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Presence of Amylose Crystallites in Parboiled Rice

LIEVE LAMBERTS,* SARA V. GOMAND, VEERLE DERYCKE, AND JAN A. DELCOUR

Laboratory of Food Chemistry and Biochemistry and Leuven Food Science and Nutrition Research Centre (LFoRCe), Katholieke Universiteit Leuven, Kasteelpark Arenberg 20, B-3001 Leuven, Belgium

Mildly, intermediately, and severely parboiled Jacinto [16% free amylose (FAM) content] and Puntal (26% FAM content) rice samples were submitted to differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). DSC thermograms revealed ungelatinized starch only in mildly parboiled rices and retrograded amylopectin in all parboiled samples. Amylose crystallites were present in intermediately and severely parboiled samples but could not be detected due to their high melting temperature. Nonparboiled and parboiled rice DSC profiles showed only type I and type II amylose−lipid complexes, respectively. Intermediately and severely parboiled rice showed a clear V_h-type (crystalline amylose−lipid complexes) with a superimposed B-type (retrograded amylopectin and/or amylose crystallites) pattern. The mildly parboiled samples showed a mix of A- (native starch crystallites) and V_h-type patterns (Puntal) and A-, V_h-, and B-type patterns (Jacinto). Mild acid hydrolysis destroyed the acid labile retrograded amylopectin crystallites and increased the relative abundance of amylose crystallites. Indeed, acid-hydrolyzed intermediately and severely parboiled samples of both cultivars showed a clear B-type diffraction pattern conclusively showing, for the first time, the presence of amylose crystallites. The melting temperature of the amylose crystallites was ca. 135 °C, and melting peaks were visible in the DSC thermograms of the intermediately and severely parboiled samples. Their levels depended on the degree of parboiling and FAM content.

KEYWORDS: Parboiled rice; amylose crystallites; retrograded amylopectin; amylose−lipid complexes; DSC; WAXD

INTRODUCTION

The level of starch in brown rice is typically ca. 76% of the dry matter (*1*). It is organized in granules, which consist of semicrystalline and amorphous growth rings (*2*), hence the description of starch as a semicrystalline entity. Rice starch granules are round, angular, and polygonal and have dimensions in the range of 2−8 μm (*3, 4*). Starch consists mainly of amylose and amylopectin. Amylose is a quasi linear polymer of α-(1→4)-linked D-glucopyranosyl units with few α-(1→6)-bonds. Rice starch amylose has a number-average degree of polymerization (DP_n) of 920−1110 and is slightly branched with 2−5 chains on average. Amylopectin has a highly branched structure because of the presence of 5−6% α-(1→6)-bonds. It has a DP_n of 8200−12800 (*4, 5*). Heating starch suspensions above the gelatinization temperature results in irreversible loss of birefringence and destruction of the molecular order (*6*). Gelatinization is accompanied by granule swelling, preferential amylose leaching, and the melting of crystallites (loss of X-ray diffraction pattern). Pasting includes all phenomena following gelatinization (*6*). Gelatinization behavior and pasting of rice starches depend on structural aspects, that is, free amylose (FAM) and lipid-complexed amylose contents and amylopectin chain length distribution (*7, 8*). Cooling of the resulting starch paste results in the formation of double helices, which aggregate and, within a short time frame, form stable amylose crystallites with a melting temperature of ca. 150 °C (*9*). At later stages, crystallization of amylopectin side chains occurs, resulting in retrograded amylopectin with a melting temperature range of ca. 55 °C (*9*). The latter crystals are rather acid labile (*10*). Miles et al. (*11*) observed for amylose as well as for amylopectin crystallites a B-type X-ray diffraction pattern. While retrograded amylopectin can be easily quantified by DSC, DSC analysis of amylose crystallites is difficult due to their high melting temperature. The low melting temperature and the acid labile character of amylopectin crystallites are caused by the short chains (DP ∼15 (*10*)). In contrast to amylopectin crystallites, amylose crystallites consist of linear chains (DP 35−40), have high melting temperatures (ca. 150 °C), and are more resistant to acid hydrolysis. Therefore, B-type crystallites originating from crystalline amylopectin and those originating from amylose crystallites can be distinguished by their different sensitivities to acid hydrolysis and by the difference in their DSC characteristics. In addition, apart from amylose crystallites, native starch crystallites (A-type crystallites) and amylose−lipid complexes (V_h-type crystallites) also resist mild acid hydrolysis (*12*).

In rice parboiling, paddy or brown rice is hydrothermally treated by soaking, heating, and drying. In contrast to paddy rice, brown rice hydrates very quickly and hence reduces

* Corresponding author [telephone (+32)-16-321649; fax (+32)-16-321997; e-mail Lieve.Lamberts@biw.kuleuven.be].

