# Wheat Starch Gelatinization in the Presence of Polydextrose or Hydrolyzed Barley β-Glucan[1]

SANG SOOK KIM [2,3] and C. S. SETSER[2]

**ABSTRACT**

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Polydextrose was fractionated (into fractions with degrees of polymerization [DP] of 3-4, 6-7, 12-16, and >20) using Sephadex G-25 gel chromatography to study the effect of solute or carbohydrate size on thermal phase transitions of wheat starch. Polydextrose and its fractions that were obtained using distilled water as an eluent were compared with 5 or 10% solutions of hydrolyzed barley β-D-glucan or sucrose at a 2:1 solution-starch ratio. Other eluents, 0.5*M* NaCl in 0.1*M* phosphate buffer and 0.1*M* ammonium acetate in 20% (v/v) ethanol, were evaluated. They resulted in contamination of polydextrose fractions by eluent salts or ions that caused a significant increase in starch gelatinization onset temperature. The 10% solutions of DP 3-4 and 6-7 polydextrose fractions were compared to maltotriose, maltotetraose, maltohexaose, and maltoheptaose. The DP 6-7 polydextrose fractions increased the gelatinization onset temperature more than the other sugars. Fractions with DP >20 resulted in a wide temperature range of starch gelatinization compared to those of the DP 3-4, 6-7, and 12-16 fractions. Hydrolyzed β-glucan increased the starch gelatinization onset temperature more than polydextrose at the 20 and 30% levels.

The starch gelatinization process in sweetened bakery products is altered by the amount and type of sweetener used. Potent sweeteners with bulking agents, such as polydextrose, which has been found to have an effect similar to that of sucrose on starch thermal transitions (Kim et al 1986), can provide alternatives to sucrose for sweetening bakery products.

Polydextrose consists of a water-soluble, randomly linked glucose polymer, lightly esterified with citrate. Some classify it as soluble dietary fiber (Olson et al 1987), and the caloric value is approximately 1 Cal/g (Figdor and Bianchine 1983). Molecular weights range from 162 to 18,000, with only 10% of the polymer molecular weights found between 5,000 and 10,000 and approximately 1.3% between 10,000 and 18,000 (Allingham 1982). In a previous study, Hansen (1987) found that molecular weights of polydextrose fractions up to 1,100 increased the onset temperature of gelatinization ($T_o$). Then, as molecular weight increased above 1,100, $T_o$ decreased, but the temperature range of gelatinization broadened. Thus, the ability of molecules to enter the starch granule could be an important factor in altering gelatinization temperature, since the exclusion limit of swollen starch granules is approximately 1,000 Da (French 1984). If this is true, some polydextrose fractions could be more efficient than others as sucrose replacements in bakery products.

Molecular weight separation frequently is done by gel chromatography. Eluents other than distilled water generally are used for gel chromatography to prevent interactions between the sample and gel material with increasing eluent ionic strength. Wen et al (1988) used 0.5*M* NaCl in a 0.1*M* sodium phosphate buffer as the eluent to identify the molecular weight distribution of hemicellulose from sugar beet pulp. Conrad et al (1977) suggested the use of 0.1*M* ammonium acetate in 20% ethanol as an eluent

[1]Contribution 90-524-J from the Kansas Agricultural Experiment Station. Research supported in part by The NutraSweet Company.
[2]Graduate student and professor, respectively, Department of Foods and Nutrition, Kansas State University, Manhattan 66506.
[3]Current address: Korean Food Research Institute, Kyonggi-Do, Korea.

because that salt can be removed by evaporation. On the other hand, Hansen (1987) used distilled water as the eluent for molecular weight fractionation of polydextrose.

