *et al.* 1979). The noncrystalline, or amorphous, portions of these molecules thus connect the crystalline layers. The ordered crystalline layers give rise to the birefringence of the granule.

Slade and Levine (1988) reported that gelatinization is a nonequilibrium melting process, actually a continuum of relaxation processes that occurs during heating of starch in the presence of plasticizing water, in which crystallite melting is indirectly controlled by the kinetically constrained, continuous amorphous surroundings. The gelatinization process will result in increased viscosity, which eventually slows down the process. At high water content, the increase in viscosity occurs after the gelatinization endotherm has been passed (Eliasson 1992). Different hypotheses have been advanced to explain the observed DSC thermal events associated with starch gelatinization. The most attractive of these views native starch as a partially crystalline polymer that, on heating in the presence of water, undergoes firstly a prerequisite second-order glass transition or softening of the amorphous phase, followed by first-order, nonequilibrium melting of crystallites (Seow and Teo 1993).

Maaruf *et al.* (1999a) reported that the gelatinization temperature of sago starch was found to increase in the presence of sucrose, whereas the gelatinization enthalpy was unaffected. The gelatinization temperature increased and then decreased as the NaCl concentration increased. The effects of sugars, emulsifiers, and starch mixtures and their interactions were an increased gelatinization temperature and enthalpy and a narrower gelatinization temperature range ($T_m - T_c$) after annealing of sago starch (Maaruf *et al.* 1999b).

Differential scanning calorimetry (DSC) is particularly well-suited to investigate the phase transitions of starch water systems, because it allows (1) study of starch gelatinization over a wide range of starch/water ratios, (2) determination of gelatinization temperatures above 100C, and (3) estimation of transition enthalpies (Biliaderis *et al.* 1980). The heating rate should be slow enough to obtain distinct and reproducible peaks for each transition. Commonly, heating rates from 1 to 10C/min are used (McNaughton and Mortimer 1982).

The objective of this study was to investigate the gelatinization temperature and enthalpy of sago starch, heated to a temperature of 120C at water:starch ratios of 0.1:1 to 4:1, using DSC. The significance of the amount of water on the mechanism of starch gelatinization was also investigated.

MATERIALS AND METHODS

Material

Sago starch (*Metroxylon sagu*) was a product of PPES Sago Industries (Mukah, Sarawak, Malaysia).

Determination of Moisture Content

Moisture content was determined according to an AOAC method (1984). Five to ten grams of starch were accurately weighed into a preweighed dish (provided with cover). The contents and dish were dried in an oven at $105 \pm 2\text{C}$ for 12 h and then removed to a desiccator, cooled and reweighed. The moisture content was expressed as percentage of lost water: original mass.

DSC Measurement

A Perkin-Elmer (Norwalk, CT) Model DSC-7 differential scanning calorimeter with an attached Unix Operating System was used in this study. The melting point and enthalpy of indium (m.p. 156.6C , ΔH_m 28.5 J/g) were used for temperature and heat capacity calibrations. An empty pan was used as a reference to balance the heat capacity of the sample pan. Starch slurries for DSC analysis were prepared by procedures modified from those described by Dorothy and Nicholas-Lauer (1990) and Jang and Pyun (1996). Starch slurries (9-11 mg) were prepared in aluminum DSC pans capable of withstanding at least 30 psia internal pressure after sealing. Pan capacity is about 20 mL.

Effect of Heating Rate

The effect of heating rate was determined according to the procedure described by Nakazawa *et al.* (1984). Starch slurries were weighed (Electronic Balance-ER 180A) into tared aluminum DSC sample pans, and distilled water was added, using a disposable syringe (1 mL/cc) to give a water:starch ratio of 1:1 (w/w), until all the granules were wetted and water was uniformly distributed across the bottom of the pan. The final weighed starch (9-11 mg) was immediately sealed using a volatile sample sealer accessory. Triplicate sample pans were equilibrated at 25C for 10 min, before they were heated from 25 to 100C at different heating rates of 1.0, 1.5, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, or 30.0C/min.

Effect of Water Content

Sago starch slurries were prepared with a range of water: starch ratios from 0.1:1 to 4:1 (water content: 9.1 to 80.0%). Starch was weighed into a tared

aluminum DSC sample pan. Distilled water was added with a disposable syringe (1 mL/cc), until the granules were wetted and water was uniformly distributed across the bottom of the pan. Pans were then hermetically sealed using a volatile sample sealer accessory. Sample pans were allowed to equilibrate for 2 h at room temperature before being heated. Triplicate sample pans were equilibrated in the DSC at 20C for 10 min before being heated from 20 to 120C at a rate of 10C/min. The volume fraction of water (ν_1) in a slurry was taken as the total volume of water divided by the total volume of starch and water.

Thermograms were analyzed using UNIX system software. The onset (T_o), peak (T_p) and conclusion temperatures (T_m) associated with the gelatinization of sago starch were measured by projecting the tangent of the point of greatest slope to its point of intersection on the temperature base line. Two major apparent endothermic transitions observed were labeled, in the manner suggested by Donovan (1979), as the G and M_1 endotherms. The combined area of the G and M_1 endotherms was used to calculate the overall gelatinization enthalpy (ΔH), which was expressed in J/g dry starch (Fig. 1).

Partial Scanning and Flory Analysis

Other pairs of pans were subjected to only partial scanning (from 20C to 57, 63, 72, 85, 87, 89, 92 or 100C) before cooling and immediate complete rescanning, using a procedure modified from that described by Slade and Levine (1988). By comparing the thermograms in the partial initial scan and the complete rescan, the thermal events that occurred during the complete rescan could be determined.

