

## DSC XXIV - Carbohydrate Studies

Al Marhoobi I. M. and Kasapis S. (2005) Further evidence of the changing nature of biopolymer networks in the presence of sugar. *Carbohydr Res* **340**, 771-774.

**Abstract:** Despite claims made in the literature that polysaccharides maintain a substantially aggregated morphology in the form of "gel particulates" or "gel islands" at a high sugar environment, results of differential scanning calorimetry (DSC) discussed now demonstrate that extensive macromolecular order is not thermodynamically stable. Gelatin, on the other hand, appears to demix from the sugar-rich domains, which promote chain association rather than inhibiting it. DSC evidence is supported by previously published transmission electron microscopy (TEM) work and mechanical analysis.

Amici E., Clark A. H., Normand V., and Johnson N. B. (2002) Interpenetrating network formation in agarose--kappa-carrageenan gel composites. *Biomacromolecules* **3**, 466-474.

**Abstract:** Thermal, mechanical, turbidity, and microscope evidence is provided which strongly suggests molecular interpenetrating network (IPN) formation by mixtures of the seaweed polysaccharides agarose and kappa-carrageenan. Over a range of ionic strength, and potassium content, there is no evidence for synergistic coupling of the networks, and simple phase separation (demixing) can definitely be ruled out. At low ionic strength, where the agarose gels first, differential scanning calorimetry evidence shows some influence of the carrageenan on the agarose ordering enthalpy, particularly at higher polymer concentrations. As the potassium level is increased, however, and the order of gelling is reversed, this effect disappears. Cure behavior for the systems at high ionic strength can be described as a simple summation of the pure component contributions. At low ionic strength, on the other hand, the modulus behavior is more complex, suggesting either a modification, in the mixture, of the kappa-carrageenan gelling parameters or a more complex modulus additivity rule.

Blennow A., Wischmann B., Houborg K., Ahmt T., Jorgensen K., Engelsen S. B., Bandsholm O., and Poulsen P. (2005) Structure function relationships of transgenic starches with engineered phosphate substitution and starch branching. *Int J Biol Macromol* **36**, 159-168.

**Abstract:** Potato tuber starch was genetically engineered in the plant by the simultaneous antisense suppression of the starch branching enzyme (SBE) I and II isoforms. Starch prepared from 12 independent lines and three control lines were characterised with respect to structural and physical properties. The lengths of the amylopectin unit chains, the concentrations of amylose and monoesterified phosphate were significantly increased in the transgenically engineered starches. Size exclusion chromatography with refractive index detection (SEC-RI) indicated a minor decrease in apparent molecular size of the amylose and the less branched amylopectin fractions. Differential scanning calorimetry (DSC) revealed significantly higher peak temperatures for gelatinisation and retrogradation of the genetically engineered starches whereas the enthalpies of gelatinisation were lower. Aqueous gels prepared from the transgenic starches showed increased gel elasticity and viscosity. Principle component analysis (PCA) of the data set discriminated the control lines from the transgenic lines and revealed a high correlation between phosphate concentration and amylopectin unit chain length. The PCA also indicated that the rheological characteristics were primarily influenced by the amylose concentration. The phosphate and the amylopectin unit chain lengths had influenced primarily the pasting and rheological properties of the starch gels.

Bocchinfuso G., Palleschi A., Mazzuca C., Coviello T., Alhaique F. and Marletta G. (2008) Theoretical and experimental study on a self-assembling polysaccharide forming nanochannels: static and dynamic effects induced by a soft confinement. *J Phys. Chem B* **112**, 6473-6483.

**Abstract:** It is well-known that the polysaccharide scleroglucan (Sclg) exhibits a triple-helix conformation (triplex) and it is able to form hydrogels in water solution. Furthermore, these hydrogels are influenced by the presence of borax, in terms of rheological and drug release properties. In previous works, we showed that the presence of borax stabilizes the intertriplex interactions and that the property variations, induced by borax, can be fully explained, considering that the Sclg triplexes can form nanochannel-like structures. In this paper, the stability of these aggregates has been experimentally studied by means of atomic force microscopy (AFM) and theoretically investigated by means of molecular dynamics (MD) simulations. The simulations indicate that the borax stabilizes nanochannel-like structures when seven triplexes are considered. The simultaneous presence of different Sclg triplexes in a narrow space strongly influences the

properties of confined water molecules in a way similar, in many aspects, to that of water molecules located in the inner part of well-defined nanochannels (e.g., diffusion inside carbon nanotubes). As a consequence, also the conformational properties of flanking regions of ScI<sub>g</sub> triplexes are influenced. Furthermore, differential scanning calorimetry (DSC) data show that the well-known conformational transition occurring at 280 K for ScI<sub>g</sub> does not take place in the presence of borax. The MD simulations suggest that such lack of transition is a direct consequence of the presence of borax. The role of Na<sup>+</sup> counterions in the hydrogel structure is also investigated

Boutebba A., Milas M., and Rinaudo M. (1997) Order-disorder conformational transition in succinoglycan: calorimetric measurements. *Biopolymers* **42**, 811-819.

**Abstract:** Differential scanning microcalorimetry was performed on succinoglycan samples from different sources in order to better understand the thermally induced order-disorder conformational transition of the polysaccharide. The shape of thermograms, as well as the melting temperature, were related to the content or distribution of the succinate groups at least in salt-free solution. With increasing polysaccharide and/or salt concentration, the change in the shape of the thermogram was attributed to a progressive screening of the succinate contribution to the order-disorder conformational transition instead of a change in the transition mechanism. In the presence of salt, contrary to the rheological behavior, the calorimetric results were found to be independent of the thermal history of the samples. This suggests a very low enthalpic contribution of the interchain interactions present in succinoglycan solutions. Possible contributions that could explain some discrepancies with results already published in the literature are discussed.

Boutebba A., Milas M., and Rinaudo M. (1999) On the interchain associations in aqueous solutions of a succinoglycan polysaccharide. *Int J Biol Macromol* **24**, 319-327.

**Abstract:** Formation of interchain associations between succinoglycan chains have been studied by comparing weight average molecular weight, intrinsic viscosity of succinoglycan as a function of the conditions to prepare the solutions (polymer concentration, the heating temperature adopted compared with T<sub>m</sub>). The different solutions obtained were characterized by their Newtonian viscosity, the storage and loss moduli and their sensitivity to the temperature. It was found that interchain associations, first stabilized mainly during the disorder-order transition convert to more stable associations by aging at temperatures below but not too far from T<sub>m</sub>. These associations appear from succinoglycan solutions characterized by an overlap parameter higher than about 8 and modify only very slightly the conformational transition parameters obtained from microcalorimetry measurements.

Cao Y. and Tan H. (2002) The properties of enzyme-hydrolyzed cellulose in aqueous sodium hydroxide. *Carbohydr Res* **337**, 1453-1457.

**Abstract:** Pure natural cellulose (softwood pulp) modified with cellulase is allowed to react with sodium hydroxide in a muller, and changes in structure and properties are investigated by FTIR and DSC. The reactivity of cellulose for some dissolving and derivatization processes is shown to be improved by an enzymatic hydrolysis and admixture with sodium hydroxide. The modified cellulose dissolved at 9% (wt) sodium hydroxide at -10 degrees C at 6% pulp consistency, while the DP of cellulose is >350.

