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Formation of thermally reversible maltodextrin gels as revealed by low resolution H-NMR

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Pulsed low resolution proton NMR (20 MHz) was applied to follow the gelation process in different thermally reversible gelling maltodextrin-water systems. Results are expressed in terms of the solidus ratio, which is the ratio of proton systems with high and low relaxation time after the application of a radio frequency pulse. The sol-gel transition process may be followed from the onset until equilibrium is reached after several days. A marked change in the signal occurs on the formation of reversible gels, which depends on the temperature, concentration, time and structural peculiarities. This behaviour is paralleled with the development of the shear modulus as well as $\Delta H°$ for melting. A linear relation between the solid-liquid ratio from NMR and X-ray crystallinity suggests that the physical basis of the NMR results is the formation of highly ordered domains as essential constituents of the gel network. Non-gelling solutions of amylopectin as well as of acetylated maltodextrins do not give 'solid' signals. Amylose is necessary for initiation and acceleration of the sol-gel transition. However, crystalline amylose in the precipitated, retrograded state gives solid signals too. It is to be concluded that the method applied is suitable for following sol-gel transitions if they are based on a highly ordered (crystalline) structure.

INTRODUCTION

In recent years, thermoreversible gels have been extensively studied with respect to the dependence of network formation and structure on the chemical composition and molecular state in solution (Kramer, 1988). Potato starch derived maltodextrins (MD) are a special group of reversibly gelling polysaccharides. Such a MD is manufactured by stepwise hydrolysis of potato starch by bacterial α-amylase according to a temperature-time programme. The hydrolysis starts in the heterogeneous phase and finishes in the homogeneous phase and the maltodextrin solution is then spray-dried to a white, flowing powder, called Stärkehydrolysenprodukt (SHP). The powder is easily solubilized in water by homogenization at room temperature or by heating to 90°C. On cooling, the solution sets to an opaque gel which melts on heating. The melting temperature depends on concentration (Richter *et al.*, 1972).

A two-phase gel structure was shown by X-ray studies. Junction zones in the gels contain crystalline domains of the B-polymorph type of retrograded amylose (Reuther *et al.*, 1983, 1984). Approximately 10–16% of the carbohydrate chains may be involved in these crystallites (Gernat *et al.*, 1987). The results of rheological and thermal measurements on these gels have recently been interpreted in terms of the thermodynamic properties of the junction zones (Schierbaum *et al.*, 1990). Their formation was proved to be a weakly cooperative process with a low entropy change. Small changes in entropy are sufficient to form thermodynamically stable networks.

Rheological investigations of the gel formation process are open to the criticism that the formation of the network will be influenced by the energy input from the measuring system.

For further characterization of MD gelling, attention should be paid to non-destructive measurements. A short measurement time for each state of the sol-gel

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transition is also desirable. NMR techniques have been adopted, to elucidate the chemical fine structure (Gidley, 1985), for determination of the bound water in granular as well as gelatinized starches (Lechert, 1976; Stute, 1980; German *et al.*, 1988; Lechert *et al.*, 1988; Radosta *et al.*, 1989). The phase structure of retrograded starches and starch gels was studied by Welsh *et al.* (1982), Gidley and Bulpin (1987) and German *et al.* (1989).

Theoretical background of measurements

In the case of reversible network formation by low DE(dextrose equivalent)-potato-starch MD, a transition will take place from a homogeneous 'structureless' solution to a two-phase system. This consists of the solid (in part crystalline) aggregation network and the liquid solution of the non-structured MD components (Schierbaum, 1988). It is to be anticipated that the protons belonging to the solid-like phase will be discerned from the protons of the liquid phase by their different behaviour in the electromagnetic field. In low resolution 20 MHz NMR spectrometry the quantity of hydrogen atoms in the sample, to be measured, is essentially constant. If a radio frequency pulse is applied for a few microseconds all the hydrogen nuclei are excited to rotate by 90° with respect to the static magnetic field (Bruker). When the pulse is switched off they return to their original state, emitting an NMR signal. The initial amplitude of this is proportional to the number of protons in the sample. The subsequent free induction decay is the sum of mechanisms with different relaxation times depending on the physical phase in which the protons exist. Hydrogen nuclei in the solid phases decay more quickly than those from liquids. Thus, the relaxation-time plot consists of superimposed signals from at least two components (Fig. 1). This is the basis for discriminating between solid ('structural') and liquid protons in the case of Bruker-Minispec pc 120. The NMR signals are measured at point SA_1 15 μs (τ_1) and at point SA_2 after 70 μs (τ_2). As it is exclusively the onset intensity at SA_0, which is really proportional to the total proton concentration, the data taken at τ_1 after 15 μs give an indication of solid plus liquid phases. The intensity at τ_2 represents the liquid phase only.

