Carbohydrate Polymers **21** (1993) 243–248

Phase equilibria and gelation in gelatin/maltodextrin systems — Part I: gelation of individual components

Stefan Kasapis, Edwin R. Morris

Department of Food Research and Technology, Cranfield Institute of Technology, Silsoe College, Silsoe, Bedford MK45 4DT, UK

Ian T. Norton & Allan H. Clark

Unilever Research, Colworth Laboratory, Sharnbrook, Bedford MK44 1LQ, UK

(Received 21 January 1993; accepted 26 February 1993)

As a prelude to studies of co-gelation with galatin, the gelation behaviour of Paselli maltodextrins SA-6 and SA-2 (DE $\approx$ 6 and 2, respectively) was mapped out over the experimentally-accessible range of temperature (T) and concentration (c), using a simple visual method to determine the time required for formation of a self-supporting network (t_g). For both samples, log t_g decreased linearly with log c and increased linearly with T. At equivalent temperatures and concentrations, SA-2 gelled between 20 and 60 times faster than SA-6.

Selected samples were monitored more rigorously by mechanical spectroscopy, taking t_g as the time at which elastic response (G') became greater than viscous response (G''). In all cases the values of t_g obtained by this procedure were lower than those from visual inspection, by a constant factor of about 3·4.

The concentration-dependence of gel moduli (G') for SA-2 and for gelatin (second-extract limed ossein; LO-2) fitted accurately to the form anticipated from cascade theory for normal polymer networks. For SA-6, by contrast, log G' varied linearly with log c over the entire range at which measurements could be made, indicating a different mechanism of structure-formation (such as the agglomeration of short, aggregated helices).

1 INTRODUCTION

Partial hydrolysis of starch to different extents of depolymerisation yields a range of commercially useful products characterised according to their 'dextrose equivalent' (DE), which gives the content of reducing end-groups relative to glucose as 100. Thus a DE of 20 corresponds to a (number average) degree of polymerisation of 5. Hydrolysis products with a DE above this value are called 'glucose syrups'; those with a lower DE are called 'maltodextrins'. The distinction is not entirely arbitrary, since it corresponds roughly to the transition from freely-soluble, short oligomers to materials with a significant proportion of chains long enough to form thermally reversible gels (Richter *et al.*, 1976; Schierbaum *et al.*, 1977). In practice, however, maltodextrin preparations are normally complex mixtures of species ranging from glucose to long polymeric chains, so that samples with the same DE prepared from different starches and/or by different processes can have quite different compositions and properties (Armbruster, 1974).

Depolymerisation of starch to maltodextrin can be achieved by acid hydrolysis (BeMiller, 1965; Robin *et al.*, 1974), enzymically (Hebeda *et al.*, 1975; Berghmans & Walon, 1977) or by a combination of both procedures (Armbruster & Harjes, 1975). A particularly interesting type of low DE maltodextrin, or 'Starch Hydrolysis Product' (SHP), is produced by the action of α-amylase on potato starch at its gelatinisation temperature, and gives thermally-reversible gels. Only potato starch has been shown to give products with this behaviour; the

Carbohydrate Polymers 0144-8617/93/$06.00

SHP obtained when maize starch is treated in the same way does not gel. The origin of the difference has yet to be explained in detail, but is likely to be associated with different patterns of branching in the parent amylopectins (Bulpin *et al.*, 1984).

SHP gels have organoleptic properties similar to those of fats, with obvious commercial applications in the production of calorie-reduced products such as low-fat spreads. Combination with gelatin allows lower concentrations of maltodextrin to be used, avoiding a 'starchy' mouthfeel. The research reported here, and in the following three papers (Kasapis *et al.*, 1993*a*, *b*, *c*), was carried out to provide background understanding for intelligent manipulation and refinement of gelatin/maltodextrin systems. A preliminary account of the principal findings has been published elsewhere (Kasapis *et al.*, 1992).

2 EXPERIMENTAL

The gelatin sample used was kindly supplied by Sanofi Bio-Industries Ltd. It was the second extract obtained from ossein by the lime pretreatment process (LO-2), a high-quality gelatin with a Bloom value of 270. This material was used directly as supplied, with no further purification or fractionation. Solutions were prepared by soaking pre-weighed amounts in distilled water at ambient temperature (typically for 2–3 h), followed by mechanical stirring at elevated temperature (10–15 min at about 80°C).

