

# Swelling and Gelatinization of Cereal Starches.

## II. Waxy Rice Starches<sup>1</sup>

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### ABSTRACT

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The swelling and gelatinization properties of waxy rice starches (essentially pure amylopectin) were studied. Low gelatinization temperature (low-GT, 64–67°C), intermediate-GT (68–71°C), and high-GT (75–79°C) starches exhibited a range of swelling factors at 80°C (low = 24–42, intermediate = 28–42, high = 29–40; maximum values were not attained by the high-GT starches). Structural analysis showed that the low-GT and high-GT starches had very similar chain lengths after debranching and on debranching of insoluble residues after lintnerization. The low-GT starches could be annealed to behave like high-GT starches, but the

latter also responded a little to annealing. It is concluded that the low-GT starches have less crystallinity and less perfect crystallites than the high-GT starches due to minor structural differences in their amylopectins. Partial hydrolysis of amorphous regions caused a large decrease in swelling factor but had only a small effect on gelatinization enthalpy. It is suggested that crystallites within the amylopectin molecule determine the onset of swelling and gelatinization, and that maximum swelling factors may relate to the molecular weight and shape of the whole amylopectin molecule.

In the preceding paper (Tester and Morrison 1990), the swelling behavior of cereal starches was shown to be primarily a property of their amylopectin (AP) content; amylose (AM) acts both as a diluent and as an inhibitor of swelling, especially in the presence of lipids (natural components of nonwaxy cereal starch granules), which can form insoluble complexes with some of the AM during swelling and gelatinization. Interpretation of results was complicated because so many factors affected swelling, and further studies were therefore carried out using waxy rice starches, which, being essentially pure AP, are not subject to interference from AM and lipids.

Rice, more than any other cereal, exhibits very wide ranges of cooking quality and rheological properties that are largely determined by the swelling, gelatinization, pasting, and retrogradation characteristics of its starch (Juliano 1985). Being a diploid cereal, rice has numerous stable starch variants commonly classified as high-, intermediate-, and low-AM and waxy (zero-AM). Each of these types normally includes varieties with low, intermediate, and high gelatinization temperatures (GT). In this study, six low-GT and six high-GT waxy rice starches with contrasting gel properties were used. In addition, swelling factor was measured using some waxy rice starches described previously (Morrison et al 1984, Morrison and Nasir Azudin 1987).

### MATERIALS AND METHODS

#### Starches

Eleven samples of waxy rice (indica type) grown under comparable conditions at the International Rice Research Institute (IRRI), Philippines, and one sample grown in Vietnam were obtained. The varieties were RD6, IR65, Khao Khao (from Vietnam), IR29, Malagkit Sungsong, IR39368-31-1-2, Inilang-ilang, Perurutong NBA, Nathasiq, Tapol, Pya Gyi Taung, and RD4. Starches from the above were isolated from milled white rice by steeping, aqueous extraction, and centrifuging through 80% (w/v) CsCl (Tester and Morrison 1990). Other starches were as described previously (Morrison et al 1984).

#### Analytical Methods

Methods for the determination of total amylose (colorimetric),  $\alpha$ -glucan, lipids, swelling factor (SF), and gelatinization temperature (GT), and enthalpy ( $\Delta H$ ) by differential scanning calorimetry (DSC) were the same as in our previous paper (Tester and Morrison 1990). Starch granules were lintnerized by steeping

for various times in 2.2M HCl at 35°C, then washing six times with water to remove the acid, and air-drying. This causes hydrolysis of  $\alpha$ -glucan, initially confined to the amorphous regions of the starch granules. Solubilized glucan was measured in the original supernatant before washing.

Native and lintnerized starches were debranched enzymically, and the  $\alpha$ -glucan chains released were analyzed by gel permeation chromatography (GPC) and by high-performance liquid chromatography (HPLC).

Native starch (5 mg) was dissolved in 990  $\mu$ l of acetate buffer (pH 3.8, 0.01M) by boiling briefly. After cooling, 10  $\mu$ l of buffer containing 540 units of isoamylase from *Pseudomonas amylo-deramosa* (Hayashibara Biochemicals, Osaka) was added. The samples were incubated at 30°C for 24 hr, with toluene present to prevent microbial growth, then boiled for 10 min to inactivate the enzyme. The insoluble residue from lintnerized starch (approximately 6.5 mg) was dissolved in 800  $\mu$ l of sodium acetate (0.01M) by boiling for 10 min, and cooled to 20–25°C; 200  $\mu$ l of acetate buffer (pH 3.72, 0.01M) containing 540 units of isoamylase and 100  $\mu$ l of buffer containing two units of pullulanase (BDH) were added to effect debranching. The samples were incubated at 37°C for 24 hr, then boiled for 10 min, cooled, centrifuged (1,550  $\times$  g, 5 min), and the supernatant was used for GPC or HPLC.

