Available online at www.sciencedirect.com
SCIENCE DIRECT
Carbohydrate Polymers 58 (2004) 71–77
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

A differential thermal analysis of the gelatinization and retrogradation of wheat starches with different amylopectin chain lengths

Kaoru Kohyama[a,*], Junko Matsuki[a], Takeshi Yasui[b], Tomoko Sasaki[a]

[a]National Food Research Institute, 2-1-12 Kannondai, Tsukuba, Ibaraki 305-8642, Japan
[b]National Agricultural Research Center for Western Region, Fukuyama, Hiroshima 721-8514, Japan

Received 12 December 2003; accepted 25 June 2004
Available online 5 August 2004

Abstract

This paper reports on the influence of amylopectin chain length distributions on the gelatinization and retrogradation of starch. Wheat starch samples with different amylopectin chain length distributions were isolated, and the gelatinization and retrogradation phenomena of the samples were studied with differential scanning calorimetry (DSC). Wheat starch containing longer side chains of amylopectin (LCA) in higher ratios exhibited a sharper and deeper peak at higher temperatures in the heating DSC curve than did starch with low ratios. The retrogradation of starch was advanced with LCA. Although the re-gelatinization temperatures for retrograded starch varied slightly, the peak depth and enthalpy for re-gelatinization were higher with high ratios of LCA. For retrograded starch, each ordered region of amylopectin was not very different, however, more number of ordered regions was formed as the ratio of LCA of amylopectin increased.

Keywords: Wheat starch; Chain length; Amylopectin; Differential scanning calorimetry (DSC); Gelatinization; Retrogradation

1. Introduction

Starch is a partially crystallized polymer material as observed by X-ray diffraction (Biliaderis, 1990). Different crystal structures are observed in starches from different origins. Cereal starch, including wheat (*Triticum aestivum* L.), has an A-type structure, while tuber starch exhibits a B-type crystal in its X-ray diffraction pattern (Biliaderis, 1991). Both polymorphs are composed of ordered arrays of double helices made up of two parallel single strands (Imberty, Chanzy, Pérez, Buléon & Tran, 1988; Imberty & Pérez, 1988; Wu & Sarko, 1978a,b). Starch consists of two glucans, which are essentially linear amylose and highly branched amylopectin, where linear alpha-(1–4)-D-glucan chains are connected through alpha-(1–6) linkages (Blanshard, 1987). Amylose or linear alpha-(1–4)-D-glucan readily forms the A-type structure at higher temperature (Hizukuri, 1961), in higher concentration (Gidley & Bulpin, 1987; Hizukuri, 1961), and with shorter chain length (Gidley & Bulpin, 1987; Pfannemüller, 1987).

When starch is heated in the presence of enough water, starch granules swell, and the crystalline organization in starch decomposes to form amorphous regions (Atwell, Hood, Lineback, Varriano-Marston & Zobel, 1988). This molecular disordering is called gelatinization, and is often observed an endothermic phenomenon using differential scanning calorimetry (DSC) (Biliaderis, 1990, 1991). Amylose alone does not exhibit a peak near the gelatinization temperature in a heating DSC curve, and the peak area for starch gelatinization generally increases with amylopectin content (Russell, 1987). Although the area of the endothermic peak observed in heating DSC for a starch–water mixture correlates with both the crystalline order as quantified by X-ray diffraction and the double-helical (molecular) order determined by nuclear magnetic resonance (NMR) spectroscopy, the endothermic peak for a starch–water mixture originates from the loss of double-helices in amylopectin rather than the loss of the crystalline structure (Cooke & Gidley, 1992). The DSC thermogram of starch varies with the origin of the starch and the DSC

* Corresponding author. Tel.: +81-29-838-8031; fax: +81-29-838-7996
E-mail address: kaoruk@nfri.affrc.go.jp (K. Kohyama).

0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.06.032

conditions, and may be influenced by the ordered structure, i.e. the double helices, of amylopectin.

The amorphous region in gelatinized starch aggregates and re-crystallizes, when gelatinized starch is kept below the gelatinization temperature. This event is known as the retrogradation of starch, which progressed more quickly at lower temperatures and a high starch concentration (Biliaderis, 1991; Paton, 1987). The number and/or the structure of the re-organized regions in retrograded starch differ from those in native starch. B-type crystals are found in retrograde cereal starch (Biliaderis, 1990) that showed an A-type structure before gelatinization. A-type crystal is known as the most thermodynamically stable form, while the B-type is the kinetically favored polymorph (Gidley & Bulpin, 1987). Retrogradation consists of two processes: the rapid gelation of amylose solubilized during gelatinization and the slower recrystallization of amylopectin (Biliaderis, 1990). The latter phenomena can be monitored by DSC, since the re-organized region in amylopectin melts again endothermally. DSC is very useful for studying the long-term retrogradation of starch as constant water content can be achieved using sealed sample pans (Nakazawa, Noguchi, Takahashi & Takada, 1985).