Two commercial maltodextrin samples were also used as supplied. These were products of the enzymic hydrolysis of potato starch, with approximate DE values of 2 and 6, respectively Paselli SA-2 and SA-6 from Avebe. Solutions were prepared in distilled water by mechanical stirring at 90°C, typically for 20 min in the case of SA-6 and 30 min for SA-2.

The experimental technique (Oakenfull & Scott, 1986, 1988) used to monitor the rate of gelation of Paselli maltodextrins was as follows. A fixed weight (10 g) of solution was placed in a series of cylindrical vials (diameter 23 mm). The samples were quenched from 90°C to the experimental temperature, maintained to within ± 0·1°C in a thermostatted water bath. The vials were then inverted sequentially and the time (t_g) required to form a gel strong enough to remain held was recorded.

Small-deformation oscillatory measurements were performed at 0·4 Hz on a Sangamo Viscoelastic Analyser, using cone and plate geometry (25 mm radius; 2° cone angle), or on a Bohlin VOR rheometer using a parallel plate system (15 mm radius; 1 mm gap) at 1% strain and frequency 1 Hz. Temperature was controlled to within ± 0·2°C by a circulating water bath and measured by a thermocouple in direct contact with the sample.

3 RATE OF MALTODEXTRIN GELATION

Estimation by visual inspection

To design meaningful experiments on gelatin–maltodextrin mixed systems, some prior knowledge of the behaviour of the individual components was required. Gelatins have a long history of industrial use, which has stimulated extensive investigation of their gelation behaviour (see for example Ledward, 1986; Djabourov *et al.*, 1988). There is, however, considerably less background information on the gelation properties of maltodextrins, because of their shorter period of industrial use (Cakebread, 1971; Harkema, 1991). Therefore the gelation behaviour of Paselli maltodextrins as a function of temperature and concentration was investigated in this study.

Gel-time measurements were made at five fixed temperatures: 5, 10, 15, 20 and 25°C, and at nine fixed concentrations spaced at intervals of 2·5% w/w over the range 20–40% w/w for SA-6 and 10–30% (w/w) for SA-2. Results obtained are listed in Tables 1 and 2, respectively. As illustrated in Fig. 1, a simple linear relationship between log t_g and log c was observed for both maltodextrin samples at each temperature.

On the assumption that the reciprocal of gel-time is directly proportional to the rate of intermolecular association to form gel junction zones, Oakenfull and Scott (1986, 1988) have used the slope of similar linear plots for other systems to derive the order of reaction and

Table 1. Gel-time data for Paselli SA-6[a]

Concentration (% w/w)	log (t_g/s) at temperatures shown				
	5°C	10°C	15°C	20°C	25°C
20·0	4·63	4·81	ND[b]	ND[b]	ND[b]
	(4·67)	(4·88)			
22·5	4·29	4·50	4·75	ND[b]	ND[b]
	(4·29)	(4·50)	(4·71)		
25·0	3·97	4·16	4·40	4·71	ND[b]
	(3·94)	(4·15)	(4·36)	(4·57)	
27·5	3·80	3·83	4·05	4·20	4·57
	(3·63)	(3·84)	(4·05)	(4·26)	(4·47)
30·0	3·43	3·47	3·75	3·81	4·22
	(3·34)	(3·55)	(3·76)	(3·97)	(4·18)
32·5	3·05	3·24	3·47	3·60	3·96
	(3·08)	(3·29)	(3·50)	(3·71)	(3·92)
35·0	2·87	2·97	3·21	3·42	3·70
	(2·84)	(3·05)	(3·26)	(3·47)	(3·68)
37·5	2·69	2·81	3·06	3·24	3·46
	(2·62)	(2·82)	(3·03)	(3·24)	(3·45)
40·0	2·45	2·67	2·90	3·05	3·33
	(2·40)	(2·61)	(2·82)	(3·03)	(3·24)

[a]The values in parentheses show the fit obtained using eqn (1).
[b]The longest gel times recorded in the table correspond to about 18 h. Experiments at temperature and concentration combinations giving longer gel times were therefore not done (ND), because of the obvious problems of continuing visual observations over longer periods.