From a practical viewpoint, the Flory analysis provides a basis for comparison of thermal stability of starch materials and allows estimation of the apparent T_m under various moisture conditions (Biliaderis 1992). According to the Flory equation (Flory 1953), the following relationship exists between the melting point of a polymer and diluent concentration:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{(R)}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot (\nu_1 - X_1 \nu_1^2) \quad (1)$$

where ΔH_u is the change in enthalpy of fusion per repeating unit of glucose, V_u/V_1 is the ratio of the molar volume of the repeating glucose unit in the starch chain to that of the diluent (water), R is the gas constant, T_m^0 (K) is the melting point of the undiluted polymer, ν_1 is the volume fraction of the diluent, and X_1 is the Flory interaction parameter. According to Flory (1953), the melting point,

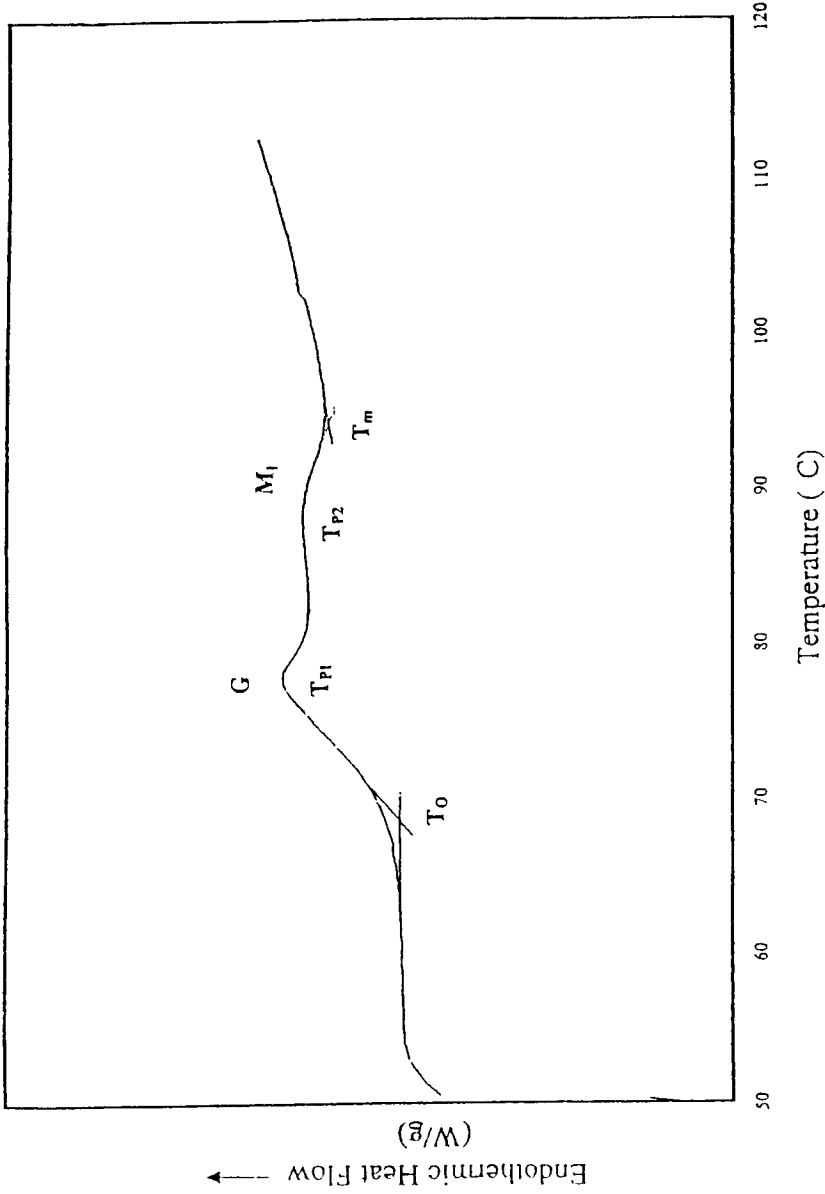


FIG. 1. DSC HEAT-FLOW CURVE OF SAGO STARCH, AT A WATER:STARCH RATIO OF 1:1, SHOWING DESIGNATED THERMAL TRANSITION TEMPERATURES

T_m , of the heated starch/water mixture was taken as the melting point of the most perfect crystallites at the upper temperature limit of the endothermic transitions. For an ideal solution, $X_1=0$; hence, Eq. (1) gives a linear relationship between ν_1 and $1/T_m$. The intercept at $\nu_1 = 0$, therefore, gives the reciprocal of the melting point of the most perfect crystallites of the undiluted polymer, $1/T_m^0$.

Statistical Analysis

Data were subjected to analysis of variance and analyzed by Duncan's multiple range test, to give statistically significant differences at a 5% level using a statistical Analytical Software package (SAS 1995).

RESULTS AND DISCUSSION

Effect of Heating Rate

Selection of the DSC heating program was particularly important, because the rate at which the temperature is raised in the furnace has a large influence on the results obtained. The heating rate is an important factor in the measurement of the gelatinization temperature of starch (Warne 1992). The thermal transition temperatures were found to increase with increasing heating rate. For heating rates from 1.0 to 30.0C/min, the values of T_o , T_{pl} and T_m progressively increased from 59.1 to 70.3, 62.8 to 78.5, and 66.7 to 95.4C, respectively. The enthalpy of gelatinization also increased with increasing heating rate, as shown in Fig. 2 and 4.

It is well established that if the process occurring during the scanning is kinetically limited, the shape of the thermogram is strongly dependent on the heating rate (Haines 1995). The effects of heating rate on the sago starch gelatinization process were carefully studied. The thermograms in Fig. 3 were obtained at nine different heating rates, and the thermograms were redrawn after subtracting the baseline heat effects. In general, the slower the heating rate, the smaller was the endotherm area and the lower the endotherm temperatures. It also appeared that the slower the heating rate of the starch, the sharper was the endotherm and the lower the peak temperature. When the heating rate was less than 10C/min, the area of the endotherm decreased; ΔH decreased from 14.5 to 2.3 J/g (Fig. 4). Warne (1992) reported that low heating rates (2 to 5C/min) give maximum peak separation, thus discouraging peak overlap, but at the expense of poorly defined peaks.