Starch from the same species or cultivar sometimes possesses different gelatinization properties due to environmental effects (Morrison, 1993; Tester & Karkalas, 2001). The temperature during plant maturation is one such factor that affects starch properties. Wheat starch (Matsuki, Yasui, Kohyama & Sasaki, 2003; Shi, Seib & Bernardin, 1994; Tester et al., 1995) as well as that from rice (Asaoka, Okuno & Fuwa, 1985; Asaoka, Okuno, Hara, Oba & Fuwa, 1989; Asaoka, Okuno, Konishi & Fuwa, 1987; Asaoka, Okuno, Sugimoto, Kawakami & Fuwa, 1984; He, Kogure & Suzuki, 1990; Hizukuri, 1969; Inouchi, Ando, Asaoka, Okuno & Fuwa, 2000), barley (Tester, 1997; Tester, South, Morrison & Ellis, 1991), potato (Hizukuri, 1969; Protserov, Wasserman, Tester, Debon, Ezernitskaja & Yuryev, 2002; Tester, Debon, Davies & Gidley, 1999), and sweet potato (Noda, Kobayashi & Suda, 2001) has a high gelatinization temperature when grown at a high environmental temperature. In rice, a higher temperature increases the number of long chains in amylopectin (Asaoka et al., 1985, 1989), and decreases the level of amylose (Asaoka et al., 1989). Shi et al. (1994) reported differences in the chain-length distributions of amylopectin, but there were variations in temperature dependence. A higher contents of amylose and starch–lipid was found in wheat starch grown at higher temperatures (Shi et al., 1994). Our previous report on four cultivars of wheat (Matsuki et al., 2003) revealed that the gelatinization temperatures elevated in correlation with the proportions of longer chains between DP 13 and 34 in amylopectin. The crystalline and double-helical structure of starch may be influenced by the environmental temperature. The molecular order of amylopectin can be detected by DSC measurement, although that of pure amylose is difficult to ascertain.

Starch samples with different amylopectin chain-length distributions were isolated from wheat grown at various temperatures (Matsuki et al., 2003). In this paper, we report on the gelatinization and retrogradation observed with DSC heating measurements and discuss the structure of the ordered regions in the amylopectin.

2. Materials and methods

2.1. Wheat starch

Four cultivars of spring wheat (Norin 3, Norin 29, Haruhikari, and Haruyutaka) were grown in a growth chamber after anthesis (Matsuki et al., 2003). The day/night temperatures (14 h/10 h) were controlled at 15/10, 20/15, 25/20, and 30/25 °C. Each cultivar and temperature condition was tested twice. Starch samples isolated as described in Matsuki et al. were stored in a desiccator containing a saturated solution of ammonium nitrate, corresponding to a relative humidity of 0.63. The water content of starch was 14.5%w/w.

Lipid associated with starch was extracted with water-saturated *n*-butanol containing 0.01% butylated hydroxytoluene and the composition of fatty acid methyl ester (FAME) was determined as described (Yasui, Matsuki, Sasaki & Yamamori, 1996). Lipid content (%) was calculated by multiplying the weight (g) of FAME/100 g starch by a factor of 1.7 (Morrison, Mann, Soon & Coventry, 1975).

The distribution of the chain lengths of the amylopectin has been described elsewhere (Matsuki et al., 2003). The distributions calculated from the elution curves resembled each other, and were characteristic of wheat amylopectin as reported by Koizumi, Fukuda & Hizukuri (1991) and Hizukuri (1996). However, the samples with shorter chains [degree of polymerization (DP) = 6–12], more often consisted of starch prepared from wheat grown at lower temperature, while those with longer chains (DP > 12) were prepared in higher ratios from wheat grown at higher temperatures. Therefore, negative correlations were found between distributions in the shorter chains and environmental temperature, while in contrast, the percentages of the longer chains with DP greater than 12 and the maturation temperature were positively correlated (Matsuki et al., 2003).

2.2. Differential scanning calorimetry

DSC measurements were performed using an SSC5200H system with a DSC120 module (Seiko Instruments Inc., Tokyo) as described by Kohyama and Nishinari (1991). Starch (5.0 mg) and distilled water (45 mg) were weighed directly in a 70 μl silver pan, and the pan was sealed hermetically. A pan containing 45 mg of water was used as a reference. The pans were heated from 25 to 130 °C at a rate of 1.0 °C/min. After the first run of heating, the pan was

quenched immediately to room temperature (20 °C) and then stored at the temperature for various lengths of time. The second run was performed from 5 to 120 °C at the same heating rate after storage. The slow heating rate (1.0 °C/min) was chosen to analyze the DSC data thermodynamically. Each sample was measured at least twice.