For GPC, 1-ml aliquots of debranched material were fractionated on a column (1,000  $\times$  16 mm) of Sepharose CL6B (Pharmacia) eluted with 0.01M KOH containing 0.005% thiomersal at 1 ml/min, and fractions were collected for analysis. The average chain length (CL) of the  $\alpha$ -glucan chains was estimated by measuring  $\lambda_{\max}$  of the I<sub>2</sub>/KI complex (Morrison and Laignelet 1983), using the relationship  $CL = 3,290 / (635 - \lambda_{\max})$  (Morrison and Karkalas 1990). Smaller aliquots were also fractionated by HPLC (Hizukuri 1986). The HPLC columns were calibrated with linear  $\alpha$ -glucans of CL 38, 54, 98, 178, 237, and 407, synthesized from maltohexaose primer and glucose-1-phosphate using potato phosphorylase (Banks et al 1971). Native starches were also separated by GPC on a column of Sepharose CL2B (Morrison et al 1984).

### RESULTS AND DISCUSSION

Only small quantities of starch from waxy rice varieties grown in France and Vietnam were available. Since these were all low-to intermediate-GT starches, single measurements of swelling were made at 80°C (Table I), approximately 10°C above GT. This is comparable with measuring the swelling factor of wheat and barley starches (GT = 57–65°C) at 70°C (Tester and Morrison 1990). The results show a range of SF (28.1–43.8) that was not correlated with GT (67.3–72.0°C) or  $\Delta H$  (12.8–14.9 J/g), indicating different swelling curves of the type shown in Figure

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1. Interestingly, E100 starch from rice grown in France differed appreciably from the same variety grown in Vietnam. Swelling differences were not due to the apparent AM content (discussed below) since the correlation was very poor ( $r = 0.506$ ,  $n = 8$ ), and swelling factors recalculated on AP content were equally variable.

Three nonwaxy starches (24.0–28.1% AM, 632–821 mg/100 g of lipid) from the same study were also available. Their GTs (73.8–74.6°C) were a little lower than for the high-GT starches described below, and their  $\Delta H$  values (13.8–14.1 J/g) were normal, but  $SF_{80}$  was only 11.5–12.6. Because all low-GT and high-GT waxy starches in the present study had  $SF_{80} > 26$ , AM and lipids inhibited swelling in rice starches as much as in other cereal starches (Tester and Morrison 1990).

The 12 waxy starches used in the main part of this study had very low levels of AM (colorimetric) and lipids (Table II) and were thus nearly pure AP. In fact, the iodine-binding capacity of rice AP, particularly from indica varieties (Hizukuri 1986, Takeda et al 1987), is sufficient to account for all of the colorimetrically determined AM in these starches. This was confirmed by GPC and HPLC of the debranched starches, which revealed negligible material at the void volume which is where debranched AM would have appeared.

Swelling curves for the 12 starches over the range 50–80°C are shown in Figure 1. Onset of swelling began a little above  $T_0$  (Table II), unlike wheat, normal and waxy barley, and maize starches, where swelling begins at or below  $T_0$  (Tester and Morrison 1990). The curves for the low-GT starches all reached plateau values (maximum SF) at 70–75°C, ranging from SF =

26 (Khao Khao and RD6) to 42 (Malagkit Sungsong). Comparable values for the high-GT starches were not determined, but extrapolation of their curves indicated a SF range of 30–50, approximately.