Recently, dietary concerns have prompted researchers to add high levels of fiber to foods. Cereal β-glucan was reported to be an effective hypoglycemic and hypocholesterolemic agent (Gordon 1989). It is a linear polysaccharide containing approximately 70% (1→4) and 30% (1→3) β-linked glucosyl residues (Dais and Perlin 1982; S. Pedersen and B. E. Norman, *unpublished data*, 1988; Woodward et al 1988). The β-glucan has a low energy value and also might serve as a bulking agent, but a successful bulk replacement for sucrose should have physical and chemical properties similar to those of sucrose. Hydrolyzed β-glucans have less viscosity and physical and chemical characteristics more similar to those of sucrose in dispersions than do intact β-glucans, which form highly viscous dispersions. The distribution of saccharides in hydrolyzed β-glucans is as follows: 0.1% DP 1, 6.0% DP 2, 54.9% DP 3, 25.4% DP 4, and 12.8% oligosaccharides greater than DP 4 (S. Pedersen and B. E. Norman, *unpublished data*). To be useful in many of the bakery products, the hydrolyzed β-glucan also should alter the starch thermal transition temperatures similarly to the way these are altered by sucrose or polydextrose.

The objective of this study was to compare the effects of different molecular sizes of oligosaccharides on thermal phase transitions of wheat starch and water dispersions, using hydrolyzed barley β-glucan and selected molecular weight fractions of polydextrose. A secondary objective was to choose a suitable eluent for the molecular weight marker preparation and fractionation of the polydextrose for the study.

## MATERIALS AND METHODS

### Gel Chromatography

Size-exclusion chromatography was done using a Sephadex G-25 (75- × 2.5-cm) column at a flow rate of 20 ml/hr. The flow rate was controlled with an LKB 2123 Microperpex peristaltic pump (LKB Co., Bramma, Sweden). An LKB 2112 fraction collector was employed to collect 3-ml fractions. Blue dextran of high molecular weight ($2 \times 10^6$) was used for the void volume determination.

*Preparation of molecular weight markers.* Total carbohydrates and reducing sugars were compared after polydextrose was fractionated using three eluents (0.5*M* NaCl in 0.1*M* phosphate buffer, 0.1*M* ammonium acetate [Fisher Scientific, Fairlawn, NJ] in 20% ethanol [Fisher Scientific], and distilled water). Total carbohydrate was measured using a Perkin-Elmer double-beam spectrophotometer (Coleman 124D, Maywood, IL) according to the method of Dubois et al (1956). The modified Park-Johnson method (Hizukuri et al 1981) was compared with the modified Nelson method (Robyt and Whelan 1968) for measuring reducing sugar, and the modified Park-Johnson method was selected because of its greater sensitivity with small quantities of the glucose and maltose reference standards. Unmodified waxy maize starch (waxy no. 1, 7340, A.E. Staley, Inc., Decatur, IL) was debranched with pullulanase (p-2138, Sigma Chemical Co., St. Louis, MO) according to the method of Craig and Stark (1984). An aliquot (5 ml, 2 mg of debranched starch per milliliter of eluent) was used for gel chromatography. The degree of polymerization (DP) of each fraction was the total carbohydrate value divided by the reducing sugar concentration.

*Eluent effect on gel chromatography and column preparation.* A Sephadex G-25 column was calibrated with maltotriose (Sigma Chemicals) and maltoheptaose (Sigma Chemicals). After the column was calibrated, 5 ml of polydextrose solutions (2 mg/ml) (Pfizer, Inc., Chemical Div., New York) were applied. Each of the three eluents (NaCl-phosphate, ammonium acetate-ethanol, or distilled water) was used for the fractionation of polydextrose. The effects of each eluent on the fractionation were evaluated by determining total carbohydrates and reducing sugars. The marker concentration was 0.5 mg/ml. Preliminary experiments determined the effect of the eluents on elution time of the fractionation process. The fractions corresponding to the molecular weight markers at the approximate DPs of 3–4 (mol wt 540–667) and 6–7 (mol wt 991–1,153) were collected using each of the eluents, frozen at −75°C (Revco model ULT 1786 A-O-C, Asheville, NC), and freeze-dried at −50°C (Virtis Co., Gardiner, NY, model 10-100). Polydextrose fractions with DP 12–16, and >20 were collected using only ammonium acetate-ethanol and distilled water. Each fraction was rechromatographed using each eluent to obtain molecular weight fractions of higher purity. Desalting of fractions obtained with NaCl-phosphate was accomplished by an additional chromatographic step using distilled water as the eluent. In addition, $^{13}$C-nuclear magnetic resonance spectroscopy according to the method by Dais and Perlin (1982) was used to identify polydextrose fractions.