Table 2. Gel-time data for Paselli SA-2[a]

Concentration (% w/w)	log (t_g/s) at temperatures shown				
	5°C	10°C	15°C	20°C	25°C
10·0	4·30	4·71	ND[b]	ND[b]	ND[b]
	(4·33)	(4·52)			
12·5	3·89	4·25	4·31	ND[b]	ND[b]
	(3·89)	(4·08)	(4·27)		
15·0	3·46	3·74	3·95	4·10	ND[b]
	(3·53)	(3·72)	(3·91)	(4·10)	
17·5	3·17	3·42	3·57	3·84	4·08
	(3·23)	(3·42)	(3·61)	(3·80)	(3·99)
20·0	2·85	3·09	3·30	3·49	3·75
	(2·96)	(3·15)	(3·34)	(3·54)	(3·73)
22·5	2·70	2·90	3·08	3·20	3·43
	(2·73)	(2·92)	(3·11)	(3·30)	(3·49)
25·0	2·59	2·74	2·93	2·98	3·23
	(2·52)	(2·71)	(2·91)	(3·10)	(3·29)
27·5	2·41	2·56	2·71	2·84	3·10
	(2·34)	(2·53)	(2·72)	(2·91)	(3·10)
30·0	2·29	2·45	2·59	2·75	3·00
	(2·16)	(2·36)	(2·55)	(2·74)	(2·93)

[a]The values in parentheses show the fit obtained using eqn (2).
[b]These experiments were again not done, for the reasons outlined in the footnote to Table 1.

hence deduce the number of chains involved in each junction. This treatment, however, does not take account of the complex relationship between the extent of intermolecular association and the resulting network properties (Clark & Ross-Murphy, 1985, 1987). In particular, as concentration is decreased below the critical gelling concentration (c_o) t_g becomes infinite, which, by the analysis of Oakenfull and Scott, would imply (wrongly) that intermolecular association into ordered junctions has been abolished (Ross-Murphy, 1991). This does not, however, diminish the usefulness of the linear relationship illustrated in Fig. 1 as a simple empirical basis for interpolation and cautious extrapolation of experimental values.

A similar empirical linear relationship (Fig. 2) was evident between log t_g and temperature, T (not log T) for fixed concentrations of both maltodextrins. Least-

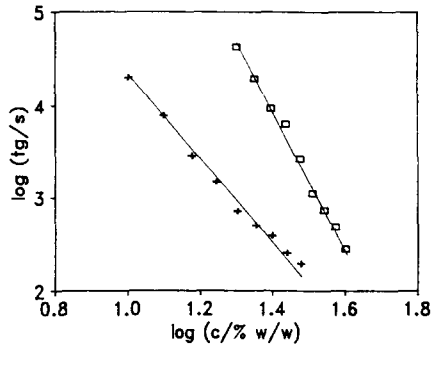

Fig. 1. Concentration-dependence of gel time (t_g, estimated visually) for SA-6 (□) and SA-2 (+) at 5°C. The concentration ranges used were 20–40% (w/w) for SA-6 and 10–30% (w/w) for SA-2.

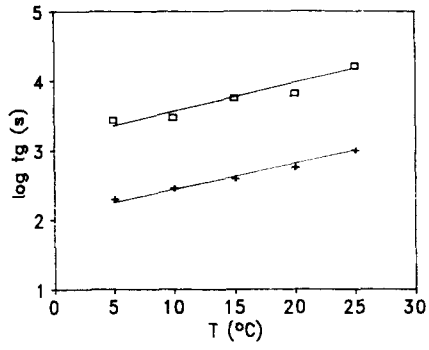

Fig. 2. Temperature-dependence of gel time (t_g, estimated visually) for SA-6 (□) and SA-2 (+) at a fixed concentration of 30% (w/w).

squares analysis yielded the following linear dependence of log (t_g/s) on log (c/% (w/w)) and T/°C for the two samples.