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processing time. Parboiling affects rice structure and texture and increases hardness. The pregelatinized starch reduces water absorption during parboiled rice cooking and hence increases rice hardness (*13*). During the cooling and drying steps, the gelatinized starch reassociates (*14*−*16*). The level of retrograded amylopectin in parboiled rice increases with the severity of the hydrothermal treatment, but reassociated amylose molecules in parboiled rice have not been detected by DSC measurements (*15*). In contrast, amylose crystallites have been detected in rice flour noodles and mungbean starch vermicelli (*17*). However, such crystallites, if present in parboiled rice samples, can reasonably be expected to contribute to cooked parboiled rice texture as they melt at temperatures exceeding those of boiling water.

Despite the above, the presence of amylose crystallites in parboiled rice has, to the best of our knowledge, never been studied, even if it seems logical to assume that, apart from amylopectin crystallites, such crystallites would also be formed, in view of their more ready formation following gelatinization (*9*). We hence investigated the impact of parboiling conditions on amylose crystallites levels in parboiled rice. To that end, mild acid hydrolysis of rice flours of nonparboiled and mildly, intermediately, and severely parboiled rice was performed. Amylose and amylose−lipid crystals in parboiled rice samples were, for the first time, studied by combined DSC and WAXD analyses. We here report the outcome of this work.

MATERIALS AND METHODS

Rice Samples. Brown rice samples (*Oryza sativa* L.) differing in amylose contents were studied. The long-grain *Indica* cultivars Jacinto and Puntal were from Mars (Olen, Belgium). The cultivar Puntal is used in industrial parboiling. Jacinto is a lower amylose rice cultivar and was also studied because we were particularly interested in learning whether we would also detect amylose crystallites in this rice.

Brown Rice Parboiling, Milling, and Grinding. Parboiling was performed on a laboratory scale. Parboiling can be executed starting from either rough rice or brown rice. In this work, as in many commercial industrial parboiling processes, brown rice was used as feedstock. It (600 g) was soaked in excess water for 30 min at 50 °C. The excess water was discarded, and the rice was rested for at least 15 min. Jacinto and Puntal reached moisture levels of ca. 30 and 29%, respectively. Mild parboiling was by steaming the soaked rice using three standard steps (10 min at 80 °C, 2 min at 100 °C, and 10 min at 105 °C). Intermediately and severely parboiled rices were produced by performing one additional steaming step (12 min at 115 °C or 17 min at 125 °C, respectively). After parboiling, the pressure was reduced to atmospheric. The rices were dried on trays for 48 h at room temperature to obtain moisture levels of ca. 11%. Milled parboiled rice was obtained by milling the brown rice samples (50 s) with a TM05C testing mill (Satake, Bredbury, U.K.). As a result, nonparboiled rice samples had a degree of milling of ca. 13%. The degree of milling of parboiled samples was ca. 10% and was hardly affected by the severity of parboiling. The milled rice kernels were ground with a laboratory mill (M20 Universal Mill, Ika, Wilmington, NC) to pass a 250 μm sieve. Samples were stored at ambient conditions until analysis.

Chemicals. All reagents and chemicals used were of at least analytical grade and obtained from Sigma (Bornem, Belgium) unless indicated otherwise.

Mild Acid Hydrolysis of Rice Flour. Mild acid hydrolysis of rice flours was performed according to the method of Jacobs et al. (*18*) with minor modifications. Flour (10.0 g) of milled nonparboiled and mildly, intermediately, and severely parboiled rice samples of both cultivars was suspended in 1.0 N HCl (0.50 L). The closed containers were stored at 37 °C, and the mixtures were gently resuspended every day. At regular time intervals, the carbohydrates in supernatants, obtained by centrifugation of the suspension (1.0 mL of the homogenized suspension, 10 min, 10000*g*), were quantified by the phenol−sulfuric acid method (*19*). After 54 days, that is, when no significant further hydrolysis of the parboiled samples was observed, the homogenized suspensions were paper filtered and the insoluble residues were washed with water until a pH of ca. 7.0 was reached.