### Differential Scanning Calorimetry

A differential scanning calorimeter (Perkin-Elmer DSC-4) equipped with a temperature controller was used and calibrated with indium metal. Wheat starch of known moisture content was weighed (3.3 mg, dry solids) into aluminum pans and 5 or 10% (w/w) solutions of the polydextrose fractions (DP 3–4, 6–7, 12–16, and >20) obtained with each of the eluents were added with a microsyringe. The pan was sealed and reweighed to determine the amount of fractionated polydextrose solution added. The fractionated polydextrose dispersion was added to approximate a 2:1 (w/w) solution-to-starch ratio. Samples were heated from 10 to 130°C at 10°C/min, using 0.5 mcal/sec sensitivity and a chart speed of 10 mm/min. An aluminum sample pan containing the appropriate amount of aluminum to balance the heat capacity of the sample was used as the reference.

For tests on the effects of contamination by eluents, 1% (w/w) polydextrose in the ammonium acetate-ethanol solution was concentrated at 40°C under vacuum to approximately 10% and then freeze-dried at −50°C for 48 hr. The starch thermal transitions (2:1 solution-starch, w/w) were measured using 5 and 10% distilled water solutions of the resulting polydextrose. Secondly, ammonium citrate (Fisher Scientific Co.) at 0.1, 1.0, 5.0, and 10.0% (w/w) levels was added to 2:1 water-starch systems, and thermal transitions were measured as given above.

Polydextrose solutions (5, 10, 20, or 30%) were compared with those of hydrolyzed barley β-glucan (Novo Industri, Bagsdaerd, Denmark). $T_o$s were measured according to Lund (1984). A digitizer (Altek Datalab Controller, model AC-30; Altek Co, Silver Spring, MD) with Microdij version 1.2 software on a Compaq computer was used to trace the area under the peak and calculate the enthalpies for starch gelatinization.

Analysis of variance with the Number Cruncher Statistical System (Hintze 1984) was used to ascertain the effects of treatments for four replications. Fisher's least significant difference values at $\alpha = 0.05$ were determined when treatment effects among samples were significant.

## RESULTS AND DISCUSSION

### Effect of Eluents on Gel Chromatography

*Molecular weight marker preparation.* Known concentrations of glucose were used to determine how accurately the DP could be calculated from measurements of total carbohydrates and reducing sugars if they were measured using each of the three eluents. Total carbohydrate sensitivity (Table I) was highest using 0.5*M* NaCl in 0.1*M* phosphate buffer and lowest for the 0.1*M* ammonium acetate. Reducing sugars were measured effectively only in the distilled water. Thus, DP could be calculated accurately only with the distilled water, and the preparation of molecular weight markers (with DP greater than 7) from debranched waxy maize starch was done using only the distilled water. The majority of the unit chains obtained from debranched waxy maize starch were in the DP range of 12–16, with a peak maximum at 14. The debranched, waxy starch was used for the DP 12–16 molecular weight marker, and polydextrose fractions with DP >20 were collected near the void volume.

*Fractionation of polydextrose.* The effects of polydextrose

fractions (DP 3–4, 6–7, 12–16, and >20) obtained using different eluents on starch thermal phase transitions were compared (Table II). No difference was found between effects on $T_o$ of 5% polydextrose fractions with DP 3–4 and with DP 6–7. The effect of 10% polydextrose fractions obtained using NaCl-phosphate on $T_o$ was the same as that obtained with ammonium acetate-ethanol for the same molecular weight fraction. When the NaCl-phosphate was used, considerably more time was required for fractionation than for the other two eluents because additional chromatographic processes with distilled water were necessary, making this procedure too time-consuming to be practical.