$$\text{SA-6:} \quad \log t_g = 0{\cdot}042\ T - 7{\cdot}54 \log c + 14{\cdot}27 \qquad (1)$$

$$\text{SA-2:} \quad \log t_g = 0{\cdot}038\ T - 4{\cdot}53 \log c + 8{\cdot}67 \qquad (2)$$

In both cases the standard deviation between observed and fitted values of log t_g was less than 0·05 (somewhat better than might have been anticipated from the rather crude nature of the measurements). The values of t_g derived from eqns (1) and (2) are listed in Tables 1 and 2, respectively, for direct comparison with the corresponding experimental values. Within the experimental range covered in this work, gelation of SA-2 is 20–60 times faster than for SA-6 at equivalent temperatures and concentrations.

It is evident from a comparison of the equations that the temperature-dependence of gel formation is closely similar in SA-6 and SA-2, indicating that the initial mechanism of intermolecular association is the same for both, and is essentially independent of DE. The concentration-dependence, however, is very much higher for SA-6, which is consistent with the smaller average chainlength bringing the system closer to c_o at equivalent absolute values of c, with consequent increased dependence of mechanical properties on concentration (Clark, 1987).

Determination by mechanical spectroscopy

Although the internal consistency of the above results is extremely gratifying and encouraging, estimation of gel times by visual inspection is not, of course, the most rigorous of procedures, and was adopted solely to allow a large number of concentration–temperature combinations for maltodextrins to be screened in a reasonable time. As a more fundamental criterion of network formation, the gelation behaviour of some representative samples was monitored by mechanical spectroscopy. Timing commenced when the maltodextrin solution (at

Table 3. Comparison of gel time as estimated instrumentally ($G' = G''$) and visually (formation of a self-supporting network)

			log (t_g/s)		
Maltodextrin	T(°C)	c(% w/w)	Instrumental	Visual	Difference
SA-6	10	27·5	3·28	3·83	0·55
		30·0	2·90	3·47	0·57
		32·5	2·74	3·24	0·50
SA-6	15	32·5	2·97	3·47	0·50
		35·0	2·71	3·21	0·50
		37·5	2·54	3·06	0·52
SA-2	20	17·5	3·27	3·84	0·57
		20·0	2·91	3·49	0·58
		22·5	2·66	3·20	0·54
SA-2	25	22·5	2·94	3·43	0·49
		25·0	2·66	3·23	0·57
		27·5	2·60	3·10	0·50
					Mean = 0·53 ± 0·03

90°C) was loaded onto the rheometer (pre-set at the required experimental temperature), and the gel time was taken as the time at which G' (elastic response), became greater than G'' (viscous response). An illustrative plot of the gel formation is shown in Fig. 3.

Gel times were determined in this way at two different temperatures for each of the maltodextrin samples, using three concentrations at each temperature, to give 12 combinations of temperature, concentration and DE. Results are listed in Table 3, in comparison with the corresponding values from visual inspection. As illustrated in Fig. 4, double logarithmic plots of the concentration-dependence of t_g by this method are again linear, and are closely parallel to the corresponding plots from visual inspection, but offset to shorter times at equivalent concentrations. The degree of offset is virtually identical for both maltodextrins, and for temperatures ranging from 10 to 25°C (Table 3), the difference between the values of log t_g from the two techniques being 0·53 ± 0·03. Thus the ratio of the observed gel times remains essentially constant, with the values obtained by visual inspection being about 3·4 times higher than the corresponding instrumental values ($10^{0.53} \approx 3.4$).

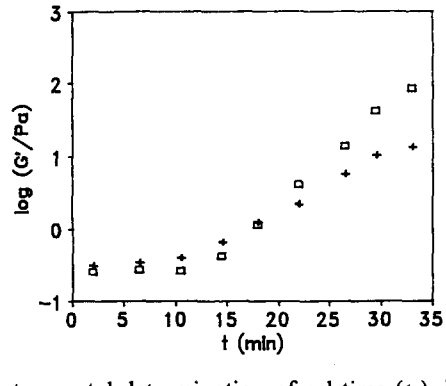

Fig. 3. Instrumental determination of gel time (t_g), illustrated for 30% (w/w) SA-6 at 10°C after quenching from 90°C. The instrumental value of t_g is taken as the time at which G' (□) becomes equal to G'' (+). Measurements were made at a frequency of 0·4 Hz and 1% strain.