The ratio SA_1/SA_2 is taken as the solid–liquid (s/l) ratio of the sample, though since it is only the *initial* intensity which is proportional to proton concentration it should be appreciated that the use of data after 15 μs is only an indication (not a measurement) of solid plus liquid phases.

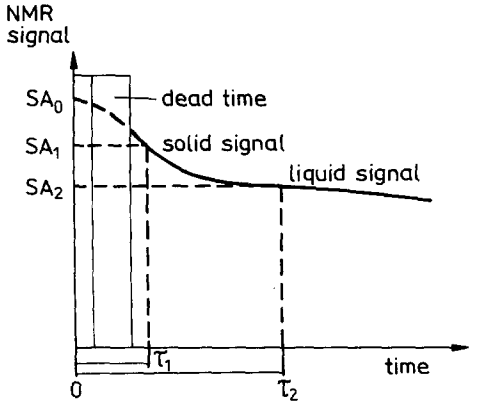


Fig. 1. The free induction decay, which follows the radio frequency radiation pulse worked on for a few microseconds on the probe sample (τ_1, τ_2: relaxation times of the entire resp. liquid signal); according to Bruker No. 30 (Bruker, 1988).

EXPERIMENTAL

Materials

Technical maltodextrin SHP

Produced by Stärkefabrik, Kyritz, FRG. DE-value 6·2%, moisture 8·0%, iodine complexing values λ_{max} 548 nm, E_{540} 0·110 (iodine concentration 10^{-4} *N*). ($\bar{P}_n$ 27 ± 3 from reducing end group measurements). Average composition: amylose ($\bar{P}_n$ 50–150), 8–11%; branched components ($\bar{P}_n < 600$), 50%; oligosaccharides ($\bar{P}_n \sim 9$), 18 ± 3%. (About 50% of the maltodextrin contains polysaccharides of greater than $\bar{P}_n \sim 62$ (Bulpin *et al.*, 1984).)

Acetyl-maltodextrin (Ac-MD)

Laboratory sample, prepared from acetylated granular potato starch Kettlitz, 1983). DE-value 6·3%, acetyl content 5·2%. $\bar{P}_n$ 26, λ_{max} 521 nm (iodine concentration 10^{-4} *N*). (The authors are indebted to Dr B. Kettlitz for providing the sample.)

Molecular weight fractions

Four molecular weight fractions were prepared by triangular fractionation of an aqueous MD solution with methanol in equal mass portions (Fig. 2).

Amylose

Amylose $\bar{P}_n$ 36 was prepared from amylose (Serva, Heidelberg) by hydrolysis with 2 N H_2SO_4 in dimethylsulphoxide (DMSO) and precipitation with methanol. (The authors are indebted to Dr F. Reuther for providing molecular weight fractions as well as amylose samples.)

Amylopectin

Commercial sample Avebe-Veendam, NdL after removing linear material (Richter *et al.*, 1969).

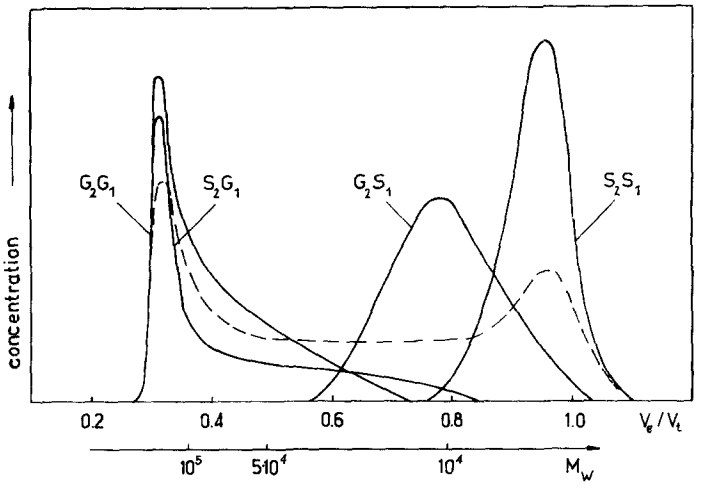


Fig. 2. Gel chromatograms of MD. Triangular fractions: G_2G_1, $\bar{P}_n$ 250 ± 40, λ_{max} 549 nm; S_2G_1, $\bar{P}_n$ 90 ± 10, λ_{max} 552 nm; G_2S_1, $\bar{P}_n$ 90 ± 10, λ_{max} 544 nm; S_2S_1, $\bar{P}_n$ 10 ± 2, λ_{max} 503 nm. (- - -) original maltodextrin (Sephadex G 200, eluant water).