2.3. Statistics

An analysis of variance (ANOVA) was performed with an SPSS package (Version 11.0J for Windows; SPSS Inc., Chicago, IL) to test the effects of environmental temperatures and cultivars. When the F-ratio was significant, the difference of the means was determined with the Tukey's multiple comparisons. Statistical significance was set at $p<0.05$.

3. Results and discussion

The lipid content of the starch samples ranged from 0.8 to 1.2%, and did not exhibit any clear dependence on environmental temperature or cultivar. The amylose content in the starch varied from 28.1 to 32.2% (mean 30.4%) (Matsuki et al., 2003), as commonly reported for spring wheat. With increasing environmental temperature, starch lipid levels were increased markedly (Shi et al., 1994) and amylose contents were increased slightly (Shi et al., 1994; Tester et al., 1995). Unlike the previous reports, there were few differences in lipid content and amylose content, and no dependency on growth temperature. The differences in the wheat starches grown at various environmental temperatures were basically due to differences in the chain length distribution of amylopectin.

ANOVA results revealed that among the four wheat cultivars, the differences in DSC parameters were small, and not statistically significant ($p>0.05$ except for peak temperature and peak width with $p>0.01$). The temperature effects on the DSC curves were common for all the cultivars. We thus analyzed the four different cultivars together, to clarify the relationships between the DSC parameters and amylopectin chain lengths.

Fig. 1 depicts typical DSC curves for starch gelatinization. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and peak width at half height (W_d) were read directly. The peak height (H_p) and enthalpy for gelatinization (ΔH) were calculated from the depth and peak area of an endothermic peak, respectively. These parameters per starch weight were less dependent on the starch concentration when the concentration was less than 10%w/w (Biliaderis, 1990; Kohyama & Nishinari, 1991). As shown in Table 1, the peak shifted to a higher temperature and became narrower and deeper with increasing growth temperature. The difference in T_c was smaller than the differences in the other parameters. The gelatinization enthalpy increased slightly at higher growth

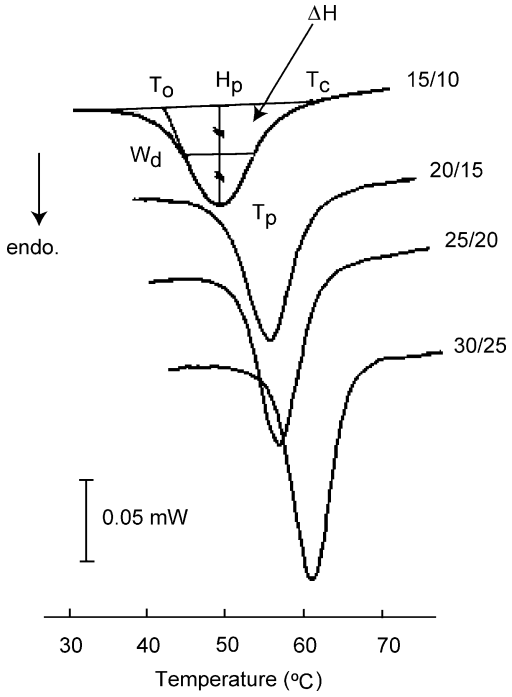

Fig. 1. Observed DSC curves for 10% w/w wheat starch. Heating rate: 1.0 °C/min. Sample: Norin 3 grown at the temperatures on the right of the curves. Examples of onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), peak width at half height (W_d), peak height (H_p) and enthalpy for gelatinization (ΔH) are shown. The latter two values are calculated in g-dry matter from the depth and peak area of an endothermic peak.

temperatures. These observations may be mainly due to the different distributions of the amylopectin side chains, since there were few differences in amylose, lipid and other starch components that could affect DSC parameters (Biliaderis, 1990). Those results confirm that high environmental temperature elevated the gelatinization temperature, as previously reported for wheat starch (Shi et al., 1994; Tester et al., 1995) as well as for various starches (Hizukuri, 1969; Asaoka et al., 1984, 1985, 1987, 1989; He et al., 1990; Tester, 1997; Tester et al., 1991, 1999; Morrison, 1993; Inouchi et al., 2000; Noda et al., 2001; Protserov et al., 2002).