It has been reported that salts are removed by evaporation if ammonium acetate in ethanol is used as an eluent for gel chromatography (Conrad 1977). In this study, however, the 5% solutions of polydextrose fractions obtained using the ammonium acetate for the fractionation process gave a higher wheat starch $T_o$ than was produced when the phosphate buffer or distilled water was used for fractionation (Table II). We suspected that ammonium citrate was formed from interaction of the citric acid associated with polydextrose and the ammonium acetate of the eluent used for the polydextrose fractionation. The results of experiments conducted to determine whether this interaction had occurred are given in Table III. The intact polydextrose dried with ammonium acetate-ethanol and redissolved in distilled water increased the $T_o$ over the level given by the original polydextrose dissolved in distilled water. Furthermore, the direct addition of ammonium citrate to polydextrose increased the $T_o$ just as the drying of the polydextrose in the ammonium acetate-ethanol had done. Examination of the fractions with $^{13}C$ nuclear magnetic resonance spectroscopy confirmed that removal of ammonium salt-ethanol by evaporation was not complete. Consequently, deionized distilled water was determined to be more appropriate for isolating polydextrose fractions than either the NaCl-phosphate or the ammonium acetate-ethanol.

### Effects of Polydextrose Fractions and Hydrolyzed Barley β-Glucan on Wheat Starch Thermal Transitions

The effects of 5 or 10% solutions of hydrolyzed barley β-glucan, polydextrose, sucrose, or polydextrose fractions (DP 3–4, 6–7, 12–16, and >20) on $T_o$ of wheat starch were compared using a 2:1 (w/w) solution-starch ratio (Tables IV and V). The addition of any of the low molecular weight carbohydrates to a simple starch-water dispersion increased ($P = 0.05$) the $T_o$. The addition of polydextrose fractions with DP 12–16 and >20 significantly ($P = 0.05$) lowered the $T_o$ from the level given by the addition of the unfractionated polydextrose. Fractions with DP 6–7 increased the $T_o$ more than any other fraction when a 10% concentration of solution and starch (2:1 ratio) was used (Table V) but not when the concentration was 5% (Table IV); then the $T_o$ was the same as for the DP 3-4 and the unfractionated polydextrose.

These data agree with those of Hansen (1987), who also found that as the size of the polydextrose fractions increased up to DP 7 (mol wt 1,150), $T_o$ was elevated. Furthermore, as DP increased above DP 7, $T_o$ did not increase as much as with the low-molecular-weight fractions. In that study, distilled water also was used as the column eluent, and in the work with the differential scanning calorimeter, a 20 or 30% concentration of solution and

**TABLE I**
**Effect of Solvents on Sensitivity to Glucose Shown by Measurement of Total Carbohydrates and Reducing Sugars**

| Solvent | Absorbance[a] | |
|---|---|---|
| | Total Carbohydrates (glucose, 100 μg/ml) | Reducing Sugars[b] (glucose, 10 μg/ml) |
| 0.5*M* NaCl in 0.1*M* sodium phosphate buffer | 1.450 | Precipitation |
| 0.1*M* ammonium acetate in 20% ethanol | 0.287 | 0.008 |
| Distilled water | 0.733 | 0.396 |

[a] Mean value of two measurements. Absorbance was measured at 480 nm for total carbohydrates and at 715 nm for reducing sugars.
[b] Measured by the modified Park-Johnson method (Hizukuri et al 1981).