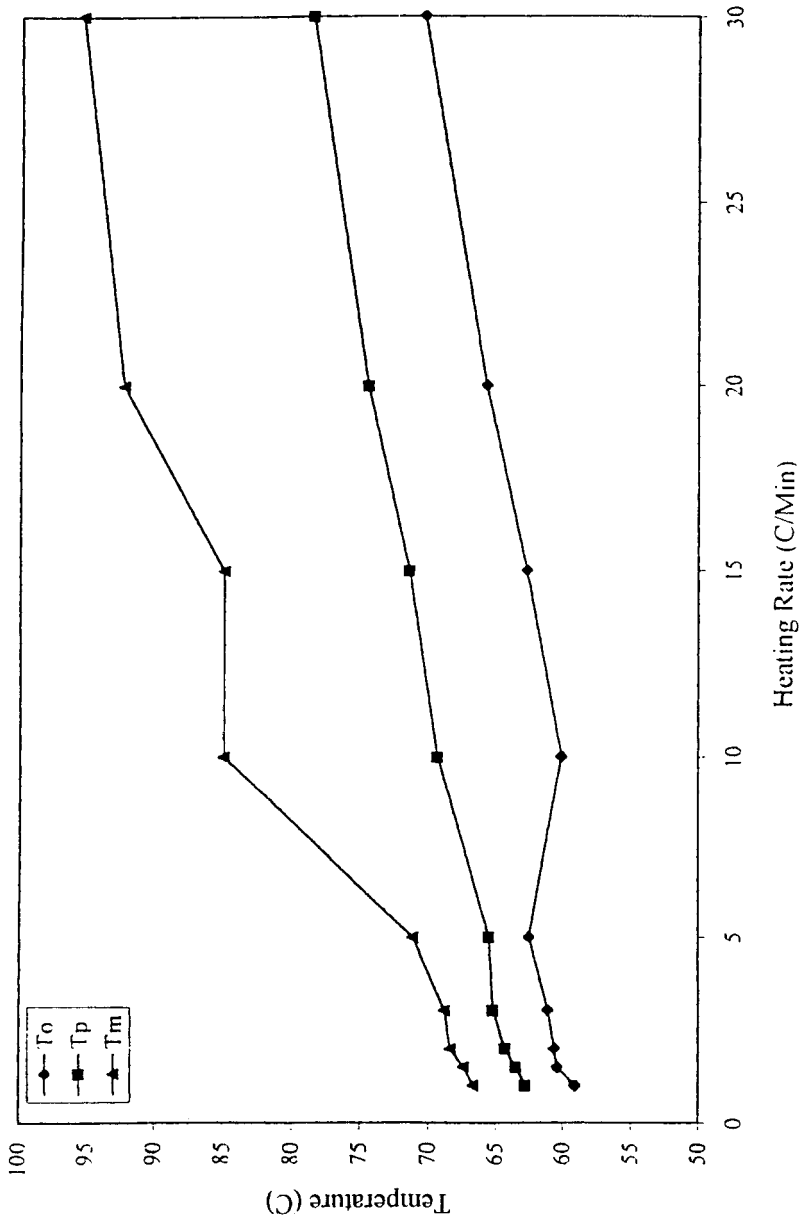


FIG. 2. EFFECT OF DSC HEATING RATE ON T_0 , T_p AND T_m TEMPERATURES FOR GELATINIZATION OF SAGO STARCH

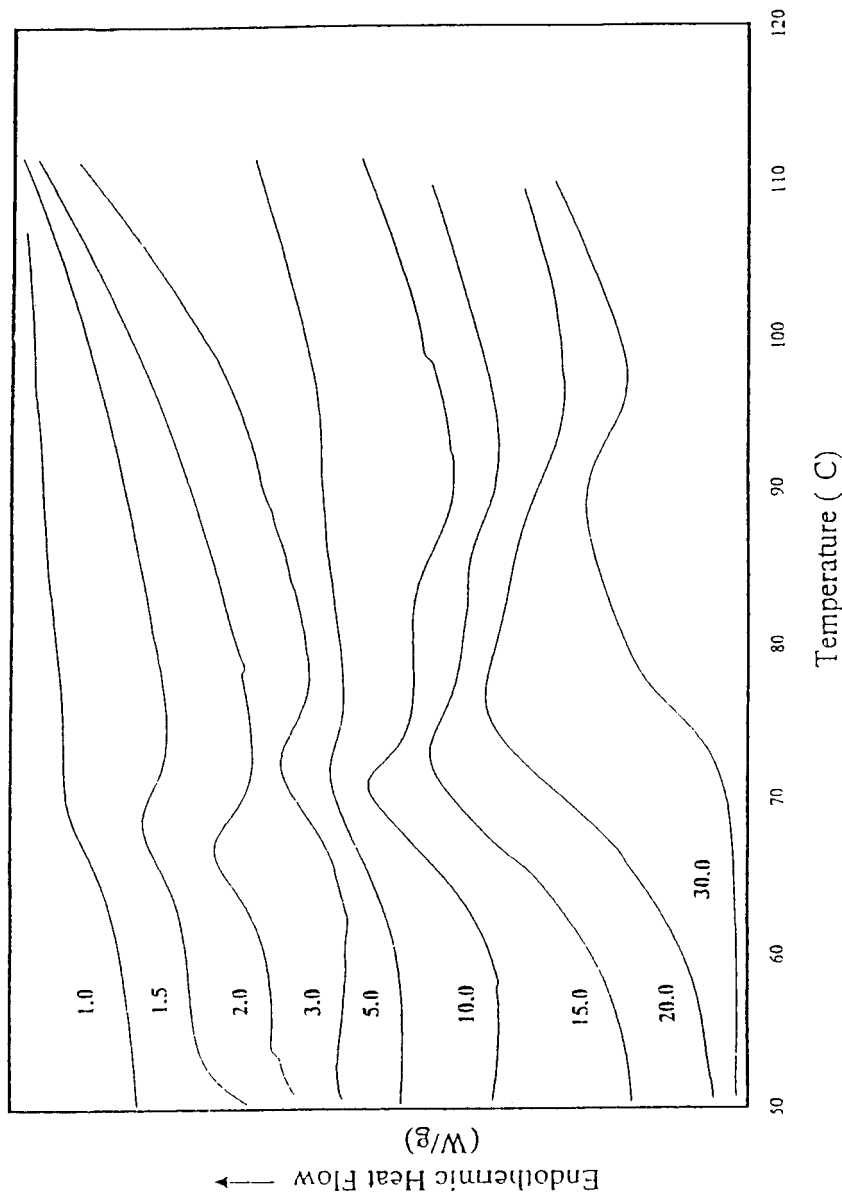


FIG. 3. DSC THERMAL CURVES FOR SAMPLES HEATED AT DIFFERENT RATES (1 TO 30C/MIN)
The water to starch ratio was 1:1.