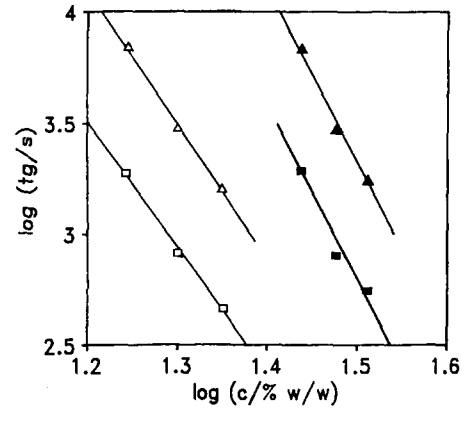

Fig. 4. Comparison of gel times (t_g) determined instrumentally (at $G' = G''$; squares) and visually (on formation of a self-supporting network; triangles) for SA-2 (open symbols) and SA-6 (filled symbols). The illustrative results shown are for 17·5, 20·0 and 22·5% (w/w) SA-2 at 20°C and 27·5, 30·0 and 32·5% (w/w) SA-6 at 10°C.

There is no conflict between the two approaches, since the instrumental criterion of the onset of gelation ($G' = G''$) corresponds to the initial development of an infinite network, whereas the requirement for the network to be self-supporting, as in the visual method, will be satisfied only at a much greater degree of cross-linking. The constant ratio of the two values, however, was unexpected, and may merit future research on other systems to determine whether the relationship is specific to maltodextrins or has more general applicability. For the moment, the systematic correlation with fundamentally valid objective measurements lends further confidence to the more empirical and subjective results from visual inspection.

In the course of these investigations, a further striking correlation was observed. Under all conditions listed in Table 3, the onset of network formation, by the criterion of $G' = G''$, was closely coincident with the development of detectable turbidity (by eye). This is consistent with intermolecular association in maltodextrin gels involving extensive helix–helix aggregation.

4 CONCENTRATION-DEPENDENCE OF *G'*

One aim of the work described above was to identify suitable conditions of temperature and concentration for investigation of the effects of thermodynamic incompatibility of gelatin and maltodextrin with both polymers present as disordered coils in solution (Kasapis *et al.*, 1993*a*; part II of this series) i.e. conditions under which the maltodextrin remains stable in solution over long periods of time. The work reported in this section was carried out in preparation for studies of mixed gels under conditions where both components can form networks within the timescale of the experiment.

In these studies (Kasapis *et al.*, 1993*b*, *c*; parts III and IV of this series) the authors followed the procedure developed in previous investigations of phase-separated mixed-gels (Clark *et al.*, 1982, 1983) of using polymer blending-laws (Takayanagi *et al.*, 1963; Clark, 1987) to relate the overall mechanical properties to those of the constituent phases. Application of this approach requires the modulus (G') to be known as a continuous function of concentration for each of the component polymers.

Although empirical fits (e.g. by a polynomial function) could be used for interpolation between measured values of G' at different concentrations, extrapolation beyond the experimentally-accessible range requires a more theoretically-valid procedure. In the present work we have used a modification (Clark, 1987) of an approach first developed by Hermans (1965), but recast in terms of the cascade formalism (Gordon & Ross-Murphy, 1975) for network formation. By this method, the concentration-dependence of modulus can be fitted to three parameters: the functionality (f), defining the number of 'binding sites' per chain; the equilibrium constant (K) between free and associated sites; and a 'front factor' (g) which scales the absolute values of modulus. These parameters are obtained by a least-squares fit of experimental data, and can then be used to derive the modulus at any concentration.

Figure 5 illustrates the time-course of gelation for a representative sample of each polymer: 15% (w/w) LO-2, 30% (w/w) SA-6 and 18% (w/w) SA-2. Development of network structure was monitored over a period of 25×10^3 s (about 7 h) at a fixed temperature of 5°C, and the final values were used in curve-fitting.