An explanation for these characteristic gelatinization and swelling properties was sought in terms of crystalline organization within the granule and the molecular structure of its AP. For this discussion, the reader is referred to the models of French (1972, 1984), Robin et al (1974, 1975), Nikuni (1978), Manners and Matheson (1981), Enevoldsen (1985), and Hizukuri (1986),

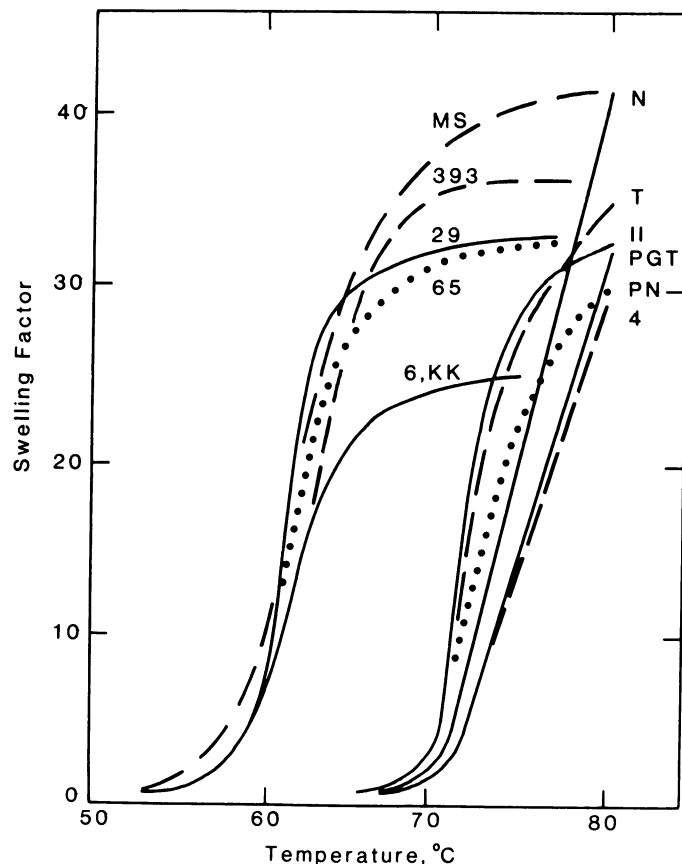


Fig. 1. Swelling curves of starch from 12 varieties of waxy rice, six with low and six with high gelatinization temperatures: IR29 (29), IR65 (65), IR39368-31-1-2 (393), RD6 (6), Khao Khao (KK), Malagkit Sungsong (MS), RD4 (4), Inilang-ilang (II), Nathasiq (N), Perurutong NBA (PN), Pya Gyi Taung (PGT), and Tapol (T).

TABLE I  
Composition, Gelatinization Properties, and Swelling Factors (at 80°C) of Nine Waxy Rice Starches from a Previous Study<sup>a</sup>

Cultivar	AM <sup>b</sup> (%)	Lipid (mg/100 mg)	GT (°C)	$\Delta H$ (J/g)	$SF_{80}$
B122	nd	nd	68.4	12.9	36.0
B124	0.4	54	72.0	13.7	39.1
B129	0.3	34	67.7	12.8	43.8
B136	0.5	24	70.5	12.8	33.4
E73	0.7	40	67.3	14.9	41.9
E100(VN) <sup>c</sup>	1.1	47	69.0	14.2	39.0
E100(Fr) <sup>c</sup>	0.4	23	70.7	12.9	35.4
E148	0	27	69.6	14.7	28.1
F13	0.3	24	69.9	14.7	31.0

<sup>a</sup> Amylose (AM), lipid, gelatinization temperature (GT), and  $\Delta H$  data from Morrison and Nasir Azudin (1987).

<sup>b</sup> Measured as amylose, but probably superlong B-chains in amylopectin, as discussed in text.

<sup>c</sup> VN = grown in Vietnam, Fr = grown in France.

TABLE II  
Composition, Gelatinization Properties, and Swelling Factors (at 80°C) of 12 Waxy Rice Starches

Cultivar	AM <sup>b</sup> (%)	Lipid (mg/100 mg)	$\lambda_{max}$ (nm)	Differential Scanning Colorimetry <sup>a</sup>				$\Delta H$ (J/g)	$SF_{80}$ <sup>c</sup>
				$T_0$ (°C)	$T_p$ (°C)	$T_r$ (°C)			
RD6	0.15	18	522	46.0	64.3	81.0	13.4	24.3	
IR65	0.94	24	526	45.6	65.7	85.3	13.7	33.3	
Khao Khao	0.32	20	522	50.1	65.9	83.3	13.4	24.2	
IR29	1.86	n.d.	534	49.6	66.1	83.0	14.22	32.4	
Malagkit Sungsong	0.39	17	526	49.3	66.8	91.6	14.4	41.9	
IR39368-31-1-2	0.79	20	526	52.0	67.3	82.3	13.9	36.3	
Inilang-ilang	9.79	14	526	59.3	75.0	90.6	15.3	32.9	
Pururutong NBA	1.97	24	530	52.3	75.7	92.6	16.2	30.5	
Nathasiq	2.32	n.d.	534	56.3	76.3	93.6	17.5	39.9	
Tapol	2.31	52	530	50.3	77.1	94.6	16.1	35.2	
Py Gyi Taung	2.31	21	532	51.3	77.6	94.3	15.7	31.3	
RD4	1.94	15	532	62.3	78.8	94.8	15.9	28.7	

<sup>a</sup> Measured as amylose, but probably superlong B-chains in amylopectin, as discussed in text.