Methods

Preparation of solutions

Maltodextrin samples were soaked in cold water and cooked under stirring until a homogeneous solution was achieved. This was immediately cooled and the amount of water loss by evaporation added. Bruker-Minispec test tubes (diameter 10 mm) were filled with 2 g of the solution, stoppered and thermostatted.

Amylose was fully dispersed in analytical grade DMSO. Immediately before interaction studies the thermostatted pure amylose-DMSO solution and the aqueous maltodextrin solution were mixed in the ratio 1 : 4 (final DMSO concentration 20%).

NMR measurements

Bruker-Minispec pc 120 with an operating frequency of 20 MHz was used in the s/l-working and s/l-calculating programme modes. Only s/l-values > 0·5% were used since lower s/l-values were imprecise because of noise. Measurements were performed at temperatures of 4, 20 and 25 °C in the concentration range 15–35% w/w until a constant s/l-value was reached.

The test tubes were removed from the thermostatic bath and immediately positioned in the probe-head. Each measurement occurred within 4 s, so constant temperature was ensured in every case. After this the test tubes were returned to the bath.

X-ray measurements

These were performed as described by German *et al.* (1989): using a 'Dron-1' (USSR) diffractometer and a CuK_α-radiation source; the angular range (2θ) was 3–40°. A glass capillary (diameter 1 mm) was filled with MD solution and crystallization was followed at 20 °C. Degree of crystallinity (%) was evaluated from the difference in intensity of the crystalline reflections in the diffractograms. (The authors are indebted to Dr E.M. Genin for performing the X-ray measurements and calculations.)

Measurement of the shear modulus

This was carried out as described by Bikbov *et al.* (1979) in uniaxial compression on cylindrical gel pieces using a dynamometric balance (Schierbaum *et al.*, 1990). In the case of concentrated MD gels, the coefficient of irreversible deformation was neglected in the calculation of the shear modulus.

DSC measurements

These were performed with DASM-4 high performance scanning calorimeter designed by Prof. Privalov (Pushchino, USSR). A platinum capillary probe-head was filled with the starch carbohydrate solutions (2–10% (w/w)). After storage (20 h at 4 °C) measurements were run against water as a reference; the heating rate was 1 K min^{-1} (see Fig. 8).

RESULTS

Maltodextrin solutions of different concentration

The progress of the gelling process is reflected by the time-dependent rise in the s/l-values (Fig. 3). A rapid increase on s/l is found at high concentrations and low temperatures. Thus, the time for s/l to reach half its final value is about 20 min for a 35% (w/w) solution at 4 °C, whereas at 25 °C and the lowest concentration (15% (w/w)) this is around 12 h. The equilibrium value takes a minimum of 24 h to be obtained. The measurements were stopped after 5 days when no further change was observed. A gel is obtained before s/l reaches half its final value but the gel point cannot be obtained from these data. The temperature is not only used in determining the initial velocity of the aggregation

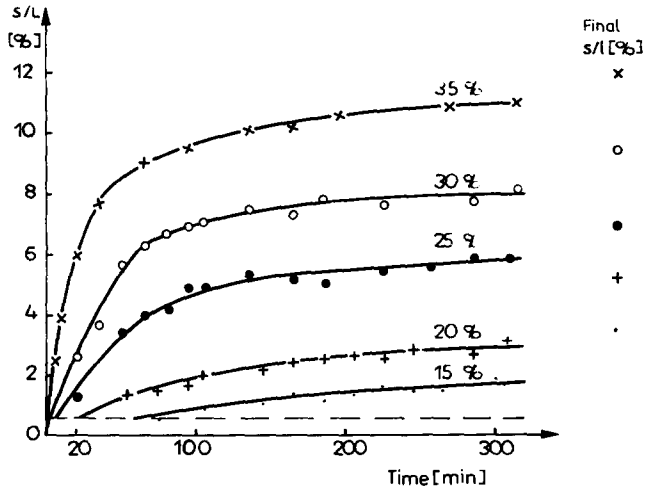


Fig. 3. Time dependence of solid-liquid proton relaxation ratio (s/l) of MD solutions at different concentrations during the first five hours of aggregation (4°C).