**TABLE II**
**Starch Gelatinization Onset Temperatures[a] (°C) Determined by Differential Scanning Calorimetry for 5 and 10% Solutions of Polydextrose at a 2:1 Solution-Starch Ratio**

| Fraction | Eluent | | |
|---|---|---|---|
| | Phosphate Buffer | Ammonium Acetate | Distilled Water |
| 5% Polydextrose | | | |
| DP[b] 3–4 | 63.7 ± 0.7 f | 65.5 ± 0.4 h | 60.1 ± 0.1 c |
| DP 6–7 | 63.4 ± 1.0 f | 64.3 ± 0.2 g | 59.9 ± 0.3 bc |
| DP 12–16 | ... | 64.3 ± 0.1 g | 59.2 ± 0.4 a |
| DP >20 | ... | 63.3 ± 0.2 f | 59.4 ± 0.3 ab |
| 10% Polydextrose | | | |
| DP 3–4 | 67.2 ± 0.2 j | 67.3 ± 0.4 j | 62.7 ± 0.1 e |
| DP 6–7 | 66.0 ± 0.4 hi | 66.5 ± 0.6 i | 63.7 ± 0.2 f |
| DP 12–16 | ... | 66.4 ± 0.7 i | 60.7 ± 0.3 d |
| DP >20 | ... | 65.6 ± 0.2 h | 60.4 ± 0.3 cd |

[a] Means and standard deviations of four measurements; means with the same letter in the entire table are not significantly different ($\alpha = 0.05$); LSD = 0.58.
[b] Degree of polymerization.

**TABLE III**
**Starch Gelatinization Onset Temperatures[a] (°C) in the Presence of Ammonium Salts with Polydextrose and in Systems Without Ammonium Salts**

| Solutions | Percent | Onset Temperature (°C) |
|---|---|---|
| Distilled water | | 58.5 ± 0.0 a |
| Polydextrose in distilled water | 5.0 | 60.1 ± 0.5 b |
| | 10.0 | 61.8 ± 0.4 c |
| Polydextrose dried in ethanol with ammonium acetate[b] | 5.0 | 65.0 ± 0.4 d |
| | 10.0 | 67.3 ± 0.2 f |
| Ammonium citrate plus polydextrose in distilled water | 0.1 | 60.3 ± 0.5 b |
| | 1.0 | 62.2 ± 0.2 c |
| | 5.0 | 66.4 ± 0.3 e |
| | 10.0 | 69.3 ± 0.2 g |

[a] Means and standard deviations of four measurements; means with the same letter in the entire table are not significantly different ($\alpha = 0.05$); LSD = 0.58.
[b] Polydextrose (1.0%) was dissolved in 0.1*M* ammonium acetate in 20% ethanol, dried, and redispersed (5 or 10%) in distilled water.

**TABLE IV**
**Starch Gelatinization Onset Temperatures and Enthalpies[a] (ΔH) for Distilled Water and for 5% Concentrations of Hydrolyzed Barley β-Glucan, Sucrose, Polydextrose, and Polydextrose Fractions at a 2:1 Ratio of Dispersion to Starch**

| Treatments | Onset Temperature (°C) | ΔH (Cal/g) |
|---|---|---|
| Distilled water | 58.5 ± 0.0 a | 2.48 ± 0.09 a |
| Hydrolyzed β-glucan | 59.7 ± 0.4 cd | 2.61 ± 0.08 b |
| Polydextrose, intact | 60.1 ± 0.5 de | 2.52 ± 0.07 a |
| Sucrose | 60.4 ± 0.2 e | 2.55 ± 0.09 a |
| Polydextrose fractions | | |
| DP[b] 3–4 | 60.1 ± 0.1 de | 2.52 ± 0.08 a |
| DP 6–7 | 59.9 ± 0.3 d | 2.51 ± 0.07 a |
| DP 12–16 | 59.3 ± 0.4 b | 2.52 ± 0.07 a |
| DP >20 | 59.4 ± 0.3 bc | 2.52 ± 0.05 a |
| Fisher's LSD | 0.42 | 0.11 |

[a] Means and standard deviations of four measurements; means within the same column with the same letter are not significantly different ($\alpha = 0.05$).
[b] Degree of polymerization.