Table 1. DSC Characteristics of Nonparboiled (NPB) and Mildly (M), Intermediately (I), and Severely (S) Parboiled (PB) Rice Samples of the Cultivars Jacinto and Puntal: Enthalpy (ΔH) and Peak Temperature (T_p) of the Melting of Native Starch (ΔH_{gel}, $T_{p,gel}$), Retrograded Amylopectin (ΔH_{retro}, $T_{p,retro}$), and Amylose−Lipid Complexes (ΔH_{AML}, $T_{p,AML}$)[a]

		native starch		retrograded amylopectin		amylose−lipid complexes	
cultivar	process	ΔH_{gel} (J/g)	$T_{p,gel}$ (°C)	ΔH_{retro} (J/g)	$T_{p,retro}$ (°C)	ΔH_{AML} (J/g)	$T_{p,AML}$ (°C)
Jacinto	NPB	14.7a	76.9a			0.4a	101.2a
	MPB	1.8b	85.9b	2.8a	53.1a	0.8b	111.6b
	IPB			6.3b	51.9a	1.6c	113.7c
	SPB			3.0a	52.3a	0.5ab	116.1d
Puntal	NPB	11.6a	74.1a			0.6a	101.2a
	MPB	2.2b	82.8b	1.7a	51.6a	1.3b	112.6b
	IPB			4.1c	52.6a	1.3b	114.5c
	SPB			3.2b	52.5a	1.2b	118.1d

[a] Values in the same column of one cultivar followed by the same letter are not significantly different ($P < 0.05$).

Levels of Free Amylose (FAM) and Proteins. FAM contents were determined on the basis of the Derycke et al. (*20*) method. The term FAM refers to the fact that the method does not include lipid-complexed amylose. Protein contents were determined according to the procedures of Lamberts et al. (*21*). All analyses were performed in triplicate, and the results are expressed on a dry matter (dm) basis.

Differential Scanning Calorimetry (DSC). DSC measurements of flours of (non)hydrolyzed nonparboiled and differently parboiled rice samples were performed as in Derycke et al. (*16*) at 66% (w/w) moisture content and a heating rate of 4 °C/min. Analyses were performed at least in triplicate.

Static Wide-Angle X-ray Diffraction (WAXD). Static WAXD measurements of flour samples of (non)hydrolyzed nonparboiled and differently parboiled rice samples were made according to the method of Derycke et al. (*16*). The static WAXD measurements of a selected set of samples were carried out in duplicate. The differences in intensities between two measurements did not exceed 0.1% over the total range of diffraction angles.

Statistical Analyses. *t*-Tests ($P < 0.05$) were performed with the Statistical Analysis System software 8.1 (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

FAM and Protein Levels. The FAM contents of the milled (non)parboiled rice samples of the cultivars Jacinto and Puntal were ca. 16 and ca. 26%, respectively. Protein contents of both cultivars were ca. 7.4%.

DSC Characteristics of Nonhydrolyzed Rice Samples. **Table 1** presents the DSC characteristics of the samples. Only the mildly parboiled rice samples showed a residual gelatinization enthalpy (ΔH_{gel}) (Jacinto and Puntal contained 12 and 19% ungelatinized starch, respectively).

Like commercial parboiled rice samples (unpublished results), all parboiled rice samples showed a retrograded amylopectin (ΔH_{retro}) melting peak. For both cultivars, the level of retrograded amylopectin was highest for the intermediately parboiled rice samples. An earlier study reported maximum amylopectin retrogradation enthalpies for waxy and amylose−extender waxy maize after heating ca. 12 °C above the gelatinization peak temperature and showed that there is an optimal temperature resulting in maximum amylopectin retrogradation (*22*). As a consequence, the differences in hydrothermal treatment due to different parboiling conditions may have resulted in differences in susceptibility to retrogradation. It may well be that intermedi-

ate parboiling made amylopectin more prone to retrogradation than those resulting from either mild or severe parboiling. Amylose crystallites were present (see below) in the processed samples but could not be detected by DSC due to their high melting temperature.

Whereas nonparboiled rice samples showed amylose−lipid complexes with a peak temperature ($T_{p,AML}$) of ca. 101 °C, $T_{p,AML}$ of the parboiled samples exceeded 110 °C. In addition, the melting temperature of the complexes increased with increasing intensity of the parboiling process (ca. 112, 114, and 117 °C for the mildly, intermediately, and severely parboiled samples, respectively). Hence, parboiling at higher temperatures resulted in more heat-stable amylose−lipid complexes. These observations indicate that rice processing at temperatures exceeding 100 °C results in the formation of type II amylose−lipid complexes, as demonstrated earlier by Biliaderis and Galloway (*23*) and Biliaderis et al. (*24*). The authors mentioned that complex I is the kinetically favored structure formed rapidly at lower temperatures (≤100 °C), whereas complex II is the thermodynamically preferred structure formed at higher crystallization temperatures (>100 °C). In addition, transformation of complex I to complex II may occur at high temperatures. Because all parboiled rice samples were processed at 105 °C (mild conditions) and higher temperatures (intermediate and severe conditions), only type II complexes were detected in the studied samples. The amylose−lipid complex enthalpy (ΔH_{AML}) seems to depend neither on cultivar nor on parboiling conditions. The presence of crystalline starch and amylose−lipid complexes in the nonparboiled and differently parboiled rice samples was further investigated by WAXD analyses.