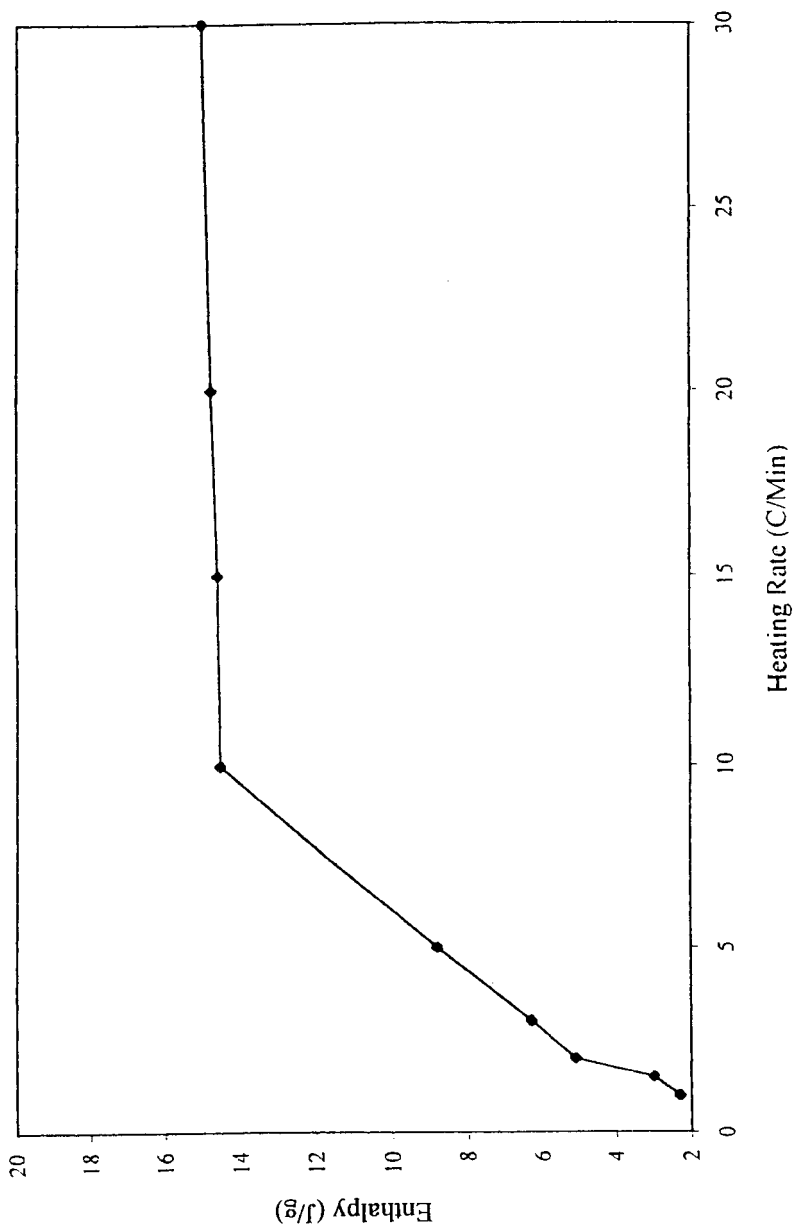


FIG. 4. EFFECT OF HEATING RATE ON GELATINIZATION ENTHALPY

Heating rates below 10C/min illustrated the case in which two thermal conversions appeared to overlap wholly or partly. In the case of sago starch, the slower the heating rate, the larger the interval between which the conversions appeared in the recording. When the heating rate was greater than 15C/min, the thermal effects taking place were recorded as progressively narrowing and closely overlapped peaks. This corresponded with ΔH increasing from 14.6 to 15.0 J/g (Fig. 4). According to Haines (1995), a rapid heating rate may allow some starch to melt before it decomposes, while at a slow heating rate, decomposition reactions may occur below the melting temperature.

In the rest of this study, a heating rate of 10C/min was used. However, the selection of a given heating rate would depend heavily on the nature of the sample under investigation, the technical capability of the DSC, and on the thermogram produced. Figure 3 shows that only at 10 and 15C/min did two endothermic transitions occur for a water:starch ratio of 1:1, and the slower the heating rate, the sharper were the endotherms produced. Warne (1992) reported that a heating rate in the region of 10C/min is generally acceptable. Many previous investigators (e.g. Maurice *et al.* 1985), studying a variety of starches, have reported that, at a water:starch ratio of 1:1, two endotherms occurred. From our study, it was concluded that the position of the endothermic peaks varied with the heating rate when other experimental conditions remained constant.

Effect of Water Content

Gelatinization and swelling are commonly designated by a temperature range or as the starting temperature at which the instrumental signal is detected. A deflection or peak in the DSC thermogram indicates a change in heat content and in the thermal properties of starch. The result of such measurements is a thermal analysis curve, and the features of this curve (peaks, discontinuities, changes of slope, etc) are related to thermal events in starch. In this study, DSC curves recorded at a heating rate of 10C/min, for temperatures between 20 and 120C, were significantly affected by water content, over a 9.1 to 80% range. The linear baselines observed before and after the gelatinization endotherm were extrapolated through the transition region. In accord with Shiotsubo (1984), the baseline of the transition region was determined as the slope of the extrapolated line that changed in proportion to the extent of the transition.

During gelatinization, dual endothermic transitions observed and depended on the water:starch ratio of the sago starch. In the presence of excess water, a single endothermic peak associated with gelatinization is typically observed. At intermediate water contents, however, this single peak is transformed into two endothermic transitions (labeled as the G and M₁ endotherms by Donovan

(1979)). At much lower water contents, the G endotherm disappears, leaving only the M_1 endotherm.

As illustrated in Fig. 1, the intersection of the largest change in slope with the baseline is referred to as the onset temperature (T_o), the minimum point as the peak temperature (T_p), and the point of return to the baseline as the melting/conclusion temperature (T_m). The DSC pan is sealed, so that water is not lost from the system during heating; hence, starch can be repeatedly recycled in the DSC. Figures 5 and 6 show the DSC thermograms of sago starch at different water:starch ratios (0.1:1 to 4:1). The relatively small endothermic transition labeled M_1 became increasingly prominent with decreasing water content. Above 66.7% water content, only one endotherm labeled G was present, with T_o and T_m temperatures of 60C and 74C, respectively.