The concentration-dependence of G' for LO-2 is shown in Fig. 6. As in previous studies (Clark *et al.*, 1983) of gelatin from a different source (acid-treated pigskin), the experimental curve could be matched with good precision by a cascade fit. The parameters of the fit are listed in the figure legend. Figure 7 shows the corresponding modulus-concentration relationships for SA-6 and SA-2. The data for SA-2 could again be matched with good precision by a cascade fit (parameters in figure legend), but the concentration-dependence of G'

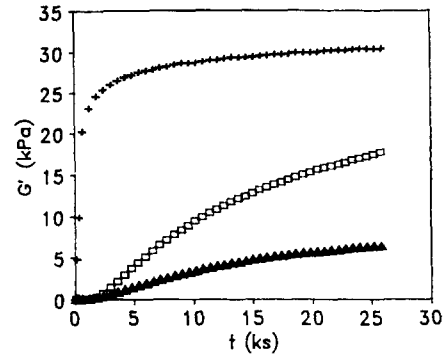

Fig. 5. Time-course of gelation (5°C; monitored by rigidity modulus, G', at 1 Hz frequency and 1% strain), illustrated for 18% (w/w) SA-2 (▲), 30% (w/w) SA-6 (□) and 15% (w/w) LO-2 (+).

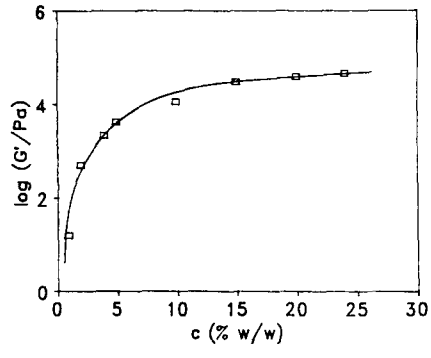

Fig. 6. Concentration-dependence of G' (25 ks; 5°C) for LO-2. The solid line shows a cascade fit with an equilibrium constant (K) of 179·2 mol litre^{-1}, a functionality (f) of 10·2 and a front factor (g) of 2·5 for an assumed molecular weight of 10^5.

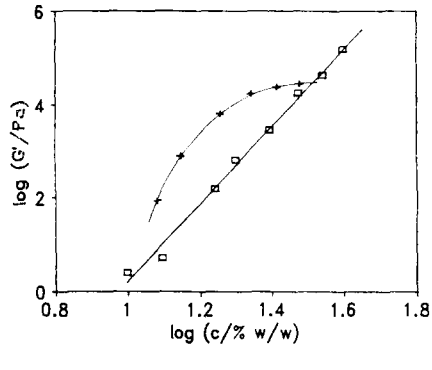

Fig. 7. Concentration-dependence of G' (25 ks; 5°C) for SA-2 (+) and SA-6 (□). The parameters of the cascade fit to the SA-2 data are: $K = 103$ mol litre^{-1}, $f = 2{\cdot}7$ and $g = 3{\cdot}5$ for an assumed molecular weight of $7{\cdot}5 \times 10^3$.

for SA-6 is entirely different in form, with log G' varying linearly with log c:

$$\log G' = 8{\cdot}28 \log c - 7{\cdot}09 \quad (3)$$

A possible interpretation of this striking difference is that SA-2, because of its higher average chainlength, is capable of forming a normal polymer network, complying with the assumptions of the cascade formalism, whereas the shorter chains of SA-6 create long-range structure in a quite different way. In the language of polymer physics, a likely alternative mechanism might be 'de-mixing', which for our system could be described from a molecular viewpoint as agglomeration of aggregated helices. However, whatever the origin of the unusual concentration-dependence for SA-6, the immediate goal of deriving a quantitative relationship between modulus and concentration could be readily achieved by using the above linear fit.

ACKNOWLEDGEMENTS

The authors are grateful to Professor S.B. Ross-Murphy for helpful discussions and the provision of a Pascal program to implement the cascade fit. The authors also thank Mr C.R.T. Brown for advice and assistance with the rheological experiments, and Mrs L. Ellis for preparing the typescripts of the four papers in this series.

REFERENCES

Armbruster, F.C. (1974). US Patent no. 3 853 706.

Armbruster, F.C. & Harjes, C.F. (1975). GB Patent no. 1 203 048.