starch (2:1 ratio) was used. No difference was found in the study by Hansen (1987) between the effects on $T_o$ of polydextrose fractions with DP 12–16 and of unfractionated polydextrose. The polydextrose fractions with DP >20 produced a lower $T_o$ than unfractionated polydextrose. In this work, the inclusion of polydextrose fractions with molecular weights higher than 2,016 (DP 12) resulted in a significantly lower $T_o$ than was obtained with the unfractionated polydextrose. In Hansen's study, the modified Nelson method (Robyt and Whelan 1968) was used to measure the reducing power of the fractions, whereas a modified Park-Johnson method (Hizukuri et al 1981) was used for this study. The modified Nelson method did not give equal reducing values for equimolar quantities of oligosaccharide. Instead, a higher DP value was calculated using the Nelson method than using the modified Park-Johnson method. The modified Park-Johnson method gave consistent values for equimolar quantities of oligosaccharides regardless of chain length. This could have resulted in DP <20 in the polydextrose fractions being considered as DP>20 in the Hansen (1987) study.

TABLE V
**Starch Gelatinization Onset Temperatures and Enthalpies[a] ($\Delta H$) for Distilled Water and for 10% Concentrations of Sucrose, Various Oligosaccharides, Hydrolyzed Barley β-Glucan, Intact Polydextrose, and Polydextrose Fractions at a 2:1 Ratio of Dispersion to Starch**

| Treatments | Onset Temperature (°C) | $\Delta H$ (Cal/g) |
|---|---|---|
| Distilled water | 58.5 ± 0.0 a | 2.48 ± 0.09 a |
| Sucarose | 60.8 ± 0.4 c | 2.60 ± 0.05 bc |
| Maltotriose | 62.5 ± 0.4 f | 2.67 ± 0.20 cd |
| Maltotetraose | 61.8 ± 0.3 de | 2.63 ± 0.05 b–d |
| Maltohexaose | 61.5 ± 0.4 d | 2.51 ± 0.16 ab |
| Meltoheptaose | 61.8 ± 0.2 de | 2.52 ± 0.07 a–c |
| Hydrolyzed β-glucan | 62.0 ± 0.2 e | 2.66 ± 0.06 cd |
| Polydextrose, intact | 61.4 ± 0.4 de | 2.67 ± 0.15 cd |
| Polydextrose fractions | | |
| DP[b] 3–4 | 62.7 ± 0.1 f | 2.55 ± 0.08 a–c |
| DP 6–7 | 63.7 ± 0.2 g | 2.51 ± 0.06 a |
| DP 12–16 | 60.8 ± 0.3 bc | 2.53 ± 0.06 a–c |
| DP >20 | 60.4 ± 0.3 b | 2.77 ± 0.10 d |
| Fisher's LSD | 0.41 | 0.15 |

[a] Means and standard deviations of four measurements; means within the same column with the same letter are not significantly different ($\alpha = 0.05$).
[b] Degree of polymerization.

TABLE VI
**Effect of Polydextrose Molecular Fractions[a] on Temperature Range[b] for Starch Phase Transitions[c]**

| Size of Fractions | Temperature Range (°C) |
|---|---|
| DP[d] 3–4 | 8.8 ± 0.3 a |
| DP 6–7 | 9.2 ± 0.3 a |
| DP 12–16 | 10.6 ± 0.8 b |
| DP >20 | 11.1 ± 1.0 b |

[a] Combined data for 5 and 10% (w/w) solutions of polydextrose fractions at a 2:1 solution–starch ratio were used.
[b] Starch thermal phase transition temperature range was obtained by measuring onset ($T_o$) and completion ($T_c$) temperatures according to the method of Lund (1984); temperature range = $T_c - T_o$.
[c] Means and standard deviations of eight measurements; means within the column with the same letter are not significantly different ($\alpha = 0.05$), LSD = 0.69.
[d] Degree of polymerization.