WAXD Patterns of Nonhydrolyzed Rice Samples. Figure 1 shows the static WAXD intensity patterns of nonparboiled and mildly, intermediately, and severely parboiled rice samples. Nonparboiled samples had clear A-type diffraction patterns with main reflections at $2\theta = 15.0°$, 17.3°, 18.0°, and 23.0°. Mildly parboiled samples also showed an A-type diffraction pattern. However, the intensity of the reflections was lower, in line with the presence of gelatinized starch.

Mild parboiling conditions resulted in a higher intensity of the reflections at $2\theta = \sim 20°$. This indicated the presence of crystalline amylose−lipid complexes (V_h-type crystallites) (*13*) in these samples. The level of crystalline amylose−lipid complexes was highest for the cultivar Puntal. In addition, for the cultivar Jacinto, the intensities of the reflections at $2\theta = \sim 17°$ exceeded those of the reflections at $2\theta = \sim 18°$, indicating small levels of amylose crystallites and/or retrograded amylopectin (B-type crystallites) in this sample. The presence of retrograded amylopectin (as detected with DSC) for the cultivar Puntal was not accompanied with a B-type diffraction pattern probably because of a too low level of retrograded amylopectin in this sample (as detected with DSC), which did not allow detecting the superimposition of A- and B-type diffraction patterns.

Intermediately and severely parboiled samples had a clear V_h-type pattern with a superimposed B-type pattern. The higher retrograded amylopectin enthalpy (ΔH_{retro}) readings of the intermediately parboiled samples than of the severely parboiled samples (Jacinto, 6.3 and 3.0 J/g of dm; Puntal, 4.1 and 3.2 J/g of dm, for intermediately and severely parboiled samples, respectively) were accompanied with higher intensities of the reflections of the B-type pattern (i.e., intensities at $2\theta = \sim 5.5°$ and $16.0 < 2\theta < 18.5°$) of these samples. This indicates that the B-type pattern at least in part originated from retrograded amylopectin.

DSC Characteristics in Relation to WAXD Patterns of Acid-Hydrolyzed Rice Samples. Panels **A** and **B**of **Figure 2** show the DSC characteristics of acid-hydrolyzed nonparboiled and mildly, intermediately, and severely parboiled rice samples of the cultivars Jacinto and Puntal, respectively. The DSC thermograms of the acid-hydrolyzed rice samples were complemented with WAXD analyses (**Figure 3**). By doing so, we were able to distinguish between acid-labile B-type crystallites originating from retrograded amylopectin and acid-resistant B-type crystallites originating from amylose crystallites.

Mild acid hydrolysis for 54 days solubilized 82% of the starch of nonparboiled rice. Mildly and intermediately parboiled rice showed 90% solubilized starch, whereas severely parboiled rice had 95% solubilized starch after 54 days of acid hydrolysis. These levels were in line with the results of Jacobs et al. (*18*), who measured 89% solubilized starch after mild acid hydrolysis (2.2 M HCl) of potato starch for 20 days.

The acid-hydrolyzed **nonparboiled rice** samples showed a clear native starch A-type pattern. A V_h-type pattern was not observed, indicating the absence of crystalline amylose−lipid complexes (**Figure 3**). Acid hydrolysis shifted the DSC melting endotherms of the native starch of the nonparboiled rice samples to higher temperatures (**Figure 2**). Whereas the peak temperatures (T_p) of the native samples were 76.9 and 74.1 °C for the cultivars Jacinto and Puntal, respectively (**Table 1**), T_p of the hydrolyzed samples were ca. 93.0 °C (**Figure 2**). Similar changes as a result of acid hydrolysis of various starches were observed earlier. Such observations have been attributed to hydrolysis of the amorphous parts in the granule (*18*, *25*, *26*). As long as they are present, such amorphous parts destabilize the native starch crystallites by water absorption and subsequent swelling in DSC analyses (*27*). As suggested by Morrison et al. (*12*), the higher T_p in acid-hydrolyzed starch is caused by the presence of longer amylopectin double helices. According to the authors, hydrolysis of the branch points may well increase the effective length of the helix-forming side chains.