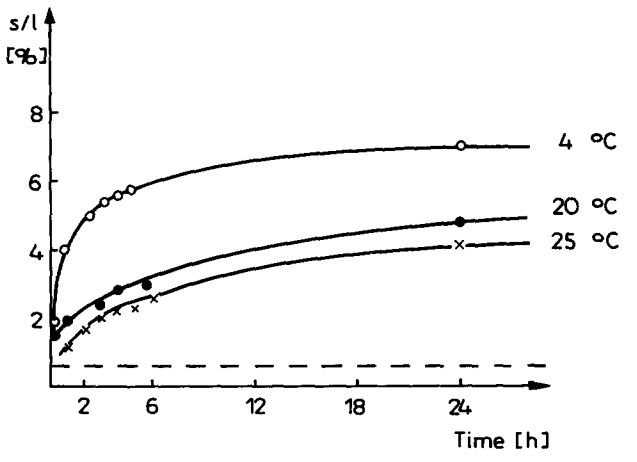


Fig. 4. Time dependence of s/l ratios of 25% (w/w) MD solutions at different temperatures.

process (Fig. 4) but also the final solid-liquid ratio (Table 1).

When the gels are equilibrated at different temperatures the highest s/l ratios are developed at the lowest temperatures (4°C). By thermostatting such gels at higher temperatures (20°C) the resulting s/l ratios are higher compared with gels which were originally formed at 20°C and then equilibrated at 4°C (Table 1). Differences in the number of structured components which arise at the gelling temperature remain when the gels are equilibrated to other temperatures. On elevating the temperature to 40°C, however, these differences become smaller and the s/l ratio at this temperature is essentially independent of gel formation temperature at concentrations ⩾25%. Under the conditions of temperature and concentration used the concentration dependence of the equilibrium s/l-values is linear (Fig. 5). Extrapolation to lower s/l-values leads to a minimum concentration for forming aggregated structures.

$\bar{P}_n$ fractions of maltodextrin

The different samples are more distinguished by the velocity of aggregation than by the maximum s/l-values. The half-value times as well as the s/l maxima may be arranged according to $\bar{P}_n$ 62 < $\bar{P}_n$ 120 < $\bar{P}_n$ 235 (Table 2). The parent MD is distinguished by high structuring velocities as well as by the height of the s/l maximum. These four samples gel at the concentration employed (Table 2). Analogous behaviour is observed for the same fractions using low shear rotational viscosity measurements.

The low molecular fraction S_2S_1 with about 50% of oligosaccharides of $\bar{P}_n \leqslant 9$ underwent phase separation and sedimentation without gelling. The s/l-value indicates that solid, structured material has been formed.

Table 1. Effect of the initial gelling temperature (4°C and 20°C) of MD gels on the s/l-values which will result after equilibrating the gel samples to higher and lower temperature levels. The lower onset temperature of gelling (4°C) in every case leads to the higher s/l-values as compared with the samples of 20°C initial gelling temperature

	t (°C)	Solid-liquid ratio (%)				
Initial gelling temp.	→ 40	2·7	3·8	5·1	6·8	8·6
	→ 20	3·6	5·3	7·0	9·6	11·5
	→ 4	3·7	5·4	8·1	10·6	13·0
Concentration →	% (w/w)	15	20	25	30	35
Initial gelling temp.	→ 20	2·3	3·7	5·5	8·1	10·0
	→ 4	2·7	4·1	6·3	8·6	10·9
	→ 40	2·1	3·2	4·9	6·9	8·6

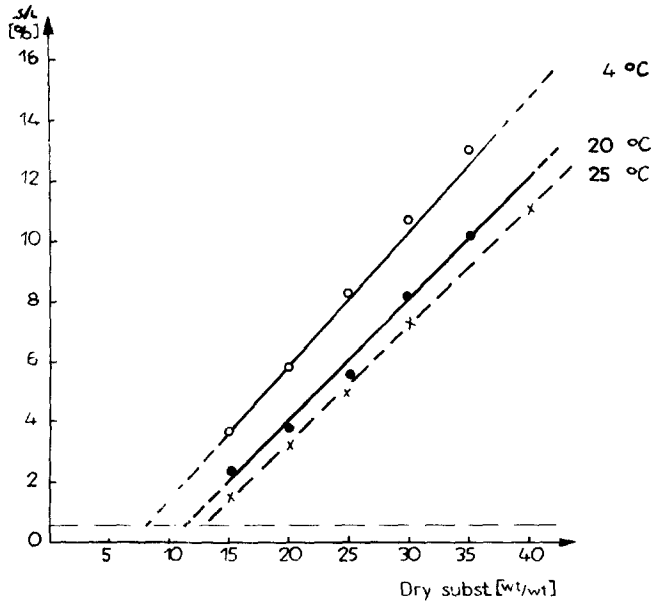


Fig. 5. Dependence of s/l-values of different MD-solutions on concentration at 4, 20 and 25°C.