The other possible cause of the growth temperature effects on starch gelatinization shown in Table 1 is annealing. Annealing is a physical process that is an observed increase in gelatinization temperature and a narrowing of the range between T_o and T_c when starch is heated in water below the gelatinization temperature for a number of hours (Tester, Debon & Karkalas, 1998). The annealing of wheat starch could be initiated when the starch contained 20%w/w moisture but it was restricted to a water content lower than 60%w/w (Tester et al., 1998). The annealing effects on elevating T_p were greater at higher annealing temperatures, but at least 15 °C below the T_o. Our results showed greater temperature effects than the annealing effect, which reported that the increase in T_p was 3 to 4 °C at most when the annealing temperature was

Table 1
Parameters of observed DSC curves for gelatinization of 10%w/w wheat starch

Environmental temperature[a]	T_o (°C)	T_p (°C)	T_c (°C)	W_d (°C)	H_p (mW/g-DM)[b]	ΔH (J/g-DM)[b]
15/10	44.2a	51.6a	66.1a	8.21c	16.07a	9.78a
20/15	49.7b	55.2b	67.9ab	6.33b	22.96b	10.85b
25/20	52.5c	56.8c	67.0a	4.98a	29.93c	11.13b
30/25	55.8d	59.9d	70.0b	4.52a	33.48d	11.46b

Mean values of four cultivars × 2 preparations × 2 replicates are presented. Values followed by different alphabetical letters with a column differ significantly ($p < 0.05$).
[a] Day (14 h)/night (10 h) temperature.
[b] g-dry matter.

25 or 35 °C (Tester et al., 1998). Thus, it is difficult to conclude that the growth temperature effects on gelatinization were due to annealing alone, although the environmental temperature was in the range in which annealing occurs.

Fig. 2 illustrates the observed DSC curves for gelatinization (first run) and retrogradation (5, 17, and 129 weeks). The peak after storage was much broader and shallower than that of the first run. The re-gelatinization peak was shifted to a higher temperature, and the depth and area increased with storage time, the same as in previous observations (Kohyama & Nishinari, 1991; Nakazawa et al., 1985). Some samples possessed T_p values exceeding that of the first run after 129 weeks of storage (one example is shown in Fig. 2). The samples prepared from wheat grown at 15/10 °C possessed a slightly higher re-gelatinization temperature (T_o and T_p) and smaller peak width than the first run, after being stored for 129 weeks. The higher re-gelatinization temperature observed may have been partly affected by annealing because the storage temperature after the first run was higher than the growth temperature. The differences in temperatures were in the range of annealing effects reported by Tester et al. (1998).

In this study, we avoided using a high starch concentration for analytical convenience, since the observed curve became less symmetrical and a second peak or shoulder sometimes appeared at higher temperatures (Biliaderis, 1990; Kohyama & Nishinari, 1991). With a low starch concentration and a high storage temperature (~20 °C), the rate of retrogradation was slow (Biliaderis, 1991; Paton, 1987). The retrogradation of wheat starch was slower than that of maize, pea and potato (Orford, Ring, Carroll, Miles & Morris, 1987), or corn and barley starches (Kalichevsky, Orford, & Ring, 1990) from rheological observations. The ΔH for 53%w/w wheat starch continued to increase after 40 days of storage at room temperature (Eliasson, 1983). For those reasons, saturation of ΔH was not observed after three years in the present condition (data not shown).

The values of ΔH for a 30%w/w concentration of wheat starch reached a saturated value after about eight days of storage at 5 °C (Paton, 1987). To achieve faster retrogradation, we also tested a higher concentration of wheat starch (36%w/w) and a lower storage temperature (5 °C) for samples grown at 15 °C and 30 °C. ΔH was saturated at around 200 h of storage for both systems, as reported previously (Paton, 1987). Retrogradation proceeded at almost the same rate for both systems. However, the saturated value of ΔH for 30 °C (5.42 J/g-dry matter) exceeded that for 15 °C (4.53 J/g-dry matter). We compared retrogradation parameters at a given duration of storage as the retrogradation rate was considered to be similar for all the starch grown at the four different environmental temperatures. Table 2 shows the data for all the samples tested. Since peaks were smaller for shorter storage periods, only ΔH was determined for 5 and 17 weeks of storage. The values of T_o and W_d did not vary with environmental temperature, unlike the first run. However, H_p and ΔH both increased with the growth temperature (Table 2). After a long storage period, T_p and T_c values elevated slightly with the growth temperature.