<sup>b</sup>  $T_0$  = onset temperature,  $T_p$  = peak temperature (= gelatinization temperature),  $T_r$  = recovery or return to baseline temperature of gelatinization endotherm,  $\Delta H$  = endothermic enthalpy.

<sup>c</sup> Swelling factor at 80°C.

and to the concept of A, B-, and C-type  $\alpha$ -(1,4)-glucan chains within the AP molecule (Peat et al 1952). In essence, amorphous regions must arise where  $\alpha$ -(1,6)-glycosidic bonds cause branching, and crystallinity can arise when adjacent unbranched segments of A- and B-chains or pairs of B-chains alone can form short double helices, and the helices then form crystalline clusters. The principal sequence of events during gelatinization is postulated to be disordering of clusters, then dissociation of double helices to give loosely ordered (semirandom) external chains (Tester and Morrison 1990).

The proportions of amorphous and crystalline material were estimated by lintnerizing starch granules. Soluble material released from low- and high-GT starches steeped in 2.2M HCl at 35°C is shown in Figure 2. Similar curves have been reported using HCl (Robin et al 1974, 1975; Maningat and Juliano 1979; Biliaderis et al 1981; Muhr et al 1984) and H<sub>2</sub>SO<sub>4</sub> (Nara et al 1983, Komiya and Nara 1986, Inouchi et al 1987). The inflection points, which probably reflect the change from initial hydrolysis of amorphous material to subsequent hydrolysis of more resistant crystalline material, indicate approximately 35% crystalline material in the low-GT starches and 50% crystalline material in the high-GT starches.

To compare amorphous contents in the low- and high-GT starches, measurements were made of soluble material after lintnerizing for three and seven days (Table III). The low-GT starches gave consistently higher yields of soluble material and

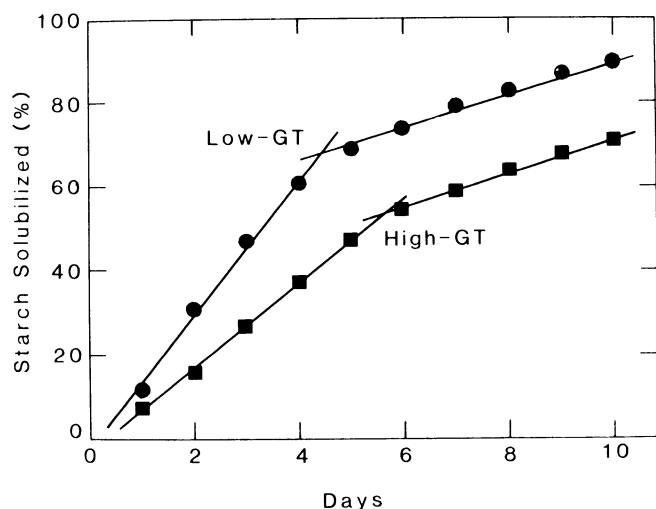


Fig. 2. Starch solubilized by steeping low gelatinization temperature (IR39368-31-1-2, ●) and high gelatinization temperature (Tapol, ■) waxy rice starches in 2.2M HCl at 35°C for various times.

TABLE III

Percentage Starch Solubilized from Low Gelatinization Temperature (GT) and High-GT Waxy Rice Starches Lintnerized for Three Days and Seven Days at 35°C

Starch	After 3 Days	After 7 Days
Low GT		
RD6	35.6	77.8
IR65	32.3	75.6
Khao Khao	32.3	76.4
IR29	30.5	79.0
Malagkit Sungsong	31.7	76.2
IR39368-31-1-2	29.6	74.5
Mean (SD)	32.0 (2.0)	76.6 (1.6)
High GT		
Inilang-ilang	18.0	55.1
Perurutong NBA	27.4	55.6
Nathasiq	17.1	53.9
Tapol	17.5	55.4
Pyta Gyi Taung	18.5	53.7
RD4	16.6	50.2
Mean (SD)	17.5 (0.6)	54.0 (2.0)

hence had less crystalline material, but there were no correlations between solubilized starch and SF<sub>80</sub>, GT, or  $\Delta$ H within the low-GT or the high-GT groups.