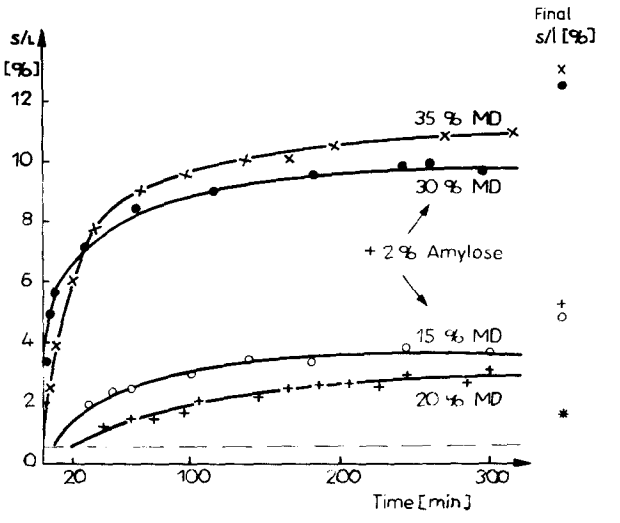


Fig. 6. Action of soluble amylose on the time dependence of the s/l-values during the initial phase of MD gel forming. (●, ○), solutions with amylose added; (×, and +), pure MD solutions for comparison; (*), final s/l-value of the pure amylose solution (%, w/w). Half-value times of s/l: 205 min, 20% MD; 65 min, 15% MD + 2% amylose; 25 min, 35% MD; 10 min, 30% MD + 2% amylose.

Action of dissolved amylose

The sol-gel transition of gelling MD samples will be accelerated when an amylose solution is added (Fig. 6). This effect is more pronounced in the low concentration systems. At the end of the gelling process the s/l-value for the samples with and without amylose are practically the same.

Acetylated maltodextrin and amylopectin

Solutions of pure Ac-MD at a concentration of 30% (w/w) and a comparable degree of hydrolysis (as compared with unsubstituted MD) did not gel. Turbid solutions, which give only a faint solid phase signal were obtained after prolonged storage times (Table 3, Fig. 7). The addition of amylose solution leads to the formation of a turbid weak gel as well as to s/l-values, which are distinctly higher than those of the Ac-MD solution and of the pure 2% (w/w) solution of amylose, which quickly retrograded. Similar interactions take place when entirely non-gelling amylopectin solutions are combined with solutions of 'free' (non-retrograded) amylose (Fig. 7).

These findings are confirmed by the result of DSC measurements with lower concentrations of the same components (Fig. 8). The pure Ac-MD solutions exhibit no melting peak, whereas the retrograded low molecular amylose had completely melted at 93·5°C. The mixed solutions of both, however, show increased melting enthalpy as well as a shift to lower melting temperatures as compared with the pure amylose system.

DISCUSSION

The method, possibilities and limitations

The transition of a homogeneous MD solution into a thermally reversible gel will be reflected by the NMR s/l

Table 2. Structure forming by $\bar{P}_n$ fractions of MD as revealed by the half-value time and maximum s/l values (for comparison: the shear modulus and the times of aggregation and apparent viscosity by rheological measurements are included (Vorwerg *et al.*, 1988))

Sample	$\bar{P}_n$	s/l half-value time (min)	Maximum s/l (%)	Shear modulus (Nm^{-1})	Aggregation time (min)	Apparent viscosity (mPa s)
Parent MD	27	42	10·7	21	25	45·6
Fractions						
G_2G_1	250	130	10·4	20	514	126·0
S_2G_1	120	60	9·8	5	172	95·5
G_2S_1	62	12	9·4	2	Non-gelling under shear	
S_2S_1	9	220	6·7	—	—	—
	Non-gelling but separation of phase					

Table 3. Interaction of non-gelling Ac-MD sample with amylose solutions (4 °C)

Sample	Concentration (%)	Maximum s/l (%)	Time (h)	State of system
Ac-MD	30	0·9	48	Turbid solution
Amylose $\bar{P}_n$ 36	2	1·7	48	Retrogradation, phase separation
Ac-MD + amylose $\bar{P}_n$ 36	28 2	2·4	45	Turbid gel