### Effects of Maltooligosaccharides on $T_o$

The 10% maltotriose solution increased the $T_o$ given by the 2:1 solution-starch more than did maltotetraose, maltohexaose, or maltoheptaose. However, polydextrose fractions with DP 6–7 increased the $T_o$ more than any of the sugars tested (Table V). Spies (1981) found a steady increase in gelatinization temperature of starch solutions containing sugars as the chain length of the sugars increased from one to four glucose units. He measured the gelatinization temperature as 50% loss of starch birefringence, using a hot-stage microscope. Increases in chain length from four to seven did not produce further increases in gelatinization temperature. Slade and Levine (1987) reported that with a series of 1:1:1 sugar-water-starch mixtures, the gelatinization temperature increased in the following order: water alone < galactose < xylose < fructose < mannose < glucose < maltose < lactose < maltotriose < maltodextrin (10 dextrose equivalent) < sucrose. Lim et al (1992) suggested that the number of hydrogen bonding sites available for interactions with the starch could determine the gelatinization temperature; thus both concentration and saccharide units would need to be considered.

Lathe and Ruthven (1956) demonstrated that maltotriose and maltotetraose delayed $T_o$ more than was expected based on molecular weights in gel permeation chromatographic experiments using starch granules as a molecular sieve. An interaction between the oligosaccharides and the starch was suspected. Studies by Brown and French (1977) using individual radioactive isotopes found maximum absorption for maltotetraose and suggested that specific binding between oligosaccharides and molecular chains in the starch amorphous phase occurred. Although a complete turn of a helix might not occur with maltotriose and maltotetraose, enough contact could occur between such oligosaccharide chains and longer starch chains to cause interactions. Interactions could stabilize the amorphous region, which could increase the glass transition temperature and then increase $T_o$.

Approximately 80% of the hydrolyzed barley β-glucans are DP 3 and 4, which contain both 1→4-β and 1→3-β linkages in the same molecule (S. Pedersen and B. E. Norman, *unpublished*

TABLE VII
**Starch Gelatinization Onset Temperature, Enthalpy, and Range[a] with Varied Concentrations of Polydextrose or Hydrolyzed Barley β-Glucan (2:1 Dispersion-Starch Ratio)[b]**

| Treatment and Concentration (w/w, %) | Onset Temperature (°C) | Enthalpy (Cal/g) | Temperature Range |
|---|---|---|---|
| Polydextrose | | | |
| 5 | 60.1 ± 0.5 a | 2.6 ± 0.1 a | 8.2 ± 0.4 ab |
| 10 | 61.8 ± 0.4 b | 2.7 ± 0.2 a | 8.9 ± 0.3 b |
| 20 | 64.2 ± 0.1 c | 2.7 ± 0.1 a | 14.6 ± 0.8 e |
| 30 | 69.5 ± 0.8 e | 2.7 ± 0.1 a | 19.3 ± 1.0 f |
| Hydrolyzed barley β-glucan | | | |
| 5 | 60.0 ± 0.5 a | 2.6 ± 0.1 a | 8.4 ± 0.4 ab |
| 10 | 62.0 ± 0.2 b | 2.7 ± 0.1 a | 8.0 ± 0.2 a |
| 20 | 66.0 ± 0.0 d | 2.7 ± 0.0 a | 9.9 ± 0.5 c |
| 30 | 70.6 ± 0.4 f | 2.7 ± 0.1 a | 11.6 ± 0.5 d |
| Fisher's LSD | 0.54 | | 0.80 |

[a] Starch thermal phase transition temperature range was obtained by measuring onset ($T_o$) and completion ($T_c$) temperatures according to the method of Lund (1984); temperature range = $T_c - T_o$.
[b] Means and standard deviations of four measurements; means within the column with the same letter are not significantly different ($\alpha = 0.05$).

*data*). The hydrolyzed barley β-glucan, with more than one type of linkage and therefore more branching than maltotriose and maltotetraose and with a greater DP than sucrose, still could have enough contact with the starch chains to result in stable associations in the starch amorphous phase and increases in the $T_o$ at the 10% concentration. Higher concentrations might be necessary compared to concentrations of sucrose because the number of interactions per molecule in the barley β-glucan would be limited.