Granule crystallinity was also estimated from the wide-angle X-ray diffraction patterns (A-type) of the starches by comparing the areas under the principal peaks. Relative areas for the low-GT starches were 70 ± 2 and for the high-GT starches 75 ± 3, but differences were not as great as expected from lintnerization and DSC enthalpy data. Relative area was loosely correlated with  $\Delta$ H ( $r = +0.864$ ,  $P < 0.05$ ) in the high-GT starches, but there was no correlation in the low-GT starches.

The DSC gelatinization endotherm gives a measure of crystallite quality (effectively double helix length) from peak temperature ( $T_p$ ) and overall crystallinity (quality × quantity) from  $\Delta$ H. The data in Table II clearly support the lintnerization and X-ray diffraction data showing more crystallinity in the second set of high-GT starches. However, it should be noted that in a previous study (Morrison and Nasir Azudin 1987) no correlations were found between  $T_p$  and  $\Delta$ H in 14 waxy rice starches, and in the present study there were none within the low-GT or high-GT groups.

Swelling factor was measured in a low-GT starch (IR39368-31-1-2) and a high-GT starch (Tapol) at various stages of lintnerization (Fig. 3). In both cases swelling power was almost completely lost after one day of lintnerization, which shows the importance of the intact structure of the AP molecule. The crystalline regions alone did not have any swelling power, but in the native starches there is no doubt that both the amorphous and crystalline segments of A- and B-chains will contribute to swelling power when heated beyond the point when crystallinity

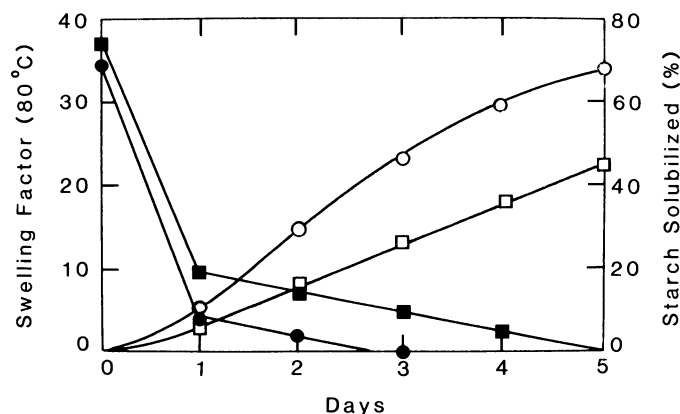


Fig. 3. Swelling factors (closed symbols) and starch solubilized (open symbols) from low gelatinization temperature (IR39368-31-1-2, circles) and high gelatinization temperature (Tapol, squares) waxy rice starches steeped in 2.2M HCl at 35°C for various times.

TABLE IV

Gelatinization Properties of Insoluble Residues from a Low Gelatinization Temperature (GT) Starch (IR39368-31-1-2) and a High-GT Starch (Tapol) After Steeping in 2.2M HCl at 35°C for Various Times

Starch/Time (days)	$T_o$ (°C)	$T_p$ (°C)	$T_r$ (°C)	$\Delta$ H (J/g)
IR39368-31-1-2				
0	52	67	82	14
1	50	62	77	11
2	49	56	75	5
3	49	55	70	2
4	NE <sup>a</sup>	NE	NE	NE
Tapol				
0	50	77	95	16
1	51	69	86	15
2	50	65	80	12
3	49	60	75	6
4	48	55	70	2

<sup>a</sup>No endotherm.

(shown by birefringence, X-ray diffraction, and the DSC endotherm) is lost.

The gelatinization endotherms of these starches were also measured during the early stages of lintnerization (Table IV). Figure 2 indicates that crystalline material was not digested to any extent during the first four days of lintnerization. However,  $T_p$  decreased steadily and  $\Delta H$  decreased towards zero, paralleling the decrease in SF (Fig. 3). Since the gelatinization endotherm is given by clusters of double helices rather than by separated double helices, some branch points are necessary to hold the clusters together (Blanshard 1987). However, after one day of lintnerization there was a much smaller decrease in enthalpy than in swelling factor, showing that the contribution of branching (destroyed by lintnerization) to cluster cohesion was comparatively small.