Crochet P., Beauxis-Lagrange T., Noel T. R., Parker R., and Ring S. G. (2005) Starch crystal solubility and starch granule gelatinisation. *Carbohydr Res* **340**, 107-113.

**Abstract:** The solubility and dissolution behaviour of A- and B-type crystals of short chain amylose were measured both directly and using differential scanning calorimetry in the temperature range 30-110 degrees C. Dissolution in the calorimeter was affected by super-heating to the extent of 24-28 degrees C. Following trends previously found by calorimetry the B-type crystal polymorph was more soluble than the A-type. Analysis of the chain composition of the dissolved material revealed a preferential solubilisation of the short chains at the lower temperatures. The solubility of both crystal polymorphs and the magnitude of the preferential solubilisation effect was reduced in the presence of 30% w/w sucrose. A comparison of calorimetric measurements of crystal dissolution and the gelatinisation of native granular waxy maize and potato starches found some broad similarities, such as transition temperatures and their composition dependence, and some differences, such as the relatively narrow temperature range of granular gelatinisation, which reflects its cooperative nature.

Falch B. H., Elgsaeter A., and Stokke B. T. (1999) Exploring the (1 → 3)-beta-D-glucan conformational phase diagrams to optimize the linear to macrocycle conversion of the triple-helical polysaccharide scleroglucan. *Biopolymers* **50**, 496-512.

**Abstract:** The immunologically important (1 → 6) comb-like branched (1 → 3)-beta-D-glucans scleroglucan, schizophyllan, lentinan, and others, exist mainly as linear triple-helical structures in aqueous solution. Partial interconversion from linear to circular topology has been reported to take place following conformational transition of the triple-helical structure and subsequent regeneration of the triplex conformation. We here report on experimental data indicating that complete strand separation of the triple-helical structure is required for this interconversion. NaOH or dimethylsulfoxide was used to induce dissociation of the triplex at combinations of concentrations and temperatures shown by calorimetry to yield a conformational transition of the triplex structures. For the alkaline treatment at 55 degrees C, it is found that up to about 30% of the material readily can be converted to the cyclic topology. This fraction increased to about 60% when the subsequent annealing of the scleroglucan in aqueous solution at pH 7 was carried out at 100 degrees C. Further increase of the annealing temperature yielded a smaller relative amount of cyclic species. The data indicate that the lower molecular weight fraction of the molecular weight distributions can be converted selectively to the macrocyclic topology by conditions that do not yield complete strand separation of the whole sample. These findings add to previous reports by providing more details about how the conditions required for the linear triplex to macrocycle interconversion relate to the conformational properties of the triple-helical structure. Copyright 1999 John Wiley & Sons, Inc.

Fringant C., Tvaroska I., Mazeau K., Rinaudo M., and Desbrieres J. (1995) Hydration of alpha-maltose and amylose: molecular modelling and thermodynamics study. *Carbohydr Res* **278**, 27-41.

**Abstract:** Hydration of alpha-maltose and amylose were investigated using molecular modelling and thermodynamics methods. The structure and energy of hydration of three low-energy conformers of alpha-maltose were determined by the MM3 molecular mechanics method. The hydration structure was found to be sensitive to the conformation of alpha-maltose and hydration numbers 10 or 11 were estimated for the different conformers. Differential scanning calorimetry and thermogravimetric analysis were used to determine the number of water molecules specifically bonded (non-freezing water) to amylose and different samples of alpha-maltose. Due to high crystallinity of alpha-maltose samples, the observed non-freezing water content was lower than predicted by molecular modelling. In contrast, the experimental number of non-freezing molecules of water per D-glucopyranose residue for amorphous amylose (nh = 3.8) is in good accordance with the value of 3.8 extracted from our calculations.

Fringant C., Desbrieres J., Milas M., Rinaudo M., Joly C., and Escoubes M. (1996) Characterisation of sorbed water molecules on neutral and ionic polysaccharides. *Int J Biol Macromol* **18**, 281-286.

**Abstract:** Ionic and neutral polysaccharides with well-defined structures were chosen to investigate the mechanism of water sorption at different relative humidities. From an experimental point of view, the freezing water was determined by DSC when the total sorbed water was obtained from thermogravimetry. The isotherms of sorption and enthalpies of interaction were determined using the combination of a microbalance and a microcalorimeter. It is shown that freezing water appears for P/P(zero) > 0.85 especially with the neutral polymers. The differential molar enthalpy of interaction is higher for P/P(zero) < 0.85 corresponding to the fixation of two water molecules forming double H-bonds; this result is confirmed by molecular modelling; saturation is obtained experimentally for 4 water molecules interacting per glucose unit. On ionic polymers, the water retention increases especially over P/P(zero) approximately 0.8 and the enthalpy of interaction is higher for the first water molecules sorbed. For P/P(zero) approximately equal to 0.8, the numbers of bound water molecules found are 2 per glucopyranosyl unit for neutral polysaccharides, 5 for glucuronan and 9-10 for carboxymethylcellulose (CMC) of DS = 2 and hyaluronan (HA).

Furuki T. (2000) Effect of stereochemistry on the anti-freeze characteristics of carbohydrates. A thermal study of aqueous monosaccharides at subzero temperatures. *Carbohydr Res* **323**, 185-191.

**Abstract:** Thermal behavior at subzero temperatures has been investigated for aqueous solutions of various monosaccharides. The heat of fusion of ice measured with differential scanning calorimetry has given linear plots against sugar concentration (wt.%), from which the amount of unfrozen water,  $U_w$ , has been determined for each monosaccharide. The results for  $U_w$  are analyzed by employing, as a measure of hydration characteristics, known physico-chemical properties of aqueous monosaccharides, such as partial molar compressibilities, etc. It was revealed that the anti-freeze characteristics of carbohydrates depend on

their stereochemistry. More water remains unfrozen in the aqueous solutions of carbohydrates having poorer compatibility with the three-dimensional hydrogen-bond network of water. Monosaccharides studied can be subdivided into three groups according to the extent of the anti-freeze effect. These results are rationalized in terms of a modified stereospecific hydration model.

Furuki T. (2002) Effect of molecular structure on thermodynamic properties of carbohydrates. A calorimetric study of aqueous di- and oligosaccharides at subzero temperatures. *Carbohydr Res* **337**, 441-450.

**Abstract:** For aqueous solutions of di- and oligosaccharides thermodynamic properties have been investigated at subzero temperatures using differential scanning calorimetry. The amount of unfrozen water observed is found to increase linearly with the glass transition temperatures of anhydrous carbohydrates. Furthermore, the amount of unfrozen water shows a linear relationship with known solution properties of aqueous carbohydrates, such as partial molar compressibility and heat of solution. The different effectiveness among various di- and oligosaccharides to avoid ice formation is associated with the combination of constitutive monosaccharides and attendant molecular structure features including the position and type of the glycosidic linkage between the constituent units. More unfrozen water is induced in the presence of a carbohydrate having a poorer compatibility with the three-dimensional hydrogen-bond network of water. A series of these results obtained imply that there is a common key of carbohydrate stereochemistry governing several different thermodynamic amounts of a given system involving carbohydrates. In this context, a modified stereospecific-hydration model can be used to interpret the present results in terms of stereochemical effects of carbohydrates.