The acid-hydrolyzed **mildly parboiled rice** samples showed both clear A- and V_h-type diffraction patterns (**Figure 3**). Moreover, for the cultivar Puntal, the intensities of the reflections at $2\theta = \sim 17°$ (indicative of A- as well as B-type) exceeded those of the reflections at $2\theta = \sim 18°$ (indicative of A-type) and a small reflection at $2\theta = \sim 5°$ (indicative of B-type) was detected. Hence, small levels of (re)associated starch (B-type crystallites) were present in this sample. As with DSC, no melting endotherm of (acid labile) retrograded amylopectin (with a T_p at ca. 52 °C) was detectable after acid hydrolysis (**Figure 2B**), so we can conclusively state that the B-type crystallites in the acid-hydrolyzed mildly parboiled sample of the cultivar Puntal originated from amylose crystallites. The DSC thermogram of the acid-hydrolyzed mildly parboiled sample of the cultivar Jacinto showed a single endotherm with a T_p at ca. 95 °C (**Figure 2A**), which most probably originated from the melting of enriched amylopectin crystallites starch. Neither crystalline amylose−lipid complex nor amylose crystallite melting was detected. The thermogram of the mildly parboiled sample of the cultivar Puntal consisted of two incompletely separated endotherms. Because the endotherms were not baseline separated, quantification of the different melting endotherms lacked accuracy. The extent of overlay of the endotherms depended on the severity of steaming conditions and made peak separation and integration difficult. Most probably, the first (T_p at ca. 95 °C) and second endotherms (T_p at ca. 125 °C) originated from melting of residual nongelatinized starch and amylose−lipid complexes or amylose crystallites, respectively.