BeMiller, J.N. (1965). In *Starch: Chemistry and Technology*, ed. R.L. Whistler & E.F. Pascall, vol. 1. Academic Press, London, pp. 495–520.

Berghmans, E.F. & Walon, R.G.P. (1977). GB Patent no. 1 470 325.

Bulpin, P.V., Cutler, A.N. & Dea, I.C.M. (1984). In *Gums and Stabilizers for the Food Industry — 2*, ed. G.O. Phillips, D.J. Wedlock & P.A. Williams. Pergamon Press, Oxford, pp. 475–84.

Cakebread, S.H. (1971). *Confectionary Production*, June, 339–44.

Clark, A.H. (1987). In *Food Structure and Behaviour*, ed. J.M.V. Blanshard & P. Lillford. Academic Press, London, pp. 13–34.

Clark, A.H. & Ross-Murphy, S.B. (1985). *Brit. Polym. J.*, **17**, 164–8.

Clark, A.H. & Ross-Murphy, S.B. (1987). *Adv. Polym. Sci.*, **83**, 57–192.

Clark, A.H., Richardson, R.K., Robinson, G., Ross-Murphy, S.B. & Weaver, A.C. (1982). *Prog. Fd. Nutr. Sci.*, **6**, 149–60.

Clark, A.H., Richardson, R.K., Ross-Murphy, S.B. & Stubbs, J.M. (1983). *Macromolecules*, **16**, 1367–74.

Djabourov, M., Leblond, J. & Papon, P. (1988). *Phys. France*, **49**, 319–32.

Gordon, M. & Ross-Murphy, S.B. (1975). *Pure Appl. Chem.*, **43**, 1–26.

Harkema, J.G. (1991). *European Food & Drink Review*, Summer, 17–18.

Hebeda, R.E., Holic, D.J. & Leach, H.W. (1975). US Patent no. 3 922 196.

Hermans, J.R. (1965). *J. Polym. Sci. A.*, **3**, 1859–68.

Kasapis, S., Morris, E.R. & Norton, I.T. (1992). In *Gums and Stabilisers for the Food Industry — 6*, ed. G.O. Phillips, P.A. Williams & D.J. Wedlock. IRL Press, Oxford, pp. 419–28.

Kasapis, S., Morris, E.R., Norton, I.T. & Gidley, M.J. (1993*a*). *Carbohydr. Polym.*, **21**, 249–59, this issue. (Part II of series.)

Kasapis, S., Morris, E.R., Norton, I.T. & Brown, C.R.T. (1993*b*). *Carbohydr. Polym.*, **21**, 261–8, this issue. (Part III of series.)

Kasapis, S., Morris, E.R., Norton, I.T. & Clark, A.H. (1993*c*). *Carbohydr. Polym.*, **21**, 269–76, this issue. (Part IV of series.)

Ledward, D.A. (1986). In *Functional Properties of Food Macromolecules*, ed. J.R. Mitchell & D.A. Ledward. Elsevier, London, pp. 171–201.

Oakenfull, D. & Scott, A. (1986). In *Gums and Stabilizers for the Food Industry — 3*, ed. G.O. Phillips, D.J. Wedlock & P.A. Williams. Elsevier, London, pp. 465–75.

Oakenfull, D. & Scott, A. (1988). In *Gums and Stabilizers for the Food Industry — 4*, ed. G.O. Phillips, D.J. Wedlock & P.A. Williams. IRL Press, Oxford, pp. 127–34.

Richter, M., Schierbaum, F., Augustat, S. & Knoch, K.-D. (1976). US Patent no. 3 962 465.

Robin, J.P., Mercier, C., Charbonniere, R. & Guilbot, A. (1974). *Cereal Chem.*, **51**, 389–406.

Ross-Murphy, S.B. (1991). *Carbohydr. Polym.*, **14**, 281–94.

Schierbaum, F., Richter, M., Augustat, S. & Radosta, S. (1977). *Dtsch. Lebensmittel-Rdsch.*, **73**, 390–4.

Takayanagi, M., Harima, H. & Iwata, Y. (1963). *Mem. Fac. Eng. Kyushu. Univ.*, **23**, 1–13.