Attention was focused next on the structure of AP to see if any aspects could be related to gelatinization and swelling behavior. Absorbance of the starch-iodine complex at 630 nm, attributed to superlong B-chains in AP rather than to traces of AM in waxy rice starches (see above), was correlated with  $\lambda_{\max}$  in the low- and high-GT starches ( $r = 0.915$ ,  $P > 0.02$ ,  $r_{\max} = +0.851$ ,  $P > 0.05$ , respectively), but it was not correlated with  $T_p$ ,  $\Delta H$ , or  $SF_{80}$  in either group of starches.

Debranched starches separated by GPC gave typical bimodal CL distributions (Table V). Similar results were obtained by HPLC (Fig. 4), the most interesting feature being a shoulder of intermediate CL ( $25 \pm 1$ ) on the fraction 2 (F2) peak of all low-GT starches that was not detectable in any high-GT starch. The CL of F2 (low-GT =  $17.7 \pm 0.4$ , high-GT =  $18.5 \pm 0.6$ ) was close to the values estimated on fractions isolated after GPC (Table V), but the CL of F1 (low-GT =  $52.5 \pm 0$ , high-GT =  $51.7 \pm 0.6$ ) was appreciably higher. Comparable values reported in the literature are CL of F1 = 13–19 and F2 = 31–57 (Juliano 1982; Asaoka et al 1984; Hizukuri 1985, 1986; Takeda et al 1987).

F2 would be composed mostly of A and B<sub>1</sub> chains and F1 mostly of B<sub>2</sub> and B<sub>3</sub> chains (Hizukuri 1986), so that B<sub>4</sub> chains would not be taken into account. There were no correlations between the CL of F1 or F2 and any parameter of either group of starches in Table II. As far as  $T_p$  is concerned, the only correlation that might be anticipated would be between the CLs of A-chains and of B-chains beyond the last branch points (i.e. external chain lengths, ECLs), which were not determined here.

However, ECL should be related to the CL of the crystalline material resistant to lintnerization. Table V shows that there were no differences between the low- and high-GT starches in this respect, all giving a single peak of CL =  $15 \pm 2$ . In a similar experiment, Maningat and Juliano (1979) obtained two peaks of CL = 18 and 30, the latter perhaps indicating incomplete

TABLE V  
Chain Length (CL)<sup>a</sup> of Fraction 1 (F1) and Fraction 2 (F2)  
of Debranched Waxy Rice Starches Before and After Lintnerization<sup>b</sup>

Cultivar	F1 (%, w/w)	Before		After CL
		CL-F1	CL-F2	
Low-gelatinization temperature				
RD6	25.4	39.0	20.2	15.7
IR65	32.7	33.0	15.7	13.2
Khao Khao	37.9	33.0	18.4	15.7
IR29	33.7	33.0	17.0	15.7
Malagkit Sungsong	27.6	36.5	15.7	15.7
IR39368-31-1-2	33.4	36.5	18.4	15.7
Mean (SD)	31.8 (4.5)	35.2 (2.5)	17.6 (1.8)	15.3 (1.0)
High-gelatinization temperature				
Inilang-ilang	30.6	36.5	18.4	14.5
Perurutong NBA	27.9	43.0	18.4	18.4
Nathasiq	29.2	39.0	20.2	15.7
Tapol	32.0	33.0	17.0	14.5
Pya Gyi Taung	28.1	33.0	20.2	15.7
RD4	32.6	39.0	20.2	15.7
Mean (SD)	30.1 (2.0)	37.3 (3.9)	19.3 (1.7)	15.7 (1.5)

<sup>a</sup> Estimated from  $\lambda_{\max}$  of fractions collected at peak modes.

<sup>b</sup> Lintnerized for seven days at 35°C in 2.2M HCl.

debranching. However, the amount of crystalline material was greater in the high-GT starches (Table III), which suggests that differences in gelatinization behavior were primarily in the physical organization of essentially similar A- and B-chains. To test this, starches were annealed by incubating at 55 or 65°C for three days, and they were then examined by DSC (Table VI).