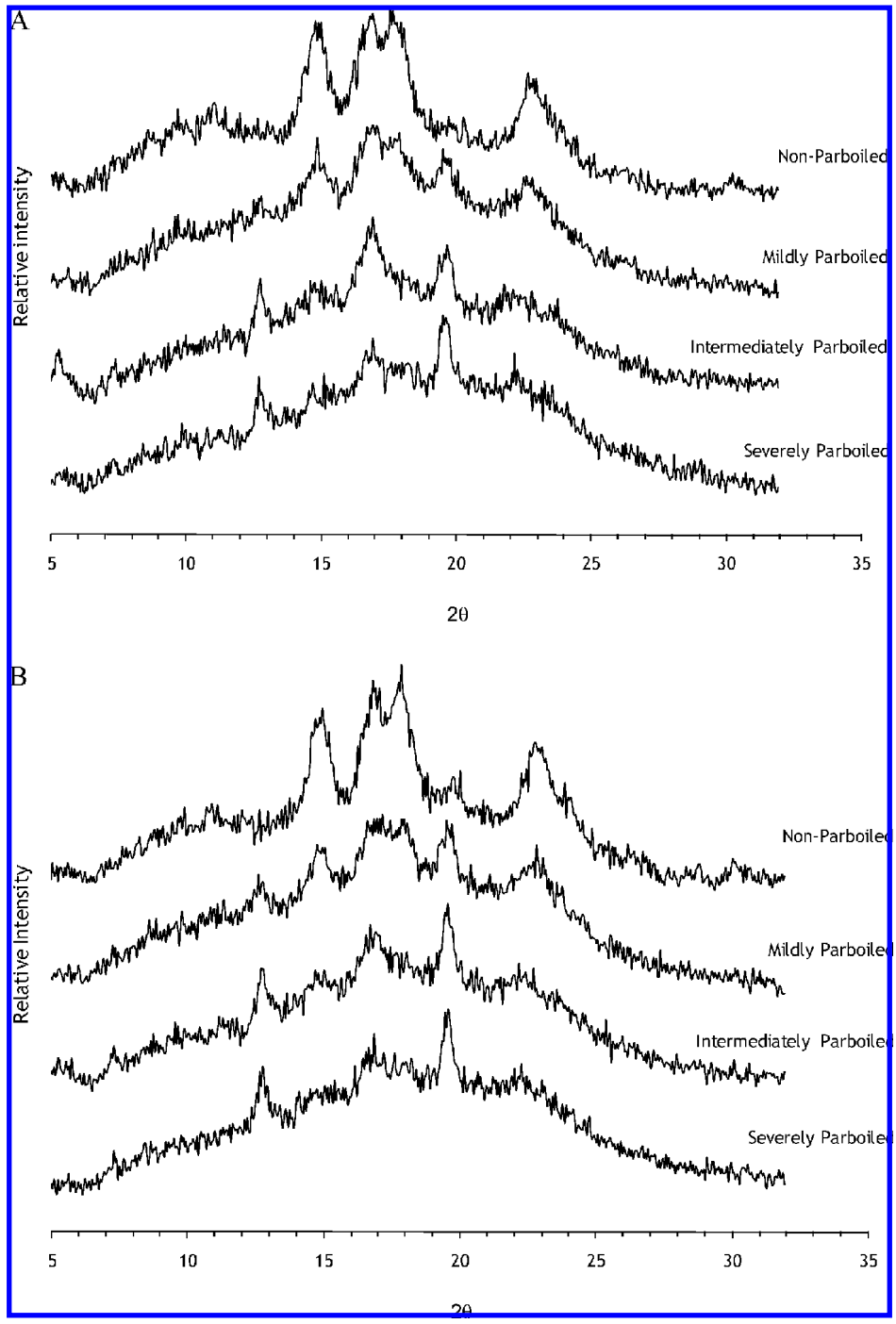

Figure 1. Static WAXD intensity patterns of nonparboiled and mildly, intermediately, and severely parboiled rice samples of the cultivars Jacinto (**A**) and Puntal (**B**). The patterns have been displaced along the ordinate to facilitate interpretation.

Indeed, Mestres et al. (*10*) observed that, following acid hydrolysis, the transition melting temperature of amylose crystallites decreases from ca. 160 to ca. 130 °C. They suggested that this may be due to stabilization of the crystallites by the amorphous regions, competition for water between the amorphous and crystalline regions of the associated amylose, and/or a weak depolymerization of the crystallites during acid hydrolysis.

The acid-hydrolyzed **intermediately parboiled rice** of both cultivars showed clear V_h- and B-type diffraction patterns (**Figure 3**). Inspection of the diffraction patterns did not allow us to exclude that some A-type crystallites were present in these samples. As in the mildly parboiled samples, no melting endotherm of retrograded amylopectin (with a T_p at ca. 52 °C) was detected (**Figure 2**). Hence, the B-type crystallites must have originated from amylose crystallites. The B-type pattern was more intense for the samples of the cultivar Puntal than for those of the cultivar Jacinto, which is in line with the higher amylose content of the former. The DSC thermogram of the intermediately parboiled samples showed three unseparated endotherms (T_p at ca. 95, 110, and 130 °C, for both cultivars). Most probably, they originated from the transition of small levels of residual amylopectin double helices, dissociation of amylose−lipid complexes, and melting of amylose crystallites, respectively. The former was explained on the basis of unwinding of residual amylopectin double helices (*16*). Whereas the nonhydrolyzed intermediately parboiled samples did not show a gelatinization endotherm (**Table 1**), the appearance of an endotherm in the acid-hydrolyzed samples most probably can