It can be suggested that the DSC curve in the temperature region of T_o reflects structural changes in the starch during the initial gelatinization stage, and that in the temperature region above T_p , the changes correspond to a viscosity increase. For water:starch ratios from 0.3:1 to 4:1, the location of the first endothermic transition (G) did not change with water content, whereas the second transition (M_1) was shifted to higher temperatures with decreasing water content. The second endothermic transition (M_1) occurred at about 73.3C, with a peak temperature at 75.8C, for sago starch in excess water (66.7%), and became broader and was shifted to higher temperatures as the water content was decreased. Lund (1984) reported that about 60% water is required for complete gelatinization, and about 25% is required to initiate gelatinization.

Donovan (1979) suggested that, in the presence of less water, the endothermic transition is characterized as a solvent-aided melting of crystallites in the starch granules. The melting is responsible for the appearance of the second peak. Peak G can be assigned to a cooperative, water-mediated melting of starch crystallites, and M_1 can be assigned to the melting of the amylopectin crystallites (Shogren 1992) or of the remaining crystallites (Burt and Russell 1983). When the water content was decreased from 56.5 to 23.1%, a biphasic endotherm (G and M_1) were observed for sago starch, and it shifted to higher temperatures as the water content was further decreased (Fig. 5 and 6). The area of the G endotherm decreased progressively, while that of the M_1 endotherm increased and became predominant at a water content of 23.1%.

This suggests the interpretation that two kinds of structures may be present or that one kind of structure may be present in two different environments. For sago starch with water contents greater than 56.5%, single endotherms (G + M_1) were observed, with peak temperatures of 70.6-73.9C and ΔH values as high as 15.7 J/g. At sufficiently high water contents, the second transition peak disappeared (Fig. 5 and 6). At a water content of 56.5%, the M_1 endotherm appeared. Biliaderis *et al.* (1980) reported that under conditions of excess water, a single endotherm representing the gelatinization process is evident. However,

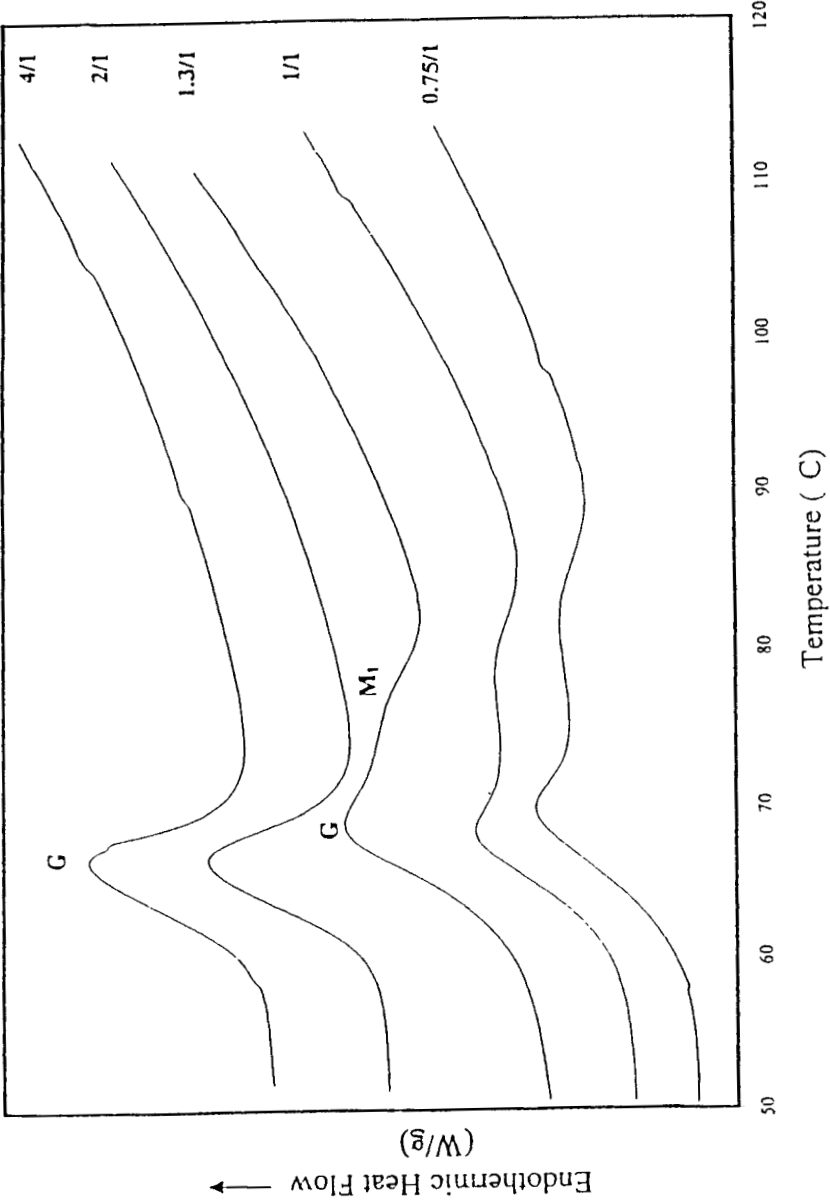


FIG. 5. TYPICAL ENDOTHERMS FOR SAGO STARCH SLURRIES WITH VARIOUS WATER:STARCH RATIOS (0.75/1 TO 4/1), HEATED TO 120°C AT 10°C/MIN