With low-GT starches, annealing at 55°C caused an increase of 15.9°C (SD 1.2) in  $T_o$ , 5.75°C (SD 0.4) in  $T_p$ , and 4.0°C (SD 1.3) in  $T_r$ , generally with a small increase in  $\Delta H$ . With some starches, gelatinization superceded annealing at 65°C, but where annealing did occur (Khao Khao and IR29) the final increases were 18.5–23.4°C in  $T_o$  and 10.1–11.6°C in  $T_p$ , making  $T_p$  higher than in the native high-GT starches (76.8°C, SD 1.4) before annealing. It is quite possible that if annealing had been done in two or three stages of increasing temperature all the low-GT starches would have attained even higher values for  $T_o$  and  $T_p$ , with no decreases in  $\Delta H$ .

With the high-GT starches, annealing at 55°C had little effect because it was too far below  $T_o$  and  $T_p$ , but annealing at 65°C caused an increase of 8.05°C (SD 1.6) in  $T_o$ , 4.5°C (SD 0.8) in  $T_p$ , and 3.0°C (SD 1.4) in  $T_r$ , with an increase of 3.25 J/g (SD 1.3) in  $\Delta H$ . Annealing at a temperature nearer  $T_p$  of the native starches was not attempted due to lack of material.

These results agree with previous observations that annealing increases the temperature of gelatinization, narrows the temperature range, and increases gelatinization enthalpy (Gough and Pybus 1971, Krueger et al 1987). The most interesting aspect of this experiment was that after annealing at 65°C, the chemically similar low-GT starches and the high-GT starches had much more similar gelatinization characteristics ( $T_o = 70.5$ –79.6, 70.0–72.7;  $T_p = 78.6$ –79.6, 81.8–83.9;  $T_r = 88.0$ –93.0, 94.7–97.0°C, respectively), and the corresponding enthalpies (approximately <16 J/g and 21–24 J/g, respectively) were more in proportion to crystallinity estimated from lintnerization (35% and 50%, respectively, from Fig. 2) than in the native starches.

Since there could have been no structural alteration in AP (branching, CL of A- and B-chains), these changes can only reflect

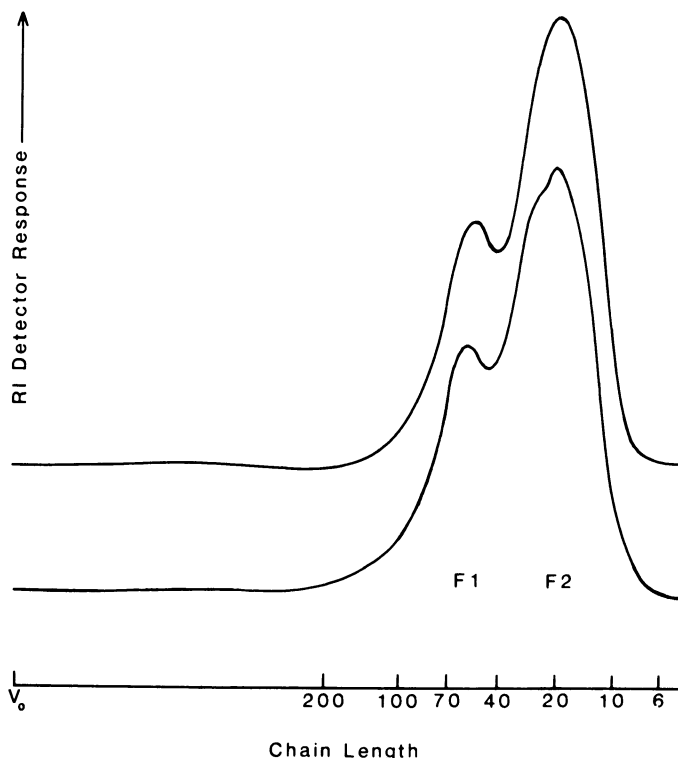


Fig. 4. High-performance liquid chromatography elution profiles of debranched waxy rice starches: upper curve = high gelatinization temperature starch (Tapol), lower curve = low gelatinization temperature starch (IR39368-31-1-2). F1 = first fraction of eluted chains, F2 = second fraction of eluted chains,  $V_o$  = void volume.

improved crystallite perfection, there being more scope for improvement in the low-GT starches, although heterogeneity caused by the intermediate CL material could be an impediment. These observations provide one explanation for the range in gelatinization properties of rice varieties grown at various locations where they would be exposed to different environmental temperatures (Morrison and Nasir Azudin 1987), which would affect the perfection of crystallites formed from essentially identical AP. However, it should be noted that with rice grown in controlled-temperature environments higher gelatinization temperatures can also be related to increased proportions of long B-chains and longer CL in debranched AP fractions separated by HPLC (Asaoka et al 1984, 1985).