Both gelatinization and re-gelatinization enthalpies after various periods of retrogradation increased with growth temperature, as shown in Fig. 3. Re-organization was estimated by the ΔH-ratio, i.e. the ΔH value for the second

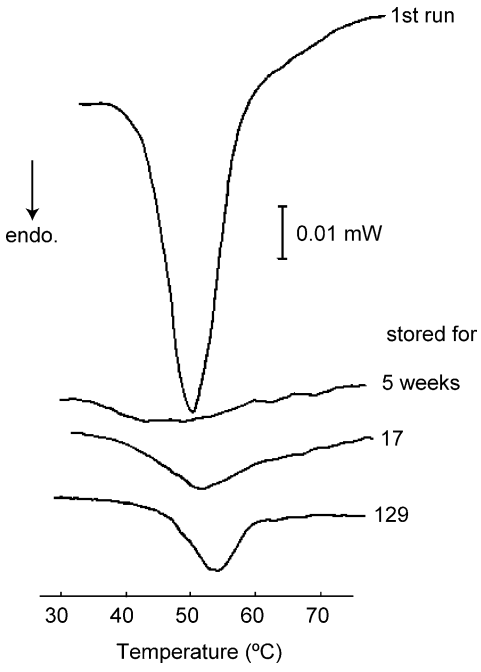

Fig. 2. Observed DSC curves for native (upper) and retrograded 10%w/w wheat starch. Sample: Norin 3 grown at 15/10 °C.

Table 2
Parameters of observed DSC curves for retrogradation of 10%w/w wheat starch

Environmental temperature[a]	Stored for 5 weeks	Stored for 17 weeks	Stored for 32 weeks					Stored for 129 weeks				
	ΔH (J/g-DM)[b]	ΔH (J/g-DM)[b]	T_o (°C)	T_p (°C)	T_c (°C)	W_d (°C)	H_p (mW/g-DM)[b]	ΔH (J/g-DM)[b]	T_o (°C)	T_p (°C)	T_c (°C)	W_d (°C)	H_p (mW/g-DM)[b]	ΔH (J/g-DM)[b]
15/10	0.81a	1.13a	38.3	49.7a	65.2	15.5	1.60a	1.32a	45.0	54.0a	62.8a	8.0	4.31a	2.23a
20/15	1.08ab	1.29a	38.2	49.5a	64.2	12.9	1.92ab	1.60ab	44.7	54.4ab	62.8a	7.9	7.18b	3.96b
25/20	1.21ab	1.52a	37.6	50.9a	63.2	13.1	2.38b	2.03b	46.3	54.8bc	63.9ab	8.0	8.38bc	4.39b
30/25	1.52b	2.50b	39.8	50.7	65.1	14.7	3.22c	2.91c	46.8	55.1c	64.9b	8.2	10.08c	5.59c

Mean values of four cultivars×2 preparations×2 replicates are presented. Values followed by different alphabetical letters with a column differ significantly ($p<0.05$).
[a] Day (14 h)/night (10 h) temperature.
[b] g-dry matter.

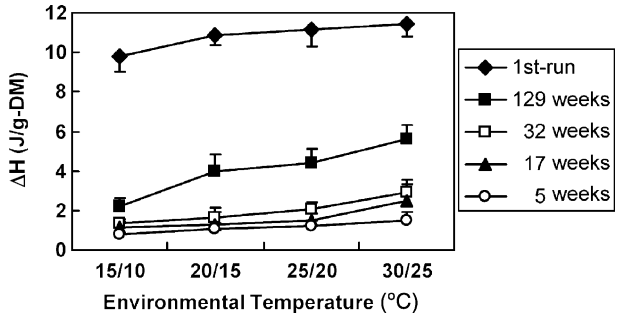

Fig. 3. Effect of growth temperature on enthalpy for gelatinization or re-gelatinization of 10%w/w wheat starch. The mean values of four cultivars×two replicates for each growth temperature are plotted. Sample cells were stored at room temperature after the first run.

run divided by that of the first run (Fig. 4). The enthalpy for re-gelatinization increased with the duration of storage. In every storage period, the ratio of the retrogradation of amylopectin was higher in samples grown at higher temperatures. This was likely affected by the higher ratio of longer chains in the amylopectin.