Genkina N. K., Wasserman L. A., Noda T., Tester R. F., and Yuryev V. P. (2004) Effects of annealing on the polymorphic structure of starches from sweet potatoes (Ayamurasaki and Sunnyred cultivars) grown at various soil temperatures. *Carbohydr Res* **339**, 1093-1098.

**Abstract:** Starches extracted from the sweet potato cultivars Sunnyred and Ayamurasaki grown at 15 or 33 degrees C (soil temperature) were annealed in excess water (3 mg starch/mL water) for different times (1, 4, 8 or 10h) at the temperatures 2-3 degrees K below the onset melting temperature. The structures of annealed starches, as well as their gelatinisation (melting) properties, were studied using high-sensitivity differential scanning calorimetry (HSDSC). In excess water, the single endothermic peak shifted to higher temperatures, while the melting (gelatinisation) enthalpy changed only very slightly, if any. The elevation of gelatinisation temperature was associated with increasing order/thickness of the crystalline lamellae. The only DSC endotherm identified in 0.6 M KCl for Sunnyred starch grown at 33 degrees C was attributed to A-type polymorphic structure. The multiple endothermic forms observed by DSC performed in 0.6M KCl for annealed starches from both cultivars grown at 15 degrees C provided evidence of a complex C-type (A- plus B-type) polymorphic structure of crystalline lamellae. The A:B-ratio of two polymorphic forms increased upon annealing due to partial transformation of B- to A-polymorph, which was time dependent. Long heating periods facilitated the maximal transformation of B- to A-polymorph associated with limited A:B ratio.

Gronwald O., Sakurai K., Luboradzki R., Kimura T., and Shinkai S. (2001) Further evidence for the gelation ability-structure correlation in sugar-based gelators. *Carbohydr Res* **331**, 307-318.

**Abstract:** Eight methyl glycosides of 4,6-O-benzylidene derivatives of the monosaccharides D-glucose, D-mannose, D-allose and D-altrose were synthesized to systematically study the effect of small configurational changes on the ability to gelate organic solvents. Among the beta anomers, only the D-mannose glycoside exhibits a strong gelation ability, whereas in the alpha-series the D-glucose and D-mannose derivatives act as versatile gelators. Also, as a general rule we found that the beta anomers possess a higher ability to gelate solvents than the alpha anomers. The gelation properties are discussed on the basis of SAXS, FTIR, differential scanning calorimetric (DSC) measurements and scanning electron microscopy (SEM) observations. The temperature-dependent SAXS measurements were carried out to elucidate the sol-gel transition temperature. The present study emphasizes that the saccharide family provides, not only valuable information of the structural requirements for the design of new gelators, but also for molecular assembly systems in general.

Guetta O., Mazeau K., Auzely R., Milas M., and Rinaudo M. (2003) Structure and properties of a bacterial polysaccharide named Fucogel. *Biomacromolecules* **4**, 1362-1371.

**Abstract:** The chemical structure of a polysaccharide named Fucogel was characterized and the position of acetylation was identified by NMR. A conformational analysis was performed on this 3-sugar repeating unit. From this, the persistence length, characterizing the stiffness of the polysaccharide, was determined and the role of the presence of acetyl group, reducing the stiffness, was pointed out. The helical conformations were also predicted, one of these being in agreement with X-ray data obtained on a similar polysaccharide. Experimental characterization of the native and deacetylated polysaccharides was developed. SEC experiments allowed us to determine the molar mass and the persistence length on the deacetylated polysaccharide. The value is in good agreement with that predicted from the molecular modeling. Microcalorimetry, rheology, and fluorescence spectroscopy demonstrated respectively that no helical conformation exists in solution but that loose interchain interactions due to the acetyl substituents exist in dilute solutions.

Guetta O., Milas M., and Rinaudo M. (2003) Structure and properties of a bacterial polysaccharide from a Klebsiella strain (ATCC 12657). *Biomacromolecules* **4**, 1372-1379.

**Abstract:** The chemical structure and the rheological behavior of the Klebsiella polysaccharide ATCC 12657 was studied and compared with data described in the literature and obtained for similar polysaccharides. The acetylated polysaccharide presents in solution a normal viscoelastic behavior with no evidence of an ordered conformation whatever the experimental conditions are. The deacetylated form can induce the formation of physical gels, in the presence of salt excess or ethanol. Microcalorimetry, optical rotation, and rheology experiments demonstrate that a thermally reversible and highly cooperative conformational transition occurs at the same temperature than a sol-gel transition. The melting of the gel and the conformational transition temperatures are dependent on the nature of cations and ionic concentration, whereas the gel strength is only influenced by polymer concentration.

Hato M., Yamashita I., Kato T., and Abe Y. (2004) Aqueous Phase Behavior of a 1-O-Phytanyl-beta-d-xyloside/Water System. Glycolipid-Based Bicontinuous Cubic Phases of Crystallographic Space Groups Pn3m and Ia3d. *Langmuir* **20**, 11366-11373.

**Abstract:** Temperature- and concentration-dependent aqueous phase diagram of a novel alkylglycoside, 1-O-phytanyl-beta-d-xyloside (beta-Xyl(Phyt)), was studied using small-angle X-ray scattering, polarizing optical microscopy, and differential scanning calorimetry. The phases found in this system include an L(c) phase, an L(alpha) phase, an H(II) phase, two inverted cubic phases of crystallographic space groups Pn3m and Ia3d, and a fluid isotropic phase, FI. The phase diagram of the beta-Xyl(Phyt)/water system is similar to that for the 1-monooleylglycerol (MO)/water system, suggesting that the phase behavior is largely determined by the overall molecular shape rather than the details of surfactant molecular structure. Moreover, the structural parameters of the beta-Xyl(Phyt) liquid crystals are also similar to those of the MO/water, due primarily to the similar molecular dimensions of two molecules. As compared to the MO/water system, however, the beta-Xyl(Phyt)/water system displays a lower value of T(K) (approximately 8.5 degrees C) and a wider temperature window for the mesophases (8.5-120 degrees C). Moreover, beta-Xyl(Phyt) is chemically more robust than MO, as the ether linkage is more stable against hydrolysis than the ester linkage and the phytanyl chain is fully saturated.

Hember M. W., Richardson R. K., and Morris E. R. (1994) Native ordered structure of welan polysaccharide: conformational transitions and gel formation in aqueous dimethyl sulphoxide. *Carbohydr Res* **252**, 209-221.