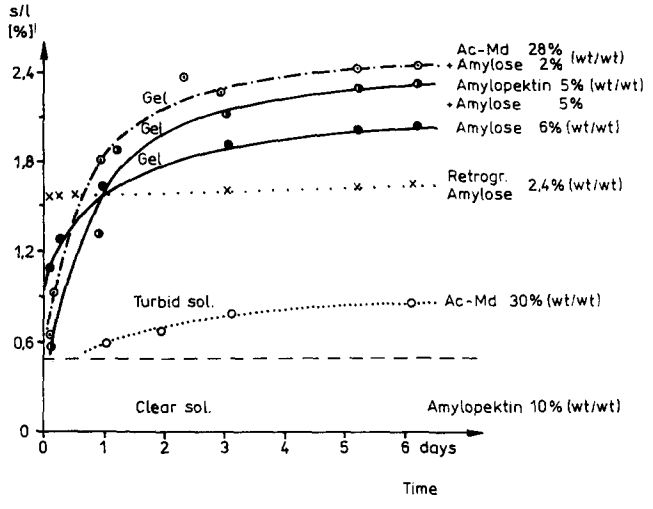
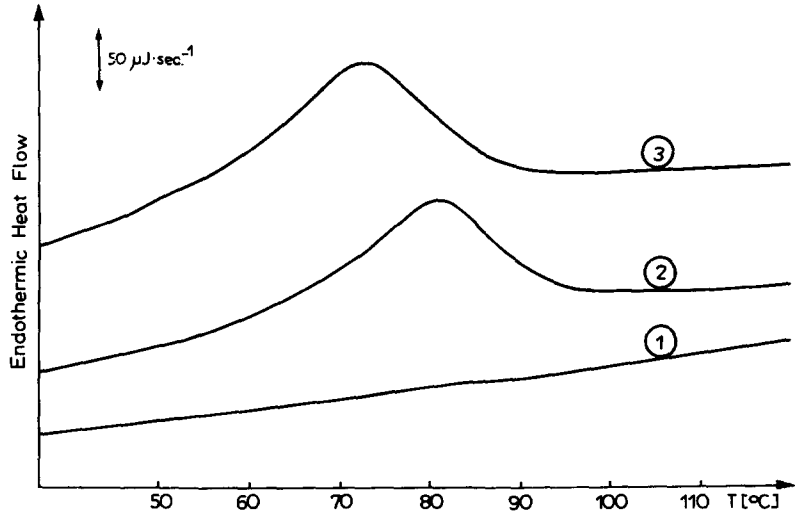


Fig. 7. Time dependence of solid-liquid ratio of pure non-gelling solutions of Ac-MD of amylopectin, of amylose solutions and of mixtures thereof.

ratio from the onset after few minutes until reaching approximately constant values after several days. Analogous time dependence has been obtained with the same MD for the X-ray crystallinity and the shear modulus (Fig. 9). The melting-enthalpy-time plot of 8% (w/w) MD solution (by DSC) exhibits a similar time dependence, but it is still rising when the other parameters have reached equilibrium (Fig. 9). The initial phase of rapid aggregation and network formation is generally followed by a long period of slow structural rearrangements. It is not possible to predict how long these rearrangements will take. In the present case no further changes in s/l-values could be observed after at most six days. Results reported by Ring *et al.* (1987) after 40 days' storage of highly concentrated amylopectin-water systems indicate that the assumption of long-time structural arrangements is realistic. Orford *et al.* (1987) distinguish between high speed irreversible crystallization of preferentially linear components and



Curve	Sample	Reference	Melting Enthalpy in J·g⁻¹	T_A	T_P in °C	T_E
①	8 % Ac-md.	water	—	—	—	—
②	2 % Amylose Pn 36	water	12.7	62.2	81.0	93.5
③	8 % Ac-md. + 2 % Amylose Pn 36	8 % Ac-md.	17.0	52.0	72.5	88.0

Sample were stored 20 hours at 4 °C before measurement

Fig. 8. DSC melting endoterms (DASM 4, heating rate 1 K min^{-1}) of solutions of Ac-MD, amylose and mixtures thereof.