One glucose unit can form at most six hydrogen bonds, however, the double-helical structure of amylose actually forms an interstrand, but no intermolecular, hydrogen bond per glucose unit (Imberty et al., 1988). For the A-type crystal, one hydrogen bond per glucose unit is formed between two double helices in a crystalline region, and another is formed with water molecules (Imberty et al.). There were few long amylopectin side chains; the proportion of long amylopectin chains with DP 35 or more was 7–8% regardless of the environmental temperature (Matsuki et al., 2003). Moreover, although some chains in amylopectin may be long enough, they are highly branched (Hizukuri, 1996; Manners, 1989). A cluster model for amylopectin that composes numbers of A-chains without branching and B-chains carrying one or more A- or other B-chains by alpha-(1–6)-linkages (Hizukuri, 1986) is widely accepted. A-chains and

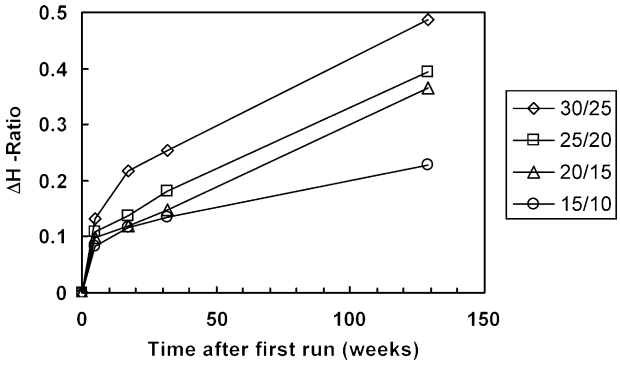

Fig. 4. Relationship between the enthalpy ratio (ΔH of the second run relative to that of the first run) and the duration of storage at room temperature. The environmental temperature after anthesis is shown in the box. The mean values of four cultivars×two replicates for each growth temperature are plotted. Sample cells were stored at room temperature after the first run.

the exterior part of B-chains contributing crystalline domains of starch are relatively short, with 12–16 glucose residues (Hizukuri, 1986). It is impossible for a long double helix to form using only the long chains, since the molecular order for native wheat starch determined by NMR is 39% (Cooke & Gidley, 1992).

Since waxy wheat starch with very low amylose content and almost pure amylopectin, exhibited a few degree higher gelatinization temperature (Yasui et al., 1996), it is unlikely that the ordered regions involve an amylose chain. If all the possible sites of hydrogen bonding (six/glucose unit) do not develop in amylopectin, we can speculate that the double helix is composed of more than two side chains of amylopectin, due to a smaller number of longer amylopectin chains. Shorter chains of amylopectin, which appear in higher proportions, may also contribute to the formation of helices. In a model system of oligosaccharides, shorter saccharides with DP$<$9 did not crystallize (Gidley & Bulpin, 1987). However, in the presence of longer chains, oligosaccharides of DP$\geq$6 units can participate in the formation of double helices (Gidley & Bulpin). In the present case, shorter amylo-pectin chains of DP$=$6–9 may also contribute to forming an ordered structure.

Assuming the ordered regions of amylopectin are created by hydrogen bondings, we can qualitatively guess the physical structure of an ordered region from the DSC endotherms of retrograded starch. The peak temperature corresponds to the size of the ordered structure because the number of hydrogen bonds relating to the size determines the energy required for cleavage in the ordered structure. Therefore, the greater crystalline regions created with more hydrogen bondings do not break until higher temperatures. The energy required for a reaction, which is the cleavage of hydrogen bondings of amylopectin in the present system, is proportionate to the frequency or number of the reacting structures in a system. The height of the DSC peak corresponds to the number of crystalline regions formed by a similar number of hydrogen bonds involving amylopectin.

The number of hydrogen bonds making an ordered structure relates to the DSC peak temperature and the number of such ordered regions corresponds to the peak height at each temperature. There are possibly two retrogradation systems. First, the longer chains in amylopectin can form rather smaller ordered regions than the native ones, while the number of ordered regions may be comparable to that in native amylopectin. Second, many shorter chains in amylopectin also form ordered regions during the retrogradation period. Fewer ordered regions are created than for native amylopectin, while the size of an ordered region is not much different from that of native amylopectin. The peak height for re-gelatinization after 129 weeks of storage at 20 °C was much smaller than that for gelatinization. A short chain can form a helical structure with a longer chain in actual amylopectin. As wheat starch grown at higher environmental temperatures contains more longer chains of amylopectin, more evidently appears in the first retrogradation process. This is why the retrogradation ratio is higher for starches from high environmental temperatures, as illustrated in Fig. 4.

As mentioned earlier, the retrogradation process is not complete. Smaller crystalline regions, which can easily be decomposed at a low temperature, are created first. Two or more ordered regions may aggregate to form a large helix during retrogradation. The large ordered regions with more hydrogen bondings are stable and keep their structure at higher temperatures. Such crystalline growth in amylopectin could result in the increase in T_p and H_p of DSC endotherms, and the decrease in W_d according to storage period (shown in Table 2).

Energy distributions of hydrogen bondings in real amylopectin systems must be considered to treat the DSC data quantitatively, however, we could qualitatively explain the ordered structures of amylopectin using a uniform energy model. It is evident that amylopectin samples with different distributions of side chains have different crystalline structures and also exhibit different retrogradation modes.