**Abstract:** Welan, in aqueous solution, has "weak gel" properties analogous to those of ordered xanthan but, unlike xanthan, shows no evidence of conformational change between 0 and 100 degrees C. When the polymer is dissolved in dimethyl sulphoxide (Me2SO) rather than in water, however, there is a massive decrease in viscosity and total loss of gel-like character. In mixtures of the two solvents, the change in rheology occurs over a narrow range of composition (approximately 85-90% v/v Me2SO for 0.5% welan). On heating and cooling in a solvent close to the lower end of the critical range (86% Me2SO), the polymer shows typical order-disorder and disorder-order transitions [as monitored by optical rotation, differential scanning calorimetry, and temperature-course of rheological change]. When solutions of disordered welan in Me2SO are poured into excess water they form cohesive strings of gel. We interpret these results as showing that: (1) the stable conformation of welan in water is the double helix structure identified by X-ray fibre diffraction in the solid state; (2) in native welan, as biosynthesised, the strands are perfectly paired, and ordered along their full length; (3) on exposure to high concentrations of Me2SO, the native structure is

dissociated into disordered coils; (4) rapid renaturation from the disordered state gives shorter helices, with exchange of partners to form a stable cross-linked network.

Hoffmann B., Milius W., Voss G., Wunschel M., van Smaalen S., Diele S., and Platz G. (2000) Crystal structures and thermotropic properties of alkyl alpha-D-glucopyranosides and their hydrates. *Carbohydr Res* **323**, 192-201.

**Abstract:** Thermotropic properties and crystal structures of alkyl alpha-D-glucopyranosides and their hydrates were estimated by X-ray, DSC and thermogravimetric measurements (TGA). Monohydrates rapidly lose their crystal water several degrees below the melting point of the anhydrous glucopyranosides. The melting points of the monohydrates measured in DSC pressure cells (chain length longer than seven) are lower, and the clearing points higher than those of the anhydrous glucosides. Layer distances of smectic and crystalline phases of anhydrous compounds were established. Melting points, densities and layer distances of the crystalline anhydrous glucopyranosides display strong even-odd effects. The strong decrease of these effects in the case of the monohydrates can be elucidated by the results of X-ray crystal structure analysis.

Hoshino E., Kubota Y., Okazaki M., Nisizawa K., and Kanda T. (1994) Hydrolysis of cotton cellulose by Exo- and endo-type cellulases from *Irpex lacteus*: differential scanning calorimetric study. *J Biochem (Tokyo)* **115**, 837-842.

**Abstract:** The mode of hydrolysis of cotton cellulose by two highly purified exo- and endo-type cellulases from *Irpex lacteus* was investigated by differential scanning calorimetry, to measure changes in the size of the amorphous region in cotton fibers with the enzymatic reaction. The cellulases induced entirely different changes in the size of the amorphous region, particularly at earlier stages of reaction. Exo-type cellulase gradually reduced the amorphous region with release of cellobiose from the initial stage of hydrolysis, but began to increase the amorphous region at more advanced stages of hydrolysis. By contrast, endo-type cellulase caused no liberation of reducing sugar at the initial stage of hydrolysis but caused a sharp increase in the amorphous region, and it thereafter caused a rapid decrease of the amorphous region, accompanied with the production of various kinds of cellooligosaccharides. The rate of size reduction of the amorphous region caused by endo-type cellulase was much higher than that by exo-type cellulase. Convergence of the decrease in the size of amorphous region during hydrolysis by endo-type cellulase is followed by the increase in this region being influenced by further hydrolysis of remained crystalline region. Substantial changes in the morphology of cotton occurred with the two cellulases after the hydrolysis stages at which the size of the amorphous region was minimum.

Jin Y., Zhang H., Yin Y., and Nishinari K. (2006) Comparison of curdlan and its carboxymethylated derivative by means of Rheology, DSC, and AFM. *Carbohydr Res* **341**, 90-99.

**Abstract:** Curdlan was carboxymethylated in an aqueous alkaline medium using monochloroacetic acid as the etherifying agent. The structure of carboxymethylated curdlan (CMc) was analyzed by FT-IR and NMR spectroscopy, which revealed that the carboxymethyl group was introduced mainly at the C-6 position as well as at the C-2 and C-4 positions. Furthermore, CMc was compared with the native curdlan by using rheology and DSC methods. It was found that in water, both polysaccharides behaved as pseudoplastic fluids and fit the power law and Herschel-Bulkley rheological models well. Both the storage shear modulus  $G'$  and the loss shear modulus  $G''$  of CMc aqueous solutions decreased and became more frequency dependent with decreasing concentration in comparison with the curdlan aqueous suspensions. The modulus-temperature curve also suggested that the gel characteristic of curdlan has been lost after chemical modification, which is consistent with the DSC results. AFM images revealed differences in the conformation of native and carboxymethylated curdlan, which changed from the aggregation of macromolecules to triple helices. All the experimental results suggest that the hydrogen bonds that bind curdlan with interstitial water to form the micelles have been destroyed completely and that the hydrophobic interactions related to the methylene groups at C-6 formed above 55 degrees C disappeared due to the introduction of the hydrophilic carboxymethyl group.

Kiseleva V. I., Krivandin A. V., Fornal J., Blaszcak W., Jelinski T., and Yuryev V. P. (2005) Annealing of normal and mutant wheat starches. LM, SEM, DSC, and SAXS studies. *Carbohydr Res* **340**, 75-83.

**Abstract:** Structure and thermodynamic properties of native and annealed wheat starches with different amylose content (from 1.5% to 39.5%) have been studied by high-sensitivity differential scanning

microcalorimetry (HSDSC), small-angle X-ray diffraction (SAXS), light (LM), and scanning electron microscopy (SEM). Starch morphology, the values of the melting cooperative unit, the thickness of crystalline lamellae and the size of amylopectin clusters as well as thermodynamic parameters characterizing surface of the face side in starch crystals were determined. Some suppositions based on different physical approaches are used for a discussion of the results concerning structural reorganization of starches on different levels of macromolecular organization.

Koroteeva D. A., Kiseleva V. I., Krivandin A. V., Shatalova O. V., Blaszcak W., Bertoft E., Piyachomkwan K. and Yuryev V. P. (2007) Structural and thermodynamic properties of rice starches with different genetic background Part 2. Defectiveness of different supramolecular structures in starch granules. *Int J Biol Macromol.* **41**, 534-547.

**Abstract:** High-sensitivity differential scanning microcalorimetry (HSDSC), small-angle X-ray scattering (SAXS), light (LM) and scanning electronic (SEM) microscopy techniques were used to study the defectiveness of different supramolecular structures in starches extracted from 11 Thai cultivars of rice differing in level of amylose and amylopectin defects in starch crystalline lamellae. Despite differences in chain-length distribution of amylopectin macromolecules and amylose level in starches, the invariance in the sizes of crystalline lamellae, amylopectin clusters and granules was established. The combined analysis of DSC, SAXS, LM and SEM data for native starches, as well as the comparison of the thermodynamic data for native and annealed starches, allowed to determine the structure of defects and the localization of amylose chains in crystalline and amorphous lamellae, defectiveness of lamellae, clusters and granules. It was shown that amylose "tie chains", amylose-lipid complexes located in crystalline lamellae, defective ends of double helical chains dangling from crystallites inside amorphous lamellae ("dangling" chains), as well as amylopectin chains with DP 6-12 and 25-36 could be considered as defects. Their accumulation can lead to a formation of remnant granules. The changes observed in the structure of amylopectin chains and amylose content in starches are reflected in the interconnected alterations of structural organization on the lamellar, cluster and granule levels.