## CONCLUSIONS

In the preceding paper (Tester and Morrison 1990), the effects of amylose and lipids on the swelling and gelatinization behavior of some cereal starches were examined. In the present study waxy rice starches that were almost pure AP were used to obtain the

TABLE VI  
Gelatinization Properties of Waxy Rice Starches  
Before and After Annealing at 55 and 65°C

Cultivar/ Annealed (°C)	$T_o$ (°C)	$T_p$ (°C)	$T_r$ (°C)	$\Delta H$ (J/g)
Low-GT <sup>a</sup>				
RD6				
...	49.7	66.0	80.0	13.2
55 <sup>b</sup>	66.8	72.5	86.0	12.5
IR65				
...	49.0	67.6	84.7	15.0
55	66.3	72.9	88.8	14.5
65	74.5	79.6	95.0	16.2
Khao Khao				
...	50.6	68.0	85.2	13.9
55	67.0	73.9	87.0	14.3
65	74.0	79.6	88.0	8.3 <sup>c</sup>
IR29				
...	52.0	68.5	83.7	13.8
55	66.7	73.9	86.7	15.4
65	70.5	78.6	90.0	12.9 <sup>c</sup>
Malagkit Sungsong				
...	51.0	67.6	85.3	14.4
55 <sup>b</sup>	66.7	73.4	90.0	14.8
IR39368-31-1-2				
...	51.3	68.3	85.7	15.0
55 <sup>b</sup>	65.7	73.9	89.7	16.4
High-GT				
Inilang-ilang				
...	65.0	76.7	90.5	17.2
55	67.3	78.6	93.0	21.4
65	74.0	82.7	95.7	20.0
Perurutong NBA				
...	64.0	77.2	93.5	18.4
55	67.0	79.1	93.3	21.2
65	70.3	81.9	94.7	21.7
Nathasiq				
...	64.7	78.8	93.3	17.8
55	66.0	80.5	95.0	21.8
65	72.7	83.0	97.0	23.6
Tapol				
...	60.0	78.0	94.0	21.1
55	66.7	79.6	95.0	24.7
65	70.0	81.8	97.0	24.2
Pyta Gyi Taung				
...	64.0	77.6	94.8	20.1
55	67.0	79.2	93.7	21.8
65	70.0	82.2	96.0	22.0
RD4				
...	63.3	80.3	94.0	19.0
55	70.7	81.7	95.3	20.7
65	72.33	83.9	96.3	21.6

<sup>a</sup> Gelatinization temperature.

<sup>b</sup> Starches incubated at 65°C gelatinized before they could anneal.

simplest possible system. These starches divided into three sets according to GT ( $T_p$  64–67°C = low-GT, 68–71°C = intermediate-GT, 75–79°C = high-GT), and each set exhibited a similar range of swelling properties above their respective onset temperatures. The experiments described in this paper were designed to investigate the contributions of granule crystallinity and AP structure to the characteristic swelling and gelatinization properties of these starches.

Different aspects of starch granule crystallinity were measured by the amount of insoluble residue after lintnerization, by the intensity of X-ray diffraction, and by DSC, and all clearly showed that the low-GT starches had more amorphous and less crystalline material than the high-GT starches. Crystallinity is perceived as clustering of double helices formed from the comparatively short free ends of A- and B-chains in AP, and it might be anticipated that the high-GT starches had longer chains and crystallites than in the low-GT starches. However, the differences found on debranching native starches and insoluble residues after lintnerization were minimal, and it seems that crystallite perfection must be the principal mechanism controlling GT in these starches. This is supported by the fact that some low-GT starches could be annealed to become like the high-GT starches. The potential to raise GT by annealing the high-GT starches appears to be less although this was not examined thoroughly due to shortage of material. The intermediate-GT material in the low-GT starches could have increased heterogeneity, and hence may be a natural mechanism to reduce total crystallinity and crystallite perfection.

Whereas some progress was made towards understanding the earlier stages of swelling and gelatinization, the results provide no explanation for the different swelling plateaus (maximum swelling factors) attained by apparently very similar starches within each set. Since this condition is reached when all crystalline order has disappeared, it must depend on more tenuous associations between the highly hydrated AP molecules. It is then conceivable that molecular weight and shape will be dominant factors (Juliano 1982, Juliano and Villareal 1987, Juliano et al 1987, Takeda et al 1989), and these will be examined in future work.

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