No direct relationship between the starch thermal transition temperature and the molecular weight of the added oligosaccharide was observed in this study, as might be predicted based on free-volume theory (Ferry 1980). According to that theory, free volume is inversely proportional to the average molecular weight. Thus, the ability of a diluent to depress $T_o$ decreases as its molecular weight increases (Boyer et al 1985), and increased $T_o$ results from increased diluent molecular weight.

The limitations inherent in the chromatographic fractionation procedure might have caused the inconsistent relationship between the molecular weight and $T_o$. Before molecular weight fractionation, the column was calibrated using known molecular weight markers (maltotriose, maltotetraose, maltohexaose, and debranched starch). The molecular weight markers for each of the fractions (DP 3–4, 6–7, 12–16, and >20) were linear molecules. Molecules with different structures and the same molecular weight could have eluted in different fractions during gel filtration. Polydextrose is heterogeneous and contains all possible branches. Thus, the polydextrose fractions eluted at the marker might not necessarily be the same molecular weight as the marker.

Hansen (1987) noted that the temperature range of starch gelatinization broadened as molecular weights of polydextrose fractions increased, although in that study no statistical analysis was done. In the present study, the temperature ranges of gelatinization for starch-water slurries containing DP 3–4 and DP 6–7 fractions were similar, as was the temperature range for those containing DP 12–16 and DP >20 fractions (Table VI). The addition of DP 12–16 and DP >20 fractions resulted in a significantly wider range of temperatures for gelatinization than those of the DP 3–4 and DP 6–7 fractions. The reason for this difference is not clear. Inherent in the gel chromatographic methodology is a greater heterogeneity near the void volume for high-molecular-weight fractions than for the low-molecular-weight fractions. Heterogeneous materials result in broad peaks relative to peaks of homogeneous ones.

Both polydextrose and hydrolyzed barley β-glucan are themselves heterogeneous carbohydrates. Polydextrose has the wider range and larger molecular weights. Approximately 88.7% of the polydextrose molecules have molecular weights between 162 and 5,000, whereas approximately 87.2% of the hydrolyzed barley β-glucan molecules have molecular weights between 180 and 664 (S. Pedersen and B. E. Norman, *unpublished data*). No differences were found between the effects of polydextrose and hydrolyzed barley β-glucan on $T_o$ at 5 and 10% concentrations. However, at 20 and 30% concentrations, the addition of the hydrolyzed β-glucan increased the $T_o$ more than did the addition of unfractionated polydextrose (Table VII). If small solutes, up to approximately 1,000 Da, penetrate the starch granule (Lathe and Ruthven 1956), more of the hydrolyzed barley β-glucan than the polydextrose might enter the starch granule at the same concentration. Thus, the small sugar molecules entering the granules could result in the occurrence of all of the possible mechanisms that have been suggested (Hansen 1987): 1) a lower water activity, 2) a greater space occupied by the solute and less space available for free water (R. C. Hoseney, *personal communication*, 1989), and 3) greater opportunities for stabilizing interactions. Polydextrose showed a wider temperature range for starch gelatinization than did hydrolyzed barley β-glucan at a 10, 20, or 30% concentration (Table VII), presumably because of the greater heterogeneity of polydextrose. Generally, impure materials have wider ranges for the melting process than do pure materials. The effect was not as apparent at the 5% concentration.

The present study indicated a size limit for molecules entering the granules, which differed according to the homogeneity of the material and, perhaps, the branching and resulting shape of the molecules. If we assume that fractions of the same molecular weight would occupy the same amount of space, then the space occupied by the fractions was not critical for controlling $T_o$ in this study. However, the space occupied by the hydrolyzed barley β-glucan probably was not the same as that occupied by polydextrose DP 3–4 fractions, and other factors likely were involved. Configuration differences between barley β-glucan and polydextrose fractions could result in the different effects on starch gelatinization $T_o$ at the same molecular weight.

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