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Role of the Molecular Weight on the Mechanical Properties of Kappa Carrageenan Gels

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ABSTRACT

Kappa carrageenans with different molecular weights were prepared by ultrasonication and preparative gel permeation chromatography; gels were prepared with different polymer and KCl concentrations. The yield stress and the elastic modulus of these gels were correlated with the molecular weight of the polymers.

INTRODUCTION

Kappa carrageenan, a sulphonated galactan extracted from many species of red algae, is extensively used in the food industry as a gelling agent (Guiseley *et al.*, 1980). The formation of a thermoreversible gel on cooling is related to the coil to helix transition for this polysaccharide (Rees, 1969). The temperature, the ionic content and the nature of the counterions regulate this conformational change and consequently the gelation of the polysaccharide (Rochas & Rinaudo, 1984). Although the properties of the polysaccharide have been extensively studied (Rees *et al.*, 1982) its gel state has not been systematically investigated (Clark & Ross-Murphy, 1987). In particular, as with many polysaccharides, the role of molecular weight on the properties of the gel has not been studied in detail, although some preliminary data have been reported by Smidsrod (1974). In contrast the properties of alginate gels have been well described by Smidsrod and Haug (1972). The molecular weight dependence they observed for the alginate gels was postulated as a general dependence for polysaccharide gels (Mitchell, 1976, 1980). For

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carrageenan the same dependence was also assumed from a comparison of the gel properties of carrageenans before and after heat processing (Ainsworth & Blanshard, 1980). This present paper describes the relationship between the mechanical properties of kappa carrageenan gels and the molecular weight of the samples.

EXPERIMENTAL

The kappa carrageenan used was the alkali treated extract from *Eucheuma cottonii* (sample 0) and was supplied from MRS (Baupte, France). Samples 9, 11, 13, 17 & 18 were obtained by ultrasonication according to Milas *et al.* (1986). Samples 1, 2, 4, 5, 6, 7, 12, 14 & 16 were obtained by preparative chromatography. In order to obtain larger quantities of low molecular weight material some samples were ultrasonicated before being chromatographed. Samples 3, 8, 10, 15, 19, 21, 22 & 23 were prepared from sample 0 by hydrolysis and were supplied by MRS.

Optical rotation measurements were made at 365 nm on a Perkin-Elmer 241 polarimeter. The gel permeation preparative chromatography was performed on the system of D. Lecacheux (Elf-Aquitaine, GRL, Lacq, France). Two stainless steel columns (100 mm i.d. × 600 mm) were packed, one with Toyosoda H.W. 55S gel and the other with H.W. 75S. The eluent was typically 0·1 M $NaNO_3$ with 0·2 g/litre NaN_3. The eluent was delivered by a Waters 590 EEF pump at a flow rate of 0·5 litre/h and the effluent was monitored by a Waters R 403 refractometer; 180 ml of solution at 0·5 g/litre was injected.

The weight average molecular weights of the samples were determined by size exclusion chromatography on two columns (Shodex B804 and B805; 50 cm length) coupled to a refractometer and a low angle light scattering photometer as previously described (Lecacheux *et al.*, 1985; Rochas & Landry, 1987). The sample of gel (diameter = 17 mm and height = 17 mm) were prepared in 0·1 M KCl as described previously (Rochas & Landry, 1988). The yield stress and the elastic modulus E were obtained at room temperature by compression on a 4301 Instron machine as previously described (Rochas & Landry, 1988).

In addition, preliminary dynamic experiments were made on a Carrimed CS 50 (Rheo, France). It was shown that the dynamic shear modulus G', slightly increased with frequency (10^{-3}–5 Hz) as previously reported by Eliot and Ganz (1975). This is consistent with the observed independence of the elastic modulus E on the crosshead speed in compression tests (Rochas & Landry, 1988). It was also shown that the relation $E = 3\ G'$ was valid. Consequently it is possible to assume that the investigated gels were isotropic.