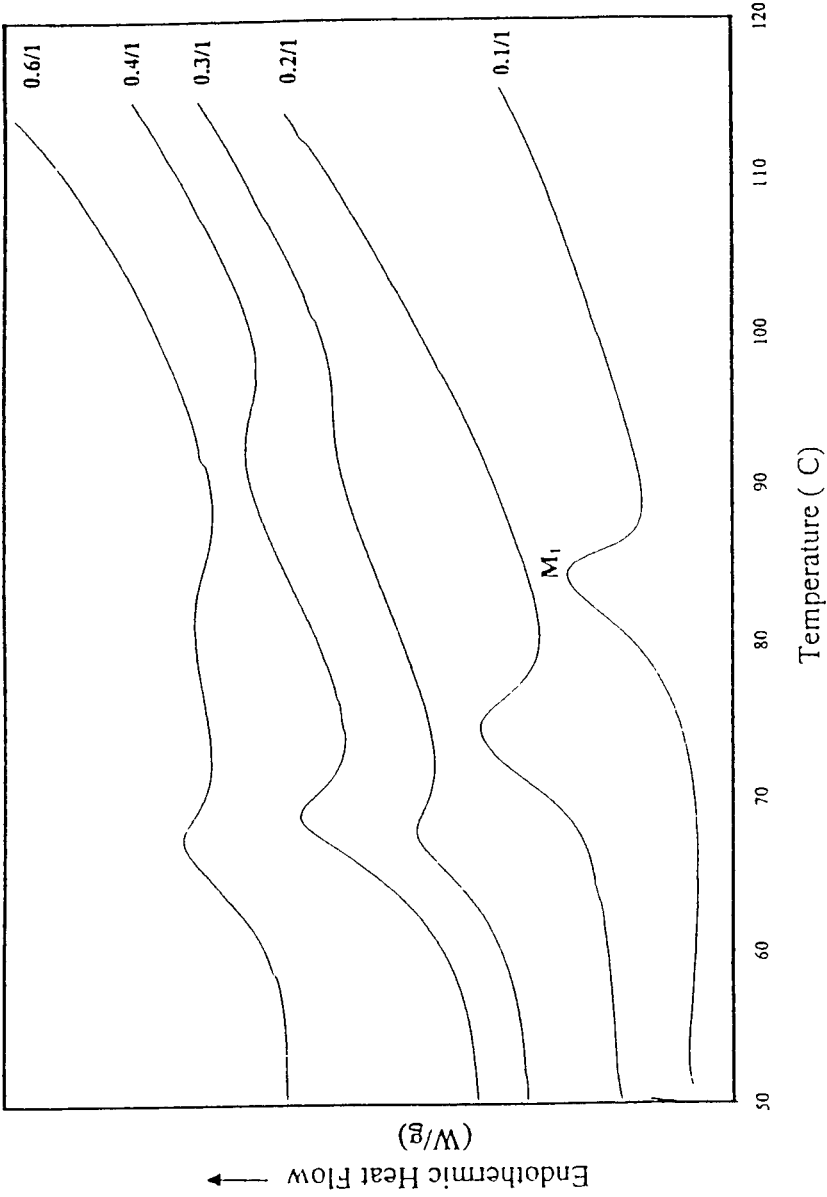


FIG. 6. TYPICAL ENDOTHERMS FOR SAGO STARCH SLURRIES WITH VARIOUS WATER:STARCH RATIOS (0.6/1 TO 0.1/1), HEATED TO 120C AT 10C/MIN

when water content is limiting, a second endotherm becomes apparent at higher temperatures, and this has been attributed to the 'true' melting of the amylopectin crystallites present in the starch granule.

In this study, the excess water content for sago starch was greater than 56.5%. In comparison, excess water contents greater than 70% and intermediate water contents from 35 to 60% have been previously reported (Donovan and Mapes 1980; Donovan 1979; Biliaderis *et al.* 1980; Evans and Haisman 1982). Wang *et al.* (1991) claimed that, regardless of starch source, the amount of water needed for complete gelatinization is 61%. Starch-water mixtures with less than 61% water are not in stoichiometric excess for the formation of gelatinized starch.

Under such limiting water conditions of less than 61%, the fraction of starch that is not gelatinized could be melted, provided that enough energy is available to such mixtures. As the ratio of water:starch decreased, the second endotherm (M_1) started to develop at higher temperatures and became predominant at low water contents. At a water content of 16.7%, the G endotherm disappeared, leaving only the M_1 endotherm, with T_0 and T_m shifted to higher temperatures (Fig. 6).

In starch-water systems in which there is limited water content, no gelatinization occurs, but in the case of sago starch, at a water content of 9.1%, a single endotherm still appeared at higher temperatures. This could represent the melting of crystallites, whereby the solid became an amorphous liquid (Maurice *et al.* 1985). When water is limited, swelling of the amorphous regions has limited effect on the crystallites, which melt at higher temperatures. The limited swelling of sago starch granules observed at low water contents is in agreement with the results of Takahashi *et al.* (1982) for potato and corn starches, with moisture contents lower than 12%, heated to the temperature of the second transition. They reported that the swelling typically associated with granules in limiting moisture did not occur. When the water content of starch approaches zero, starch granules melt at their decomposition temperature (Takahashi *et al.* 1982).

Figures 5 and 6 show that when the water:starch ratio decreased, the endotherm peak area also decreased. Also, the size of the endotherm appeared to decrease slightly as the starch concentration increased. The gelatinization enthalpy remained substantially the same, 15.2-15.8 J/g for high-moisture sago starch slurries, but decreased significantly when the water:starch ratio decreased below 1.3:1 (Table 1). This may have been due to limited swelling of the amorphous regions of the sago starch granules.

Cooke and Gidley (1992) used ΔH as an indicator of the degree of starch molecular order and proposed that the higher the ΔH , the longer are the chain lengths in the ordered regions. Therefore, the ΔH obtained for sago starch (15.2-15.8 J/g) seems to suggest that the average chain length in the ordered

regions of sago starch is shorter than for potato (16.7-17.3 J/g) or tapioca (16.9 J/g) starches but longer than for wheat (9.7 J/g) starch.

TABLE 1.

ENTHALPIES (ΔH) AND MELTING TEMPERATURE RANGES FOR GELATINIZATION OF SAGO STARCH AT DIFFERENT WATER CONTENTS

Water: Starch Ratio	4:1	2:1	1.3:1	1:1	0.75:1	0.6:1	0.4:1	0.3:1	0.2:1	0.1:1
ΔH (J/g) ¹	15.8 ^a ± 1.0	15.5 ^a ± 0.5	15.2 ^a ± 0.1	14.5 ^b ± 0.2	11.2 ^b ± 0.3	8.0 ^c ± 0.6	5.3 ^d ± 0.5	3.3 ^d ± 0.6	0.8 ^c ± 0.4	0.9 ^c ± 0.4
Melting Temperature Range ($T_m - T_o$)	16.6	18.0	19.7	25.0	-	-	-	-	-	-

$\alpha = 0.05$ ¹ Value are average ± standard deviation based on triplicates
Means with the same letter are not significantly different

Figure 7 shows that the T_o and T_{p1} occurred essentially at constant temperatures for water:starch ratios of 4:1 to 0.3:1, but increased for water:starch ratios of 0.2:1 to 0.1:1. At water:starch ratios of 1.3:1 to 0.3:1 and 4:1 to 0.3:1, a progressive shift of T_{p2} (M_1 endotherm) and T_m , for sago starch was observed. Sago showed a melting temperature range of 16.6-18.0 in excess water (66.7-80.0%) (Table 1). This $T_m - T_o$ value was lower than reported values for adzuki bean (23), smooth pea (30) and lentil (35) starches (Biliaderis *et al.* 1980). It can be concluded from our T_o , T_{p1} , T_{p2} , T_m and $T_m - T_o$ results that sago starch can be gelatinized more easily than other starches.