References

Asaoka, M., Okuno, K., & Fuwa, H. (1985). Effect of environmental temperature at the milky stage on amylose content and fine structure of amylopectin of waxy and nonwaxy endosperm starches of rice (*Oriza sativa* L.). *Agricultural and Biological Chemistry*, *49*, 373–379.

Asaoka, M., Okuno, K., Hara, K., Oba, M., & Fuwa, H. (1989). Effects of environmental temperature at the early developmental stage of seeds on the characterization of endosperm starches of rice (*Oriza sativa* L.). *Denpun Kagaku*, *36*, 1–8.

Asaoka, M., Okuno, K., Konishi, Y., & Fuwa, H. (1987). The effects of endosperm mutations and environmental temperature during development on the distribution of molecular weight of amylase in rice endosperm. *Agricultural and Biological Chemistry*, *51*, 3451–3453.

Asaoka, M., Okuno, K., Sugimoto, Y., Kawakami, J., & Fuwa, H. (1984). Effect of environmental temperature during development of rice plants on some properties of endosperm starch. *Starch/Stärke*, *36*, 189–193.

Atwell, W. A., Hood, L. F., Lineback, D. R., Varriano-Marston, E., & Zobel, H. F. (1988). The terminology and methodology associated with basic starch phenomena. *Cereal Food Worlds*, *33*, 306–311.

Biliaderis, C. G. (1990). Thermal analysis of food carbohydrates. In V. R. Harwalker, & C.-Y. Ma (Eds.), *Thermal analysis of foods*. London: Elsevier.

Biliaderis, C. G. (1991). The structure and interaction of starch with food constituents. *Canadian Journal of Physiology and Pharmacology*, *69*, 60–78.

Blanshard, J. M. V. (1987). Starch granule structure and function: a physicochemical approach. In T. Galliard (Ed.), *Starch: properties and potential*. Chichester: Wiley.

Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinisation:orgin of the enthalpic transition. *Carbohydrate Research*, *227*, 103–112.

Eliasson, A.-C. (1983). Differential scanning calorimetry studies on wheat starch-gluten mixtures II. Effect of gluten and sodium stearoyl lactylate on starch crystallization during ageing of wheat starch gels. *Journal of Cereal Science*, *1*, 207–213.

Gidley, M. J., & Bulpin, P. V. (1987). Crystallisation of malto-oligosaccharides as models of the crystalline forms of starch: minimum chain-length requirement for the formation of double helices. *Carbohydrate Research*, *161*, 291–300.

He, G.-C., Kogure, K., & Suzuki, H. (1990). Development of endosperm and synthesis of starch in rice grain 3. Starch property as affected by the temperature during grain. *Japanese Journal of Crop Science*, *59*, 340–345.

Hizukuri, S. (1961). X-ray diffractometric studies on starches VI. Crystalline types of amylopectin and effect of temperature and concentration of mother liquor on crystalline type. *Agricultural and Biological Chemistry*, *25*, 45–49.

Hizukuri, S. (1969). The effect of environmental temperature of plants on the physicochemical properties of their starches. *Journal of Japanese Society of Starch Science*, *17*, 73–88.

Hizukuri, S. (1986). Polymodal distribution of the chain lengths of amylopectins, and its significance. *Carbohydrate Research*, *147*, 342–347.

Hizukuri, S. (1996). Starch: analytical aspects. In A.-C. Eliasson (Ed.), *Carbohydrates in food* (pp. 347–429). New York: Marcel Dekker.

Imberty, A., Chanzy, H., Pérez, S., Buléon, A., & Tran, V. (1988). A revisit to the three-dimensional structure of B-type starch. *Journal of Molecular Biology*, *201*, 365–378.

Imberty, A., & Pérez, S. (1988). The double-helical nature of the crystalline part of A-starch. *Biopolymers*, *27*, 1205–1221.

Inouchi, N., Ando, H., Asaoka, M., Okuno, K., & Fuwa, H. (2000). The effect of environmental temperature on distribution of unit chains of rice amylopectin. *Starch/Stärke*, *52*, 8–12.

Kalichevsky, M. T., Orford, P. D., & Ring, S. G. (1990). The retrogradation and gelation of amylopoctins from various botanical sources. *Carbohydrate Research*, *198*, 49–55.

Kohyama, K., & Nishinari, K. (1991). Effect of soluble sugars on the gelatinization and retorogradation of sweet potato starch. *Journal of Agricultural and Food Chemistry*, *39*, 1406–1410.