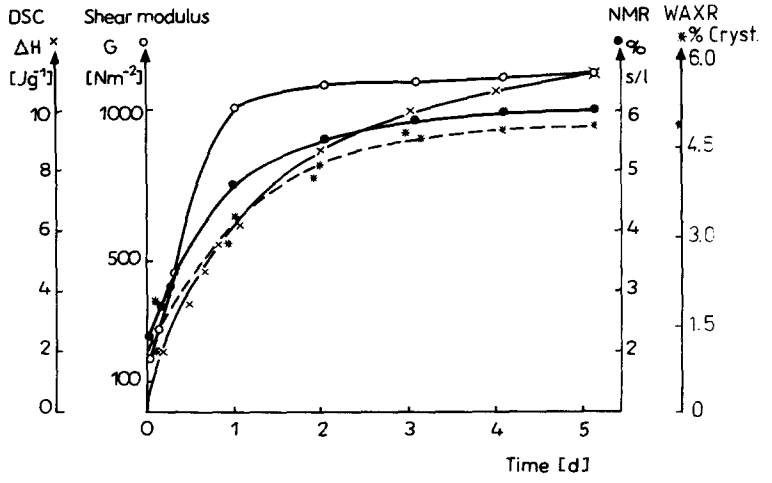


Fig. 9. Time dependence of sol-gel transition of MD-solution as characterized by low resolution-NMR, ●, wide angle X-ray-scattering, *, shear modulus, O, (20% w/w) and DSC-measurements (8% w/w), ×.

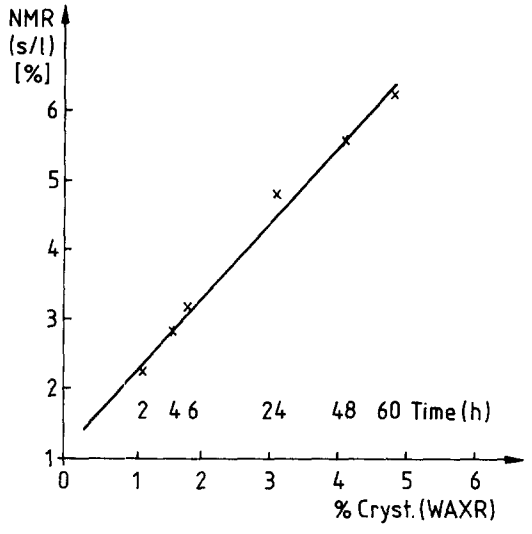


Fig. 10. Linear proportionality between s/l-values and %-degree of X-ray crystallinity (25% w/w, 20 °C).

the slow rearrangement of the amylopectin chains.

The degree of X-ray crystallinity was linearly related to the solids content over the first 60 h of aggregation (Fig. 10). It is important to remark that the formation of solid structures will be detected by NMR in the liquid pre-gel state. The detection of crystalline components by X-ray scattering or solid phase material by NMR relaxation measurements is indicative that separation of phases starts at the beginning of the gelling process. Structural elements were detected in 35% (w/w) gelling MD solutions from storage and loss moduli (G' and G''), beginning about 16 min after the temperature drops below 30 °C (Bulpin *et al.*, 1984). It is to be stressed, on the other hand, that no solid-liquid values are observed in solutions which exhibit amorphous scattering in X-ray diffraction analysis. Such solutions consist of non-gelling Ac-MD solutions or freshly prepared MD solutions at low concentrations (Reuther *et al.*, 1984). The s/l dependence on temperature and concentration shows the same behaviour as other characteristic gel properties. Approaching the melting temperature lowers the s/l ratio. Molten gels behave like water and other liquids without any structured components. This property is in accordance with the loss in apparent low shear viscosity (Vorwerg *et al.*, 1988), with X-ray small-angle scattering results (Reuther *et al.*, 1983) as well as with the findings of Bulpin *et al.* (1984) using high resolution ^{13}C-NMR studies.

The dependence of the final s/l ratio on concentration at different temperatures exhibits a linear relationship from 15% to 35% (w/w). Similar behaviour can be derived from the X-ray wide-angle scattering results on gelling maltodextrins of 10–25% (w/w) (Gernat *et al.*, 1987) as well as from the shear moduli of starch gels and waxy maize amylopectin gels of 10–25% (w/w) (Ring, 1985; Ring *et al.*, 1987). A linear dependence shear modulus versus concentration of MD solutions is valid only for the 15–25% (w/w) range (Vorwerg *et al.*, 1988). This is indicative of a limiting concentration in gel properties because there is a maximum aggregate density, whereas the number of structured (crystalline) components may be further increased.

The time dependence of the s/l-values over the first five hours at various concentrations did not fit first-order kinetics (Fig. 11). From this it follows that a fully intramolecular reation is unlikely.

The $\bar{P}_n$ dependence of gelation is similar for the rheological and s/l measurements. The gelling fraction $\bar{P}_n$ 235 (Table 2) needs more aggregation time but exhibits the highest s/l ratio, equilibrium viscosity and shear modulus. The fraction $\bar{P}_n$ 62 aggregates with the highest velocity both in low shear rheology as well as in non-destructive NMR s/l measurement but the gel, if formed, is rather weak (Vorwerg *et al.*, 1988).