While the values of T_o and T_p were independent of the starch concentration over the range 20-80%, T_m and T_{p2} increased with decreasing water content, especially for starch slurries with concentrations greater than 50% (Fig. 5). The heat of gelatinization, as determined from the endotherm area, was independent of starch concentration at concentrations lower than 50%. However, it decreased in the higher concentration range. This result, together with the T_m profile, suggests that at water concentrations lower than 50% the amount of water present was insufficient to fully gelatinize the sago starch granules.

Partial Scanning and Flory Analysis

A plot of $1/T_m$ versus ν_1 for sago starch is shown in Fig. 8. Linear regression analysis of the experimental data gave a significant correlation ($R^2 = 0.96$). For sago starch, a T_m^0 value of 431.7K (158.7C) was obtained by

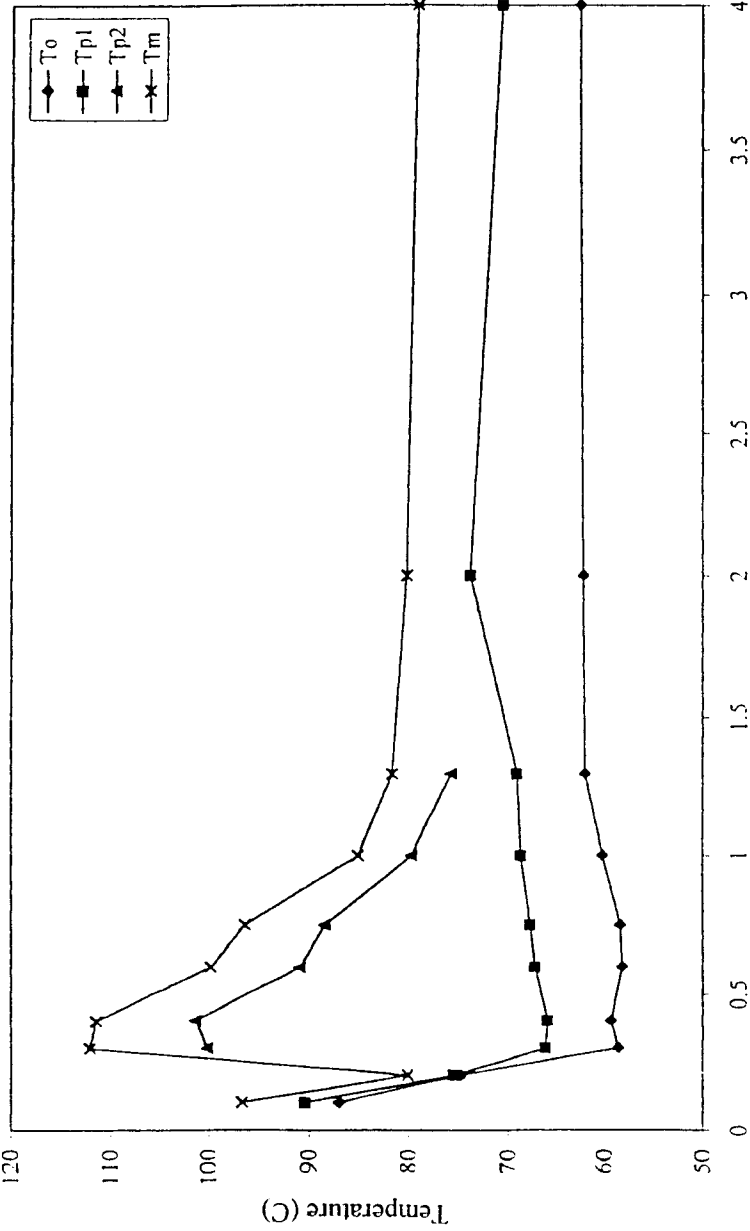


FIG. 7. EFFECT OF WATER:STARCH RATIO ON THERMAL TRANSITION TEMPERATURES ASSOCIATED WITH GELATINIZATION OF SAGO STARCH

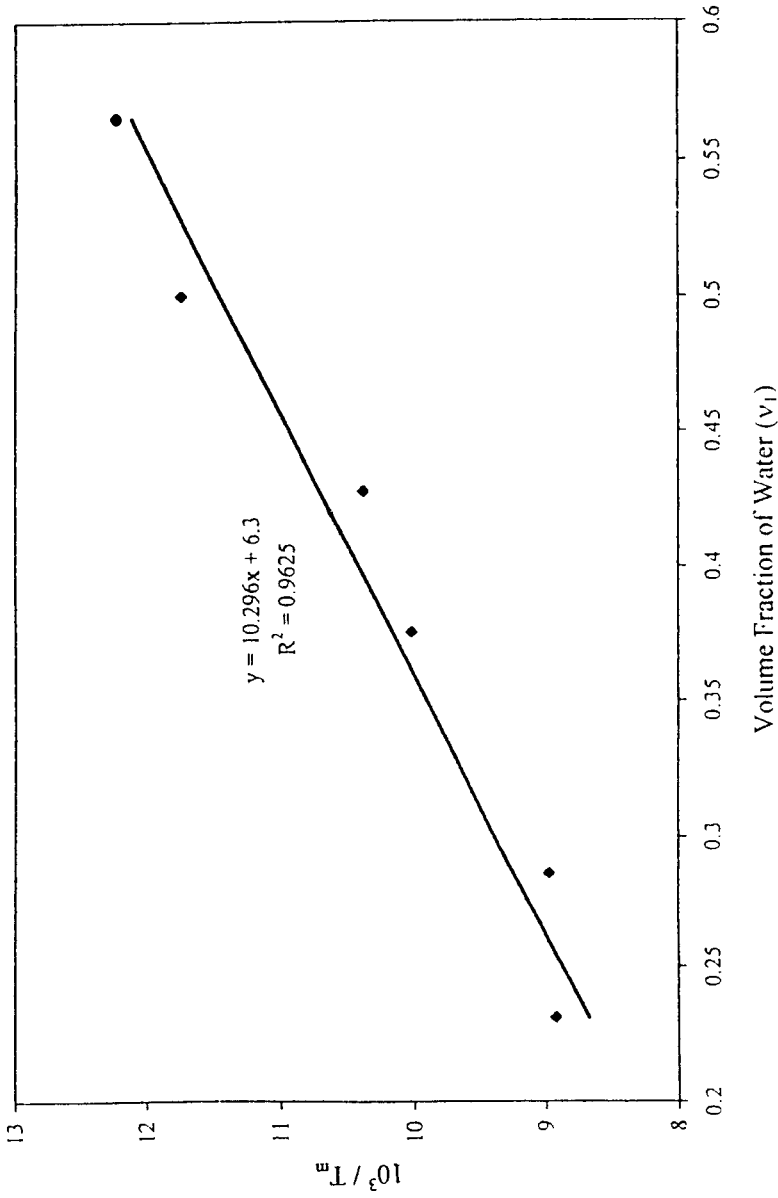


FIG. 8. PLOT OF $1/T_m$ VERSUS VOLUME FRACTION OF WATER (v_1) FOR THE ENDOTHERM ASSIGNED TO THE MELTING OF THE MOST STABLE CRYSTALLITES

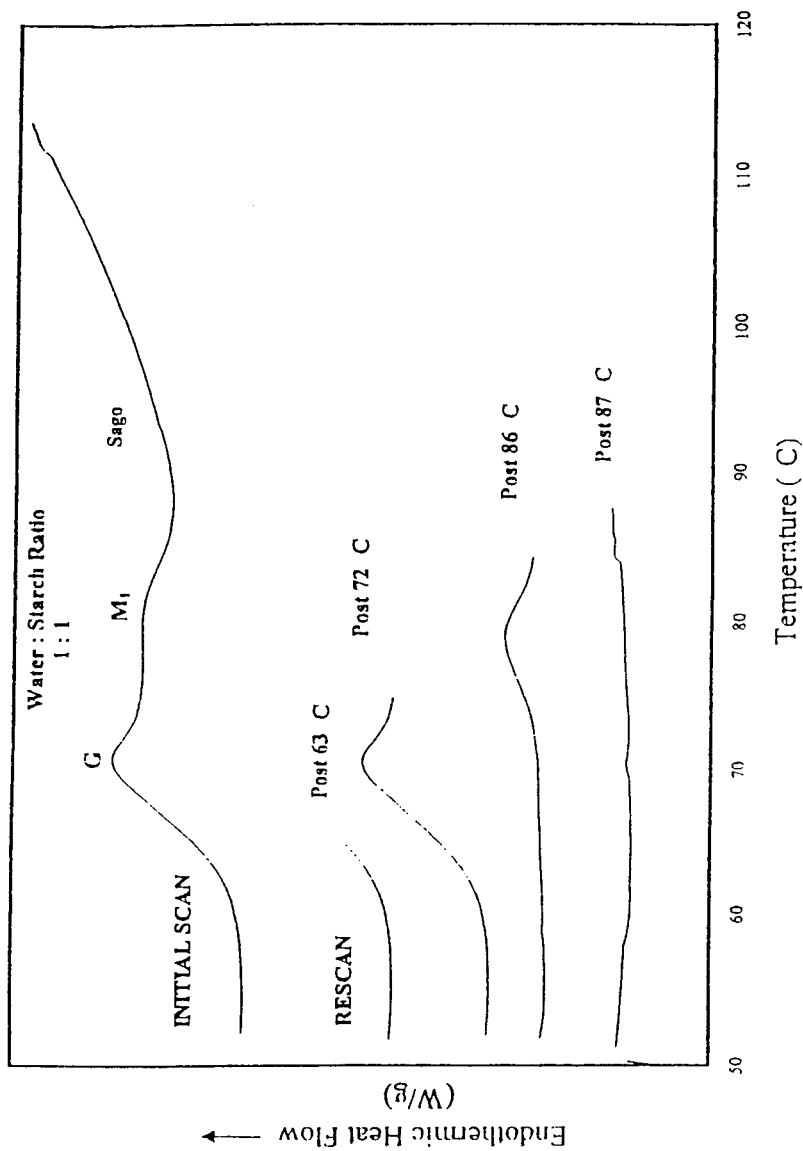


FIG. 9. DSC HEAT-FLOW CURVES OF SAGO STARCH: TOP-INITIAL SCAN AT 10C/MIN FOR NATIVE STARCH; OTHERS-RESCANS AT 20C/MIN IMMEDIATELY FOLLOWING PARTIAL SCANNING AT 10C/MIN FROM 20C TO THE MAXIMUM TEMPERATURE INDICATED

extrapolation to $\nu_1 = 0$. This value is comparable to previously reported values of 210C for wheat (Lelievre 1973) and 168C for potato (Donovan 1979) starches. Differences in T_m^0 values may be related to various factors, of which the granular organization and its inherent crystallinity are probably the most important.

The composite diagram of DSC heat-flow curves for sago starch, shown in Fig. 9, demonstrated that an initial heating to at least 86C was required (for a heating rate of 10C/min and a water content of 50%) to complete the nonequilibrium melting process associated with gelatinization of native starch as originally conceptualized by Maurice *et al.* (1985) and Slade and Levine (1988). Partial initial scanning to temperatures ≥ 63 C, but less than 86C, resulted in only partial melting (Slade and Levine 1988), as evidenced in the rescans by a peak in the melting profile (Fig. 9). This peak area decreased with increasing maximum temperature in the range 63–86C of the partial scan, but disappeared completely yielding a featureless thermogram, as evidenced by a flat baseline from 20–100C after initial heating to ≥ 86 C (Slade and Levine 1988). In accord with previous findings by Slade and Levine (1988), we concluded that 85C represents the effective T_m at the 'end of melting' for native sago starch heated at 10C/min with 50% total water content.

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