Le Bail P., Rondeau C., and Buleon A. (2005) Structural investigation of amylose complexes with small ligands: helical conformation, crystalline structure and thermostability. *Int J Biol Macromol* **35**, 1-7.

**Abstract:** Crystalline amylose complexes were prepared with decanal, 1-butanol, menthone and alpha-naphthol. Their crystalline structure and the related helical conformation, determined by wide angle X-ray diffraction (WAXD) and <sup>13</sup>C CPDAS solid state NMR, were assigned to V6I, V6II, V6III and V8 types, respectively. It was possible to propose some hypotheses on the possible nature of interactions and especially intra-/inter-helical inclusion. Some shifts in the NMR C1 carbon signals were attributed to the presence of ligand in specific sites inside the structure for a same type of V6 helical conformation. Moreover, the crystallinity and polymorphic changes induced by desorption/rehydration were studied. A general increase of the carbon resonances sharpness upon rehydration has been observed, but also a V6II-V6I transition when decreasing the water content. Differential scanning calorimetry (DSC) experiments were also performed to approach the thermostability of the four types of complex and also the way they form again after melting/cooling sequences.

Lawal O. S. (2004) Succinyl and acetyl starch derivatives of a hybrid maize: physicochemical characteristics and retrogradation properties monitored by differential scanning calorimetry. *Carbohydr Res* **339**, 2673-2682.

**Abstract:** Starch isolated from a hybrid maize (8535-23) was chemically modified by succinylation and acetylation. No pronounced difference was observed between the X-ray pattern of native starch and modified starch samples, and the samples gave the characteristic A pattern of cereal starches. Onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), concluding temperature ( $T_c$ ) and enthalpy of gelatinisation ( $\Delta H$ ), reduced after succinylation and acetylation, but gelatinisation temperature range increased following starch modifications. Modifications reduced starch retrogradation.

Lehmann U., Jacobasch G., and Schmiedl D. (2002) Characterization of resistant starch type III from banana (*Musa acuminata*). *J Agric Food Chem* **50**, 5236-5240.

**Abstract:** Banana starch (*Musa acuminata* var. Nandigobe) was evaluated for its use in generating resistant starch (RS) type III. Structural, physicochemical, and biological properties of these products were analyzed. The investigated process includes debranching of the native starch and retrogradation under different

storage temperatures and starch concentrations. After enzymatic debranching, a high amount of low-molecular-weight polymers with a degree of polymerization between 10 and 35 glucose units beside a higher molecular weight fraction were found. The resulting products comprised RS contents of about 50%. After heat-moisture treatment, the RS yield increased up to 84%. Peak temperatures of about 145 degrees C found in DSC measurements pointed to a high thermal stability of the RS products. In vitro fermentations of the RS products, carried out with intestinal microflora of healthy humans, resulted in a molar ratio of acetate:propionate:butyrate of about 49:17:34. The established method allowed the production of a high-quality RS with prebiotic properties for health preventing applications.

Lewen K. S., Paeschke T., Reid J., Molitor P., and Schmidt S. J. (2003) Analysis of the retrogradation of low starch concentration gels using differential scanning calorimetry, rheology, and nuclear magnetic resonance spectroscopy. *J Agric Food Chem* **51**, 2348-2358.

**Abstract:** The retrogradation of 5, 10, 15, and 25% corn starch gels was measured using differential scanning calorimetry (DSC), rheology, and an array of NMR spectroscopy techniques. During the initial (<24 h) stage of retrogradation, an increase in G' corresponding to an increase in the number of solid protons participating in cross-relaxation (M(B)(0)) was observed for all four concentrations studied. During the latter (>24 h) stage of retrogradation, amylopectin recrystallization becomes the dominant process as measured by an increase in  $\Delta H(r)$  for the 25% starch gel, which corresponded to a further increase in. A decrease in the molecular mobility of the liquid component was observed by decreases in (17)O T(2), (1)H D(0), and T(2A). The value for T(2B) (the solid transverse relaxation time) did not change with concentration or time indicating that the mobility of the solid component does not change over time despite the conversion of the highly mobile starch fraction to the less mobile solid state during retrogradation.

Lourdin D., Colonna P., Brownsey G. J., Noel T. R., and Ring S. G. (2002) Structural relaxation and physical ageing of starchy materials. *Carbohydr Res* **337**, 827-833.

**Abstract:** The structural relaxation during the ageing of an amorphous maltose and a starch-sorbitol mixture was examined using a range of physical techniques. Heat capacity, measured by differential scanning calorimetry, showed an overshoot in the glass-transition region, the size of which was temperature and time dependent. Volume relaxation measurements were made at different ageing temperatures in the range T(g) -15 to -30 K. The volume decreased with increasing ageing time, in an essentially linear fashion with log time. The mechanical behaviour of the materials showed a progressive embrittlement on ageing. For both materials, the mechanical relaxation time increased with ageing, and the material became stiffer. Investigation of the effect of physical ageing on transport properties was also performed using conductivity measurements on a maltose-water-KCl mixture. A decay in conductivity, which was almost linear with log time, was observed. The structural relaxation was modelled using the Tool-Narayanaswamy approach to describe the calorimetric data.

MacLaughlin F. C., Mumper R. J., Wang J., Tagliaferri J. M., Gill I., Hinchcliffe M., and Rolland A. P. (1998) Chitosan and depolymerized chitosan oligomers as condensing carriers for in vivo plasmid delivery. *J Control Release* **56**, 259-272.

**Abstract:** Chitosan is a polysaccharide that demonstrates much potential as a gene delivery system. The ability of a commercially available chitosan and depolymerized chitosan oligomers to condense plasmid was determined using TEM and microtitration calorimetry, while the diameter and stability of the resultant complexes were measured using laser light scattering. Selected complexes were physically stable to challenge with both serum and salt solutions. Parameters such as chitosan molecular weight, plasmid concentration and charge ratio influenced such stability. The effect of including a pH-sensitive endosomolytic peptide on the physicochemical properties of the complex was determined. The presence of a pH-sensitive endosomolytic peptide enhanced the levels of reporter gene expression in Cos-1 cells 4-fold. A selected complex containing a lytic peptide was administered in the upper small intestine and colon of rabbits, and reporter gene expression was measured in defined intestinal tissues. Reporter gene expression was enhanced in defined intestinal tissues, although levels of expression remained low. The combination of strong complex stability and low in vivo expression levels suggest that uptake and/or decomplexation, but not endosomal release, may be the critical rate-limiting steps in the uptake process.

Mazzobre M. F., Aguilera J. M., and Buera M. P. (2003) Microscopy and calorimetry as complementary techniques to analyze sugar crystallization from amorphous systems. *Carbohydr Res* **338**, 541-548.