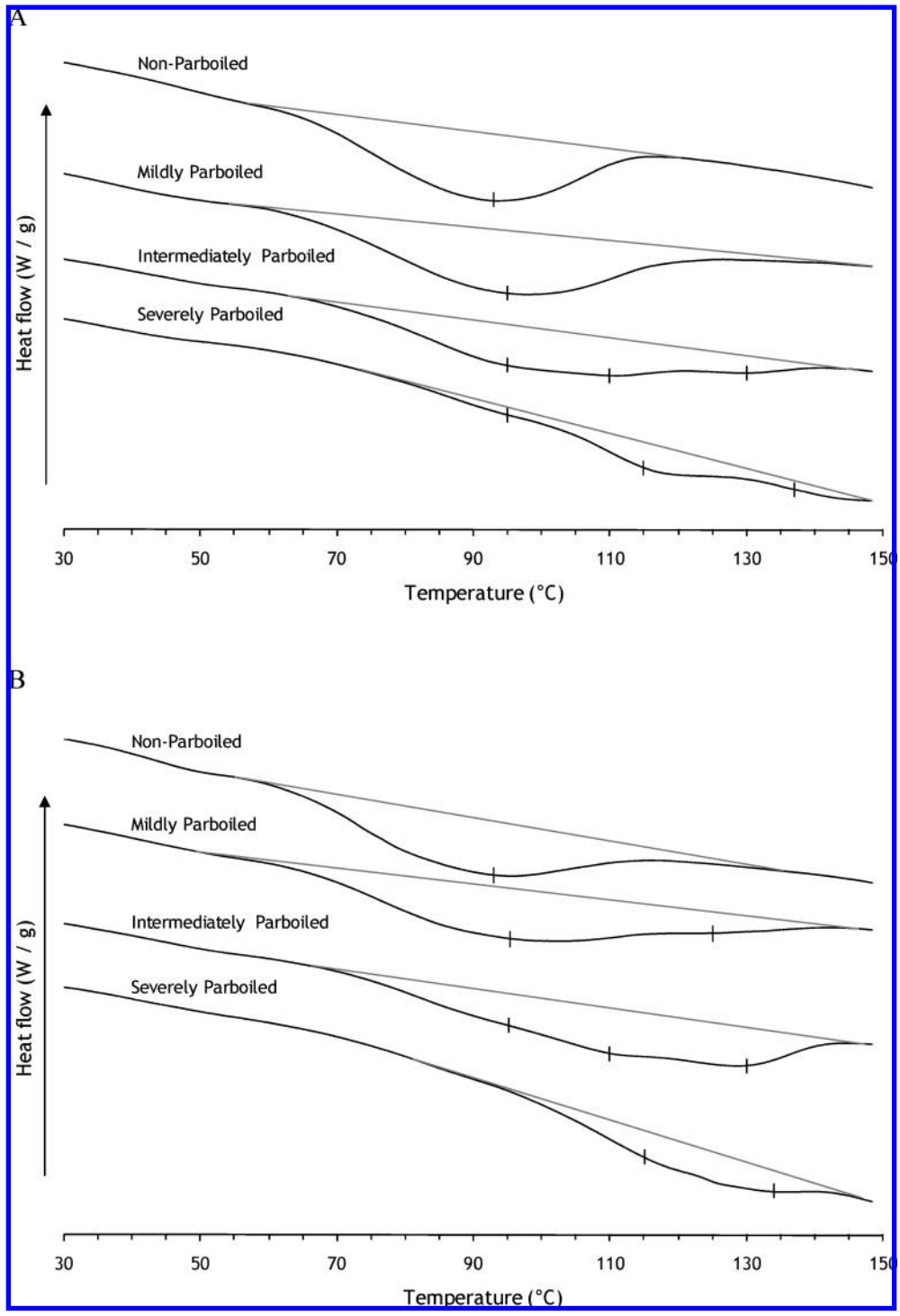

Figure 2. DSC thermograms of acid-hydrolyzed (1.0 N HCl, 37 °C, 54 days) nonparboiled and mildly, intermediately, and severely parboiled rice samples of the cultivars Jacinto (**A**) and Puntal (**B**). The marks on the thermograms indicate peak temperatures.

be ascribed to the increased concentration of the crystalline material. The relative size of the third endotherm of the acid-hydrolyzed sample of the cultivar Puntal was larger than that of the cultivar Jacinto. Hence, these observations indicated that the level of amylose crystallites was larger in the cultivar Puntal than in the cultivar Jacinto. These DSC results were also confirmed by the higher reflections at $2\theta = \sim 5°$ and $2\theta = \sim 17°$ for Puntal than for Jacinto.

The WAXD patterns of the acid-hydrolyzed **severely parboiled samples** were very comparable to those of the acid-hydrolyzed intermediately parboiled samples (**Figure 3**). The DSC thermogram of acid-hydrolyzed severely parboiled Jacinto consisted of three unseparated endotherms with T_p at ca. 95, 115, and 137 °C (**Figure 2**). These endotherms most probably had the same origin as those of the acid-hydrolyzed intermediately parboiled rice samples (cfr. supra). The DSC thermogram of the acid-hydrolyzed severely parboiled Puntal showed only two unseparated endotherms with T_p at ca. 115 and 135 °C. Again, the last endotherm was more pronounced for the cultivar Puntal. Probably, no residual amylopectin double helices were present in this sample. This agrees well with the lower melting temperature of the starch of this cultivar than of Jacinto (**Table 1**).