RESULTS

Characteristics of the samples

For the different samples (Table 1) it is possible to correlate the intrinsic viscosity at 25°C in 0·1 M NaCl and the weight average molecular weight using a power law with a correlation coefficient of 0·992. Because the exponent of this relation 0·95 is very close to one the weight average molecular weight is close to the viscosity average molecular weight. Consequently the Mark–Houwink relation can be written as

$$[\eta] = 3{\cdot}110^{-3} M^{0{\cdot}95} \quad \eta \text{ in ml/g}$$

It is then possible to rapidly estimate the molecular weight of a sample from its intrinsic viscosity. Due to the value close to one of the exponent of this relation we observe that the fractions with high polydispersity are as close to the correlation line (Fig. 1) as the fractions with low poly-

TABLE 1
Characteristics of the Different Fractions of Kappa Carrageenan

Samples	*[η] ml/g*	$\bar{M}_w$	I^a	*Samples*	*[η] ml/g*	$\bar{M}_w$	I^a
0	819	690 000	5				
1	1 480	1 202 000	3·2	13	410	240 000	1·5
2	1 150	833 000	2·9	14	300	133 000	
3	875	581 000	5·1	15	269	113 000	
4	815	507 000	2·5	16	255	130 000	
5	690	419 000		17	220	126 000	
6	675	454 000		18	196	121 000	1·4
7	630	371 000		19	175	92 000	
8	615	380 000	5·8	20	170	101 000	1·6
9	610	360 000	2·7	21	96	58 000	
10	560	338 000	4·4	22	46·4	31 700	
11	495	307 000		23	12·5	6 560	
12	415	220 000					

[a] *I* is the polydispersity.

dispersity. The samples obtained by chromatography or ultrasonication show a very sharp conformational transition (Fig. 2). The polydispersity of the samples does not affect the broadness of the transitions as shown for a 1:1 blend of two fractions of very different $\bar{M}_w$ ($1{\cdot}2 \times 10^6$ and $1{\cdot}3 \times 10^5$). In addition the mid-point T_m of the transition is not dependent on the molecular weight (Table 2). The curves of the hydrolyzed samples (Fig. 3) are different from the other samples but they are similar to the curves obtained from hydrolyzed fractions by Snoeren (1976). As shown above, the broadness of the transition is not due to the polydispersity of the fraction; it is possible that the hydrolysis slightly modifies the chemical structure of the carrageenan. This is particularly true for the extensively hydrolyzed sample 23 ($\bar{M}_w$ 6500).

Role of the molecular weight on the gel

The role of molecular weight on the yield stress and on the elastic modulus of the gel was determined with different values for the polymer concentrations and salt concentrations.

For the different concentrations of polymer used it was observed that the elastic modulus steadily increased with molecular weight, increasing up to a critical value of $M_c = 180{\cdot}000$ (Fig. 4). This critical value M_c is independent of the polymer concentration and the ionic content (Fig. 5). This value probably represents the maximum possible length of the molecule used to build the network. Beyond this limit the modulus remains constant and independent of the molecular weight. From the intercept of the curve of E versus M_w (Fig. 4) with the molecular weight axis it is possible to obtain the lowest molecular weight required to form a gel (i.e. $E > 0$).

Using this value we can verify that a 'macroscopic' gel is obtained when the polymer concentration is higher than the overlapping concentration C^* (here a 'macroscopic' gel means that the network completely fills the container). For example a $(4 \pm 0{\cdot}5)\ 10^4$ M_w is required to obtain a gel at 10 g/litre in 0·1 M KCl (Fig. 4).

The overlapping concentration C^* of this sample is well approximated by the relationship obtained by Graessley (1980) $C^*[\eta] = 0{\cdot}77$. Using the Mark–Houwink relation to obtain the intrinsic viscosity, from the molecular weight $\bar{M}$, required for gel formation, the Graessley relationship gives $C^* = 10 \pm 1$ g/litre. The same agreement between the experimental C^* and the calculated values is obtained from the molecular weight at concentrations of 5 and 20 g/litre. The value of $[\eta]$ is obtained for the coil conformation. It is assumed to be a good