**Abstract:** A comparison of microscopic and macroscopic techniques to evaluate sugar crystallization kinetics is presented using amorphous lactose and lactose-trehalose mixtures. Polarized light video microscopy (PLV) and differential scanning calorimetry (DSC) were applied to measure crystallization kinetics, induction times and time for complete sugar crystallization at different storage temperatures (60-95 degrees C). DSC was also employed to measure the glass transition temperature (T<sub>g</sub>) of the systems. PLV permitted direct observation, in real time, of growth of individual crystals and morphological aspects at a scale not detected by DSC. Taking the average of several microscopic observations, the results for temperature dependence of crystallization rate and time to complete lactose crystallization were similar to those obtained by DSC. Both PLV and DSC techniques showed that the presence of trehalose delayed lactose crystallization, without affecting the T<sub>g</sub> value. For the analysis of sugar crystallization in amorphous systems, PLV and DSC proved to be complementary techniques. Validation of results obtained by PLV with results from DSC opens a new area of microstructural analysis of crystallizing systems.

Miller D. P., de Pablo J. J., and Corti H. (1997) Thermophysical properties of trehalose and its concentrated aqueous solutions. *Pharm Res* **14**, 578-590.

**Abstract:** PURPOSE: To address the lack of fundamental thermophysical data for trehalose and its aqueous systems by measuring equilibrium and non-equilibrium properties of such systems. METHODS/RESULTS: Differential scanning calorimetry (DSC) and dynamic mechanical analysis were used to measure glass transition temperatures of trehalose and its solutions. X-ray diffractometry was used to verify the structure of amorphous trehalose. Controlled-stress rheometry was used to measure viscosity of several aqueous trehalose systems at ambient and sub-ambient temperatures. Over this temperature range, the density of these solutions was also measured with a vibrating tube densimeter. The equilibrium phase diagram of aqueous trehalose was determined by measuring the solubility and freezing point depression. CONCLUSIONS: Our solubility measurements, which have allowed long times for attainment of chemical equilibrium, are substantially different from those reported earlier that used different techniques. Our measurements of the glass transition temperature of trehalose are higher than reported values. A simple model for the glass transition is presented to describe our experimental observations.

Oh E. J., Choi S. J., Lee S. J., Kim C. H. and Moon T. W. (2008) Modification of granular corn starch with 4-alpha-glucanotransferase from *Thermotoga maritima*: effects on structural and physical properties. *J Food Sci* **73**, C158-C166.

**Abstract:** Corn starch was converted using alpha-1,4-glucanotransferase from *Thermotoga maritima* (T<sub>m</sub> alpha GT), a hyperthermophilic bacterium, without inducing gelatinization, and the structural changes and physical properties of the modified starches were investigated. Enzyme modification was induced at 65 degrees C for 8, 16, or 24 h, and the morphology of the modified starches was observed with light and scanning electron microscopy. Granule integrity was mostly maintained after enzyme treatment, although some granules were partially fragmented as evidenced by enlarged surface pores and some cracks. The modified starches had lower apparent amylose levels than raw starch. The molecular weights of amylose and amylopectin molecules in the treated starches were lower than those of raw starch, and the amount of branched molecules, which had much lower molecular weights, also increased in the treated starches. The chain-length distribution of amylopectin showed an increased number of shorter branched chains. The modified starches showed a wider melting temperature range and a lower melting enthalpy than that of raw starch. The X-ray diffraction pattern of the modified starches showed typical A-type starch peaks, but the relative crystallinities were lower than that of raw starch. The solubility and paste clarity of the modified starches were much higher than those of raw starch. The modified starch gels maintained their rigidity over the whole frequency range tested and showed thermoreversibility between 4 and 75 degrees C. These results suggest that T<sub>m</sub> alpha GT can be used to produce granular corn starch, which contains amylose and amylopectin having lower molecular weights and a thermoreversible gelation property

Ojinnaka C., Jay A. J., Colquhoun I. J., Brownsey G. J., Morris E. R., and Morris V. J. (1996) Structure and conformation of acetan polysaccharide. *Int J Biol Macromol* **19**, 149-156.

**Abstract:** Acetan is an anionic bacterial polysaccharide. The chemical repeat unit consists of a cellobiose unit solubilised by attachment of a charged pentasaccharide sidechain to one of the glucose residues. The repeat unit contains two sites of acetylation. <sup>1</sup>H and <sup>13</sup>C NMR studies, coupled with both basic-methylation and mild-methylation studies, have shown that acetylation occurs at C6 on the (1,2)D-Man and the (1,3,4)D-Glc residues. A variety of techniques including NMR, optical rotation, circular dichroism and

DSC show evidence for a thermoreversible conformational order (helix)-disorder (coil) transition for acetan in aqueous solution. The studies suggest that acetylation of the backbone does not prevent helix formation.

Ojinnaka C., Brownsey G. J., Morris E. R., and Morris V. J. (1997) Effect of deacetylation on the synergistic interaction of acetan with locust bean gum or konjac mannan. *Carbohydr Res* **305**, 101-108.

**Abstract:** It has been discovered that deacetylation of the bacterial polysaccharide acetan promotes synergistic interactions with either locust bean gum (LBG) or konjac mannan (KM). Acetan is similar in structure to xanthan, and adopts a similar 5-fold conformation in the solid state. Like xanthan, it shows a thermally reversible order (helix)-disorder (coil) transition in solution. Both polymers have a cellulosic backbone with charged (anionic) sidechains attached at O-3 of alternate glucosyl residues, but the sidechains in acetan are longer (pentasaccharide rather than trisaccharide) and do not contain pyruvic substituents. Acetan has two sites of acetylation, one at O-6 of the inner mannosyl residue of the carbohydrate sidechains (as in xanthan) and the other on the polymer backbone (believed to be at O-6 of the branched glucosyl residues). Solutions of acetan or deacetylated acetan were equilibrated against 10 mM potassium chloride (to stabilise the ordered conformation) and were mixed (at 25 degrees C) with solutions of LBG or KM, also equilibrated against 10 mM potassium chloride. Unlike xanthan, native acetan showed no evidence of synergistic interaction with either LBG or KM. After deacetylation, however, large enhancements were observed in dilute-solution viscosity, and thermoreversible gels were formed at higher concentrations. With KM as co-synergist, gel melting was accompanied by an intense endotherm in differential scanning calorimetry. The magnitude of this endotherm increased with storage time at 25 degrees C, reaching a final value of  $\Delta H$  approximately 15.9 J/g (in comparison with  $\Delta H$  approximately 5.0 J/g for the order-disorder transition of deacetylated acetan alone). It is suggested that interaction occurs by formation of heterotypic junctions between the acetan backbone and unsubstituted regions of the plant polysaccharide, and that the acetate groups on native acetan promote solubility and hence inhibit association.

Ridout M. J., Brownsey G. J., Morris V. J., and Cairns P. (1994) Physicochemical characterization of an acetan variant secreted by *Acetobacter xylinum* strain CR1/4. *Int J Biol Macromol* **16**, 324-330.

**Abstract:** Chemical mutagenesis has been used to produce mutants of *Acetobacter xylinum* NRRL B42 that are cellulose-negative and that produce variants of the acetan structure deficient in the side-chain sugar residues. The product of *A. xylinum* strain CR1/4 has been shown to possess a tetrasaccharide repeat unit with the side chain terminating in glucuronic acid. X-ray diffraction studies of oriented fibres suggest that the polysaccharide CR1/4 forms a fivefold helix with a pitch of 4.8 nm. Light-scattering studies on CR1/4 solutions suggest a molecular weight of  $1.2 \times 10^6$  with radii of gyration values of 86 nm (aqueous solution) and 67 nm (0.1 M NaCl solution). The magnitude of the measured radii of gyration and the shape of the Holtzer plots suggest that CR1/4 can be described as a stiff coil. Preliminary differential scanning calorimetry data show melting behaviour consistent with order-disorder transitions of a charged helical structure. Rheological studies have revealed new synergistic interactions of CR1/4 with locust bean gum. Comparative studies of acetan and CR1/4 show that decreasing the length of the side chain enhances the solution viscosity.