It is obvious from the non-gelling but aggregating and sedimenting oligosaccharide fraction, as well as

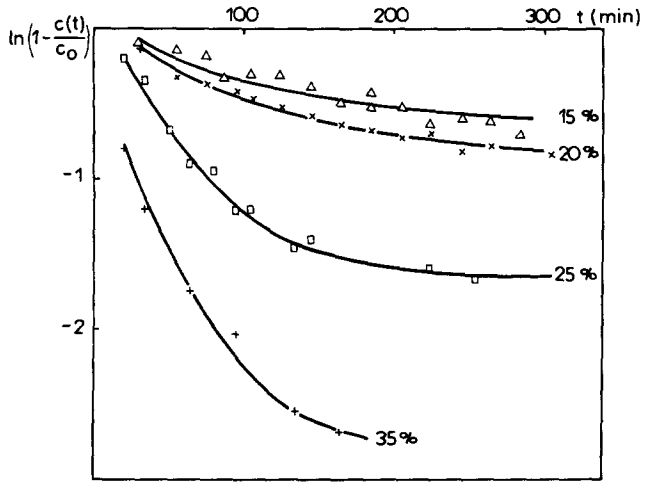


Fig. 11. s/l-ratio versus time plotted according to the 1st order kinetic of reaction.

from the retrograded amylose ($\bar{P}_n \sim 36$), that the formation of solid phases or crystalline components is what is detected by the low resolution NMR measurements. Consequently, the measured s/l-values will cover gelled, crystalline or retrograded systems. It is not the gel state which will be measured but the formation of highly ordered structures which are an essential constituent of the gel. It is necessary to remark that thermal reversibility and irreversibility cannot be distinguished by the NMR s/l measurements. Crystallinity in retrograded amylose will be detected in the same way as in thermally reversible gels.

Concluding remarks on maltodextrin network formation

Undoubtedly the linear fraction in the dissolved state is responsible for initiation and acceleration of gel formations. This statement results from the experiments in which soluble amyloses were added to solutions of gelling MD as well as to non-gelling solutions of Ac-MD or amylopectin. In the case of maltodextrin solutions (Fig. 6) the effect is more pronounced in the initial phase. The final s/l-values are increased more at lower maltodextrin concentrations. In the non-gelling solutions, amylose initiates the formation of a gel structure. The maximum s/l-values are higher in every case than those of the pure amylose (Table 3, Fig. 7), but no retrogradation took place when the amylose solution was mixed with the other carbohydrate solutions in contrast to the behaviour of the pure amylose solutions. These observations may be interpreted by the assumption that the outer linear chains of the amylopectin will interact with the amylose, so preventing their self-association and formation of a hydrated common network. From the experimental values, it can be suggested that these interacting linear units of the branched molecules contribute to the amount of ordered structure in the gel. The available chain length and the concentration will determine the density of the interaction.

In the case of acetylated maltodextrins, the degree of substitution as well as of hydrolysis are both responsible for limiting gel formation and for the initiation of gelation on amylose addition (Schierbaum *et al.*, 1986). This simple interaction model was first established on the basis of rheological measurements (Vorwerg *et al.*, 1988) and is now confirmed by the results of NMR s/l results.

Further support is given by the results of DSC measurements. Non-gelled Ac-MD gives no melting enthalpy, but when gelation resulted on amylose addition, the enthalpy developed by this system is higher than that of pure amylose. Compatibility between soluble amylose and branched chain molecules seems to be necessary for the formation of a maltodextrin gel. Low cooperativity of interactions (Schierbaum *et al.*, 1990) as well as low molecular α-glucosidic chains (Burchard, 1985) may be responsible for this type of gel behaviour. The findings of Gidley (1989) and Pfannemüller (1989) about double-helix formation of α-glucosidic chains of 10–12 anhydroglucose units and the statement of Gidley and Bulpin (1987), that branched molecules may participate in network formation, support the present authors' assumption.

Compared with the results on higher molecular starch components compatibility and amylose network formation, the authors' findings deviate from the results and derived structure models which were published by Ring *et al.* (1985), Kalichevski and Ring (1987) and Miles *et al.* (1984, 1985). Incompatibility has been shown for high molecular weight amyloses and amylopectins, whereas demixing does not take place for the lower molecular weight maltodextrin systems investigated here. The present authors suggest that the molecular level of the interacting components as well as their composition are responsible for the different results and interpretations. Further work will be needed on the pre-conditions for network structure in connection with thermally reversible or irreversible behaviour of two-phase starch gels.

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