Miles et al. (*11*) stated that starch gelatinization in excess

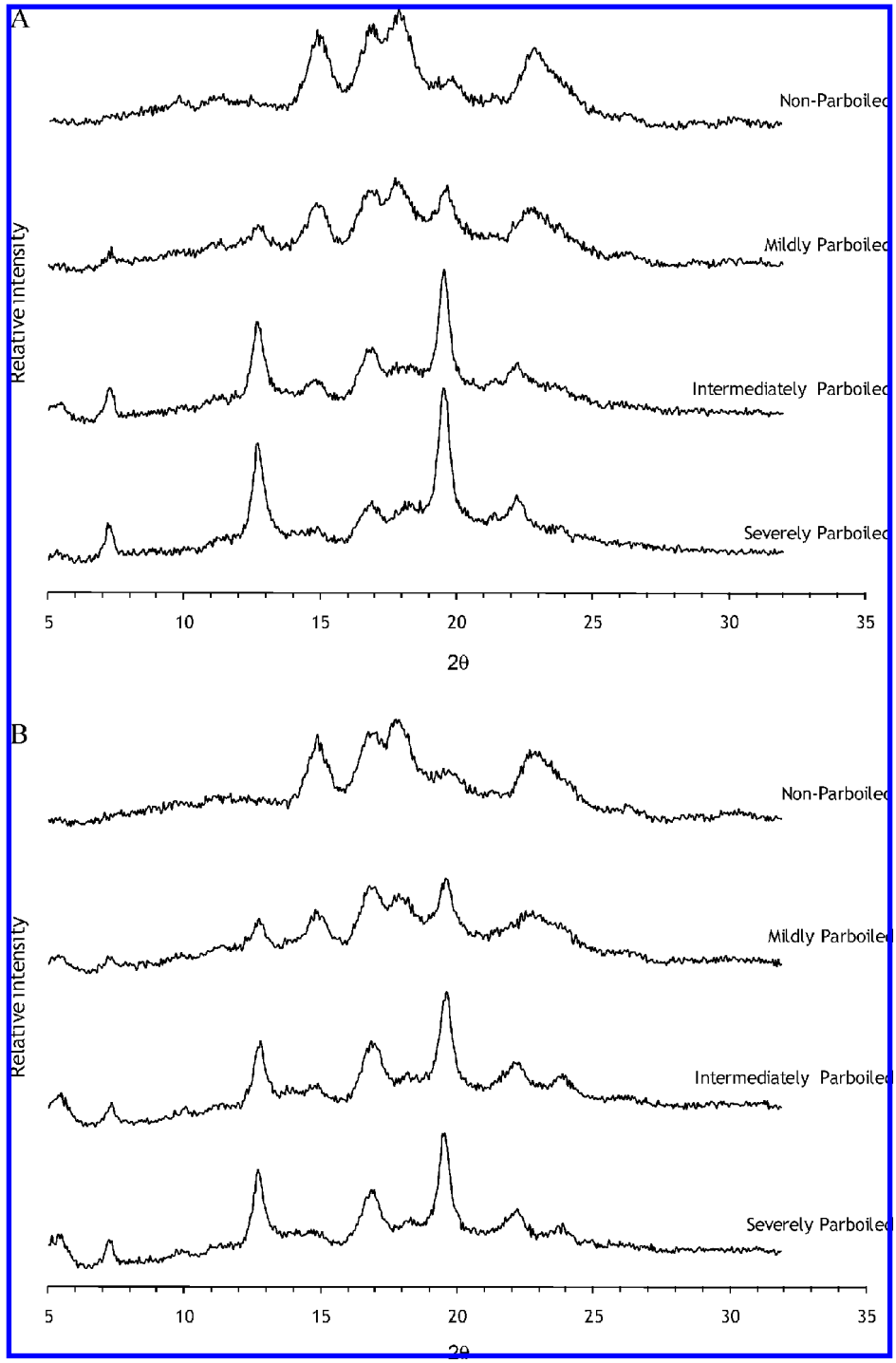

Figure 3. Static WAXD patterns of acid-hydrolyzed (1.0 N HCl, 37 °C, 54 days) nonparboiled and mildly, intermediately, and severely parboiled rice samples of the cultivars Jacinto (**A**) and Puntal (**B**). The patterns have been displaced along the ordinate to facilitate interpretation.

water leads to remnants of starch granules, enriched in amylopectin and embedded in an amylose matrix. The latter consists of a three-dimensional network comprising short segments strongly linked to one another by junction zones. These junction zones may correspond to amylose crystallites. As the water content during parboiling is limited, it can be questioned whether the amylose crystallites in parboiled rice have the same nature as in starch gels (excess water). By analogy with what has been described for bread (*28*), it is conceivable that, in parboiled rice, part of the amylose is leached and part of it is present in the center of the starch granules (the outer starch layers are then enriched in amylopectin). The leached amylose may form a continuous network in which the granules are embedded. However, the amylose in the center of the granule may form ordered structures as well and, consequently, may have an impact on the rigidity of the starch granule remnants (*29*). Because the amylose crystallites in parboiled rice have melting temperatures exceeding 100 °C, they may have an impact on the texture properties of the cooked parboiled rice by influencing the starch rigidity. Their exact influence on cooked parboiled rice texture requires further research.

In conclusion, our results, for the first time, convincingly show the presence of amylose crystallites in parboiled rice. The level of amylose crystallites seems to depend on both the parboiling conditions and the cultivar. Mildly parboiled rice showed lower amylose crystallites levels than intermediately and severely

parboiled rice samples. The cultivar with the higher FAM level (Puntal) had more amylose crystallites than that with the lower FAM level (Jacinto).

ABBREVIATIONS USED

FAM, free amylose; ΔH_{AML}, amylose−lipid complex melting enthalpy; ΔH_{gel}, gelatinization enthalpy; ΔH_{retro}, retrograded amylopectin melting enthalpy; dm, dry matter; DSC, differential scanning calorimetry; DP_n, number-average degree of polymerization; DP, degree of polymerization; T_p, peak temperature; $T_{p,AML}$, peak temperature of melting of amylose−lipid complexes; $T_{p,retro}$, peak temperature of melting of retrograded amylopectin; WAXD, wide-angle X-ray diffraction.

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