Ridout M. J., Brownsey G. J., York G. M., Walker G. C., and Morris V. J. (1997) Effect of o-acyl substituents on the functional behaviour of *Rhizobium meliloti* succinoglycan. *Int J Biol Macromol* **20**, 1-7.

**Abstract:** The effects of selective removal of acetyl or succinyl substituents on the functionality of succinoglycan polysaccharide have been studied by comparing the behaviour of the polysaccharides isolated from native *Rhizobium meliloti* strain Rm1021, and genetically modified *R. meliloti* species. Removal of the succinyl groups was found to dramatically improve pseudoplasticity of the aqueous succinoglycan samples and also increase the cooperativity of the order-disorder transition exhibited by the polysaccharide. Removal of the acetyl substituent led to a decrease in the order-disorder transition temperature, whereas the removal of the succinyl groups led to an increase.

Sereno N. M., Hill S. E. and Mitchell J. R. (2007) Impact of the extrusion process on xanthan gum behaviour. *Carbohydr. Res* **342**, 1333-1342.

**Abstract:** Processing xanthan gum by extrusion and subsequent drying produces a biopolymer showing particulate, rather than molecular behaviour in aqueous solution. This form of xanthan disperses very readily to give a viscosity that is strongly dependent on salt concentration. On heating above the

temperature of the order-disorder transition as determined by calorimetry, there is a viscosity transition that is indicative of the irreversible loss of the particulate structure. It is suggested that the extrusion process melts and aligns xanthan macromolecules. On cooling reordering will occur but in the highly concentrated environment in the extruder (approximately 45% water w/w), inter-molecular association between neighbouring macromolecules cannot proceed to completion due to kinetic trapping. As a consequence a network structure is created maintained by associations involving ordered regions. A xanthan solution can be prepared from this particulate material by dispersing and subsequent heating far more readily than can be achieved with non-processed xanthan.

Spigno G., Pizzorno T. and De Faveri D. M. (2008) Cellulose and hemicelluloses recovery from grape stalks. *Bioresour. Technol.* **99**, 4329-4337.

**Abstract:** In this work, two mild chemical fractionation procedures were compared to separate and recover lignocellulosic components from grape stalks. The first method consisted of mild acid hydrolysis for hemicelluloses separation, followed by an alkaline/oxidative step for lignin solubilization, while in the second method the acid hydrolysis was preceded by an alkali steeping phase. Influence of the length of the first step of both methods (from 2 to 24h) on monosaccharides and cellulose yields was investigated. The first method allowed a higher sugar recovery for longer times, and a slightly lower amount of cellulose. Cellulose residues from both the methods were comparable for cellulose content and thermal profile (studied by differential scanning calorimetry). Acid hydrolysis of the first step was carried out also in autoclave, showing that xylan degradation could be described by a first order kinetics where at higher temperature the presence of a fast reaction and a slow reacting fraction must be accounted for.

Takemasa M. and Nishinari K. (2004) The effect of the linear charge density of carrageenan on the ion binding investigated by differential scanning calorimetry, dc conductivity, and kHz dielectric relaxation. *Colloids Surf B Biointerfaces* **38**, 231-240.

**Abstract:** The effect of the linear charge density of natural polyelectrolyte, carrageenan, on the ion binding to carrageenan molecules in relation to the gelation was investigated by using the dielectric relaxation spectroscopy, dc conductivity, optical rotation, and differential scanning calorimetry (DSC). Although carrageenan is an anionic polysaccharide, carrageenan molecules in the helix state at low temperatures can bind not only cation, such as potassium and cesium, but also anion, such as iodide. The dc conductivity steeply decreases just below the coil-helix transition temperature, which indicates the binding of ion to the carrageenan molecules in the helix state due to the increase of the linear charge density compared with that in the coil state. The addition of NaI promotes the helix formation, and prevents from aggregation of helices, which was suggested by the results of the dynamic shear modulus and the DSC, and resulted in an increase of the relaxation amplitude of the lowest frequency relaxation (approximately kHz) attributed to the fluctuation of the tightly bound counter ions along the high charge density region (helix). It is concluded that binding of iodide induces (1) the increase in the amount of tightly bound counterions to carrageenan molecules and (2) the formation of non-aggregated helix.

Tiziani S., Sussich F., and Cesaro A. (2003) The kinetics of periodate oxidation of carbohydrates 2. Polymeric substrates. *Carbohydr Res* **338**, 1083-1095.

**Abstract:** A study of the kinetics of periodate oxidation on a series of dextran oligomers and polymers is carried out by isothermal microcalorimetry. In addition to these substrates, some dimeric carbohydrates and hyaluronan were studied. Rate constants were calculated from the calorimetric decay curves, which, properly corrected for calorimetric response, are proportional to the rate of periodate conversion. The dependence of the kinetic rates on the molecular weight of dextran samples and on the substrate concentration, is described in terms of the much higher rates of terminal reducing units. The presence of two sites with comparable reaction rates makes the analysis of the calorimetric curves difficult, even in the simple overall pseudo-first-order condition. The suitability of a phenomenological treatment of kinetic data is explored.

Villain-Simonnet A., Milas M., and Rinaudo M. (1999) Comparison between the physicochemical behaviour of two microbial polysaccharides: RMDP17 and rhamnan. *Int J Biol Macromol* **26**, 55-62.

**Abstract:** This paper concerns the properties of two ionic polysaccharides with very close chemical structures. pH metric and conductimetric measurements showed that they behave similarly from a polyelectrolytic point of view. From optical rotation and differential scanning calorimetry (DSC)

measurements, the two polymers probably adopt a double helical conformation which is destabilised by deacetylation. The main differences concern the stability of this ordered conformation and the ability of these double helices to associate to form gels. The results support a higher thermal stability of the ordered conformation for deacetylated RMDP17 (about 8 degrees C), whereas deacetylated rhamosan has a better ability to form gels.

Villain-Simonnet A., Milas M., and Rinaudo M. (2000) A new bacterial polysaccharide (YAS34). I. Characterization of the conformations and conformational transition. *Int J Biol Macromol* **27**, 65-75.  
**Abstract:** This paper concerns the study of the conformational transition of a new exopolysaccharide (YAS34) using experimental techniques such as optical rotation, conductimetric and microcalorimetric measurements as a function of temperature. The behaviors of this polysaccharide in the acid or sodium salt form are compared; a deacetylated sample is also prepared to demonstrate the role of substituents. For the native structure (never heated), a conformational transition is observed but the deacetylated polysaccharide exhibits no ordered conformation. Multidetector size exclusion chromatography (SEC) analyses and conductimetric experiments allowed to determine the nature of each conformation and the molecular dimensions. From these results, it is suggested that the native conformation is a double helix which by heating over  $T_m$  (temperature corresponding to half conformational transition) dissociates into disordered single chains. In the acid and sodium salt forms, by cooling below  $T_m$ , an ordered conformation is restored. This conformation seems to be an intramolecular double helix 'hairpin-like turn' (called renatured conformation). Nevertheless an irreversible denaturation is obtained progressively in the sodium salt form when the time of heating over  $T_m$  increases. The conformation of the deacetylated polysaccharide corresponds to that of a single flexible chain (disordered conformation). The conformational transition for the native conformation was studied also in relation to the polyelectrolytic character of the polysaccharide: stability as a function of salt nature and salt and polymer concentrations was investigated for the polymer initially in the sodium and acid forms.