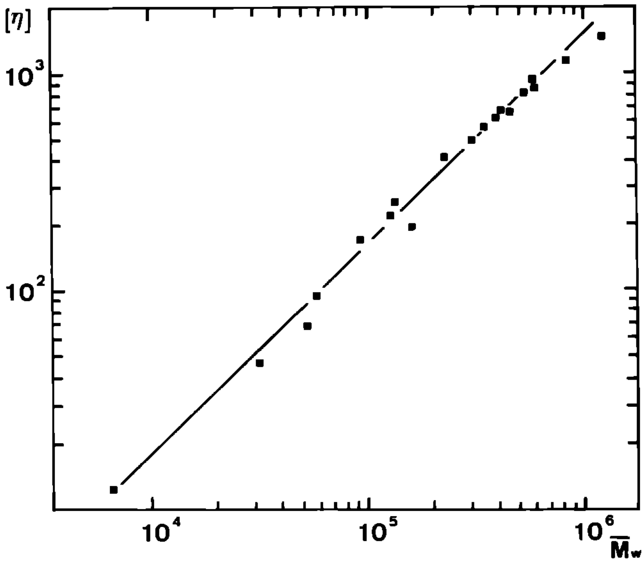

Fig. 1. Double-logarithmic plots of the intrinsic viscosity [η] versus the weight average molecular weight of kappa carrageenan in 0·1 M NaCl at 25°C.

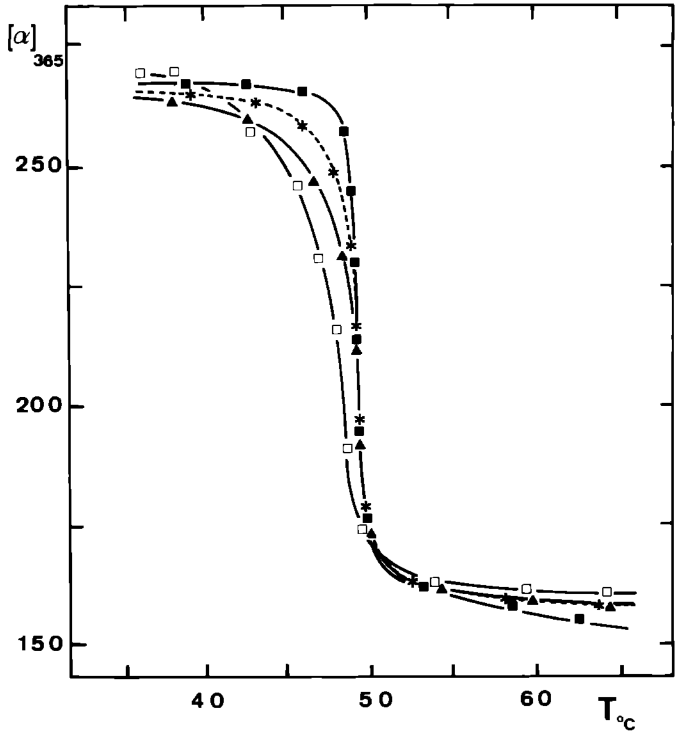

Fig. 2. Optical rotation temperature dependence (cooling, 25°C/h) of different fractions of kappa carrageenan in 0·1 M KCl, $C_p = 0{\cdot}5$ g/litre, ■ fraction 1, ▲ fraction 16, □ fraction 20, * blend of fraction 1 (0·25 g/litre) and fraction 16 (0·25 g/litre).

TABLE 2

T_m (Cooling) for Different Fractions, Determined from the Temperature Dependence of the Optical Rotation, Polymer Concentration 0·5 g/litre, 0·1 M KCl

Fraction									
GPC	$\bar{M}_w$	1 202 000	833 000	507 000	419 000	360 000	Mixture[a]		
	T_m (°C)	49·8	49·7	49·4	49·7	49·7	49·4		
Ultrasonication	$\bar{M}_w$	638 000	259 000	232 000	212 000	119 000	68 000		
	T_m (°C)	49·4	49·2	49·3	48·7	48·7	46·8		
Hydrolysis	$\bar{M}_w$	581 000	380 000	338 000	113 000	92 000	58 000	31 700	6 560
	T_m (°C)	49·5	49·3	49·2	48[b]	48[b]	41[b]	44[b]	29[b]

[a] Blend of fraction $\bar{M}_w = 1{\cdot}2 \times 10^6$ (0·25 g/litre) and $\bar{M}_w = 1{\cdot}3 \times 10^5$ (0·25 g/litre).

[b] The transition is broad and the amplitude of the transition is lower than the amplitude of a classical transition. A consequence is poor precision in the determination of T_m.