Koizumi, K., Fukuda, M., & Hizukuri, S. (1991). Estimation of the distribution of chain length of amylopectins by high-performance liquid chromatography with pulsed amperometric detection. *Journal of Chromatography*, *565*, 233–238.

Manners, D. J. (1989). Recent developments in our understanding of amylopectin structure. *Carbohydrate Polymers*, *11*, 87–112.

Matsuki, J., Yasui, T., Kohyama, K., & Sasaki, T. (2003). Effects of environmental temperature on structure and gelatinization properties of wheat starch. *Cereal Chemistry*, *80*, 476–480.

Morrison, W. R. (1993). Cereal starch granule development and composition. In P. R. Shewry, & K. Stobart, *Seed storage compounds. Biosynthesis, interactions, and manipulation* (pp. 175–190). Oxford: Oxford University Press.

Morrison, W. R., Mann, D. L., Soon, W., & Coventry, A. M. (1975). Selective extraction and quantitative analysis of non-starch lipids from wheat flour. *Journal of the Science of Food and Agriculture*, *26*, 507–521.

Nakazawa, F., Noguchi, S., Takahashi, J., & Takada, M. (1985). Retrogradation of gelatinized starch studied by differential scanning calorimetry. *Agricultural and Biological Chemistry*, *49*, 953–957.

Noda, T., Kobayashi, T., & Suda, I. (2001). Effect of soil temperature on starch properties of sweet potatoes. *Carbohydrate Polymers*, *44*, 239–246.

Orford, P. D., Ring, S. G., Carroll, V., Miles, M. J., & Morris, V. J. (1987). The effect of concentration and botanical source on the gelation and retrogradation of starch. *Journal of the Science of Food and Agriculture*, *39*, 169–177.

Paton, D. (1987). Differential scanning calorimetry of oat starch pastes. *Cereal Chemistry*, *64*, 394–399.

Pfannemüller, B. (1987). Influence of chain length of short monodisperse amyloses on the formation of A- and B-type X-ray diffraction patterns. *International Journal of Biological Macromolecules*, *9*, 105–108.

Protserov, A., Wasserman, L. A., Tester, R. F., Debon, S. J. J., Ezernitskaja, M. G., & Yuryev, V. P. (2002). Thermodynamic and structural properties of starches extracted from potatoes grown at different environmental temperatures. *Carbohydrate Polymers*, *49*, 271–279.

Russell, P. L. (1987). Gelatinization of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *Journal of Cereal Science*, *6*, 133–145.

Shi, W.-C., Seib, P. A., & Bernardin, J. E. (1994). Effects of temperature during grain-filling on starches from six wheat cultivars. *Cereal Chemistry*, *71*, 369–383.

Tester, R. F. (1997). Influence of growth conditions on barley starch properties. *International Journal of Biological Macromolecules*, *21*, 37–45.

Tester, R. F., Debon, S. J. J., Davies, H. V., & Gidley, M. J. (1999). Effect of temperature on the synthesis, composition and physical properties of potato starch. *Journal of the Science of the Food and Agriculture*, *79*, 2045–2051.

Tester, R. F., Debon, S. J. J., & Karkalas, J. (1998). Annealing of wheat starch. *Journal of Cereal Science*, *28*, 259–272.

Tester, R. F., & Karkalas, J. (2001). The effects of environmental conditions on the structural features and physico-chemical properties of starches. *Starch/Stärke*, *53*, 513–519.

Tester, R. F., Morrison, W. R., Ellis, R. H., Piggott, J. R., Batts, G. R., Wheeler, T. R., Morison, J. I. L., Hadley, P., & Ledward, D. A. (1995). Effects of elevated growth temperature and carbon dioxide levels on some physicochemical properties of wheat starch. *Journal of Cereal Science*, *22*, 63–71.

Tester, R. F., South, J. B., Morrison, W. R., & Ellis, R. P. (1991). The effects of ambient temperature during the grain-filling period on the composition and properties of starch from four barley genotypes. *Journal of Cereal Science*, *13*, 113–127.

Yasui, T., Matsuki, J., Sasaki, T., & Yamamori, M. (1996). Amylose and lipid contents, amylopectin structure, and gelatinization properties of waxy wheat (*Triticum aestivum*) starch. *Journal of Cereal Science*, *24*, 131–137.

Wu, H.-C. H., & Sarko, A. (1978a). The double-helical molecular structure of crystalline B-amylose. *Carbohydrate Research*, *61*, 7–25.

Wu, H.-C. H., & Sarko, A. (1978b). The double-helical molecular structure of crystalline A-amylose. *Carbohydrate Research*, *61*, 27–40.