Wangsakan A., Chinachoti P., and McClements D. J. (2001) Maltodextrin-anionic surfactant interactions: isothermal titration calorimetry and surface tension study. *J Agric Food Chem* **49**, 5039-5045.  
**Abstract:** Interactions between maltodextrin (DE = 10) and an anionic surfactant (sodium dodecyl sulfate, SDS) were studied in a buffer solution (pH 7.0, 10 mM NaCl, 20 mM Trizma, 30.0 degrees C) using isothermal titration calorimetry (ITC), surface tension, differential scanning calorimetry (DSC), and turbidity techniques. ITC measurements indicated that the binding of SDS to maltodextrin was exothermic and that, on average, one SDS monomer bound per 24 glucose units of maltodextrin at saturation. Surface tension measurements indicated that there was a critical surfactant concentration (approximately 0.05 mM SDS) below which surfactant and maltodextrin did not interact and that the amount of surfactant bound to the maltodextrin above this concentration increased with increasing maltodextrin concentration. Turbidity measurements indicated that the solutions remained transparent at all maltodextrin (0-1 wt %) and SDS (0-20 mM) concentrations studied, which suggested that phase separation did not occur. DSC measurements indicated that no phase transitions occurred between 10 and 110 degrees C for maltodextrin solutions (0.5 wt %) in the presence or absence of surfactant. A phase diagram was developed to describe the interactions between SDS and maltodextrin.

Wursch P. and Gumy D. (1994) Inhibition of amylopectin retrogradation by partial beta-amylolysis. *Carbohydr Res* **256**, 129-137.  
**Abstract:** The rate of retrogradation of amylopectin solution differs from one starch variety to another and it is thought to be due to the different length of the external chains of amylopectin. A shortening of the external chains of waxy maize and potato amylopectin was performed with beta-amylase. Partial beta-amylolysis produced a significant fraction of chains having 2-6 glucose units. A high linear correlation ( $R > 0.97$ ) was found between the enthalpy of retrograded amylopectin measured by DSC, or percent solid measured by low frequency pulsed NMR, and average external chain length. No retrogradation appeared to occur when the external chains of both amylopectins had 11 or less glucose units on average. The inhibition of retrogradation appears to be caused primarily by the presence of very short external chains, which hinders the reassociation of the long external chains.

Yoshida K., Teramoto A., Nakamura N., Kikuchi K., Miyazaki Y., and Sorai M. (2003) Static water structure detected by heat capacity measurements on aqueous solutions of a triple-helical polysaccharide

schizophyllan. *Biomacromolecules* **4**, 1348-1356.

**Abstract:** Heat capacity measurements were made on aqueous solutions of a triple-helical polysaccharide schizophyllan by precision adiabatic calorimetry over a wide range of concentrations 30.45-90.93 wt % at temperatures between 5 and 315 K. The heat capacity curves obtained were divided into four groups depending on the weight fraction of schizophyllan  $w$  regions I-IV. In region I, triple-helices with the sheath of bound water, structured water, and loosely structured water forming layers around the helix core are embedded in free water. In region II, there is no free water, and loosely structured water decreases until it vanishes, but structured water stays constant with increasing  $w$ . In region III, bound water remains unaffected, but structured water decreases with increasing  $w$  by overlapping each other. Finally, in region IV, only schizophyllan and bound water exist, the latter decreasing upon increasing  $w$ . The maximum thickness of each layer is 0.18(3) nm for bound water, 0.13(4) nm for structured water, and 0.23(6) nm for loosely structured water, and these layers of water are at the enthalpy levels of 53%, 93.7%, and nearly 100%, respectively, between ice (0%) and free water (100%).

Yoshida H., Nozaki K., Hanashiro I., Yagi F., Ito H., Honma M., Matsui H., and Takeda Y. (2003) Structure and physicochemical properties of starches from kidney bean seeds at immature, premature and mature stages of development. *Carbohydr Res* **338**, 463-469.

**Abstract:** Starches from kidney bean (*Phaseolus vulgaris* L. cv. Toramame) seeds at the immature, premature, mature stages of development were examined. The starch content increased from 94, 219 to 265 mg per seed. Starches showed the C(a)-crystalline type composed of small (<5 micrometer) and large (10-35 micrometer) granules, with the large granules largely increasing with maturity. The amylose content increased from 21, 26 to 27%, and rapid viscosgrams and DSC thermograms suggested that the mature-stage starch was gelatinized with ease. The amylose increased in size from DPn 820, 1000 to 1080 and a number of chains per molecule (NC) from 3.3, 4.2 to 4.5. The branched amylose was a minor component (11-18% by mole) with NC 20-22. The amylopectin was similar in CL (23), beta-amylolysis limit (59%), and chain-length distribution, but reduced in size (DPn 17,100-5270) and increased in content of phosphorus (114-174 ppm) with an increase in the amount of phosphorus linked to C-6 of the glucose residue (8-66%).

Zhang G., Foegeding E. A., and Hardin C. C. (2004) Effect of sulfated polysaccharides on heat-induced structural changes in beta-lactoglobulin. *J Agric Food Chem* **52**, 3975-3981.

**Abstract:** The mechanism that leads to a decreased aggregation of beta-lactoglobulin in the presence of dextran sulfate and lambda-carrageenan was investigated by assessing changes in the denaturation thermodynamics and protein structure. Differential scanning calorimetry results showed that the denaturation temperature ( $T_p$ ) was about 4.6 degrees C higher in the presence of dextran sulfate, as compared with beta-lactoglobulin alone, whereas in the presence of lambda-carrageenan the difference in  $T_p$  was about 1.2 degrees C. Changes in protein structure studies using near-UV circular dichroism (CD) provided support for the calorimetric results. The transition midpoint ( $T_m$ ) for denaturation of beta-lactoglobulin was about 5 degrees C higher in the presence of dextran sulfate than that found with beta-lactoglobulin alone and about 2 degrees C in the presence of lambda-carrageenan. Thermal modifications of the tertiary structure of beta-lactoglobulin were irreversible at temperatures above 67 degrees C; the addition of dextran sulfate reduced the extent of such modifications. Far-UV CD studies indicated that the addition of dextran sulfate or lambda-carrageenan did not affect secondary structure changes of beta-lactoglobulin upon heating. These studies indicate that dextran sulfate and lambda-carrageenan can enhance the stability of beta-lactoglobulin and thereby inhibit heat denaturation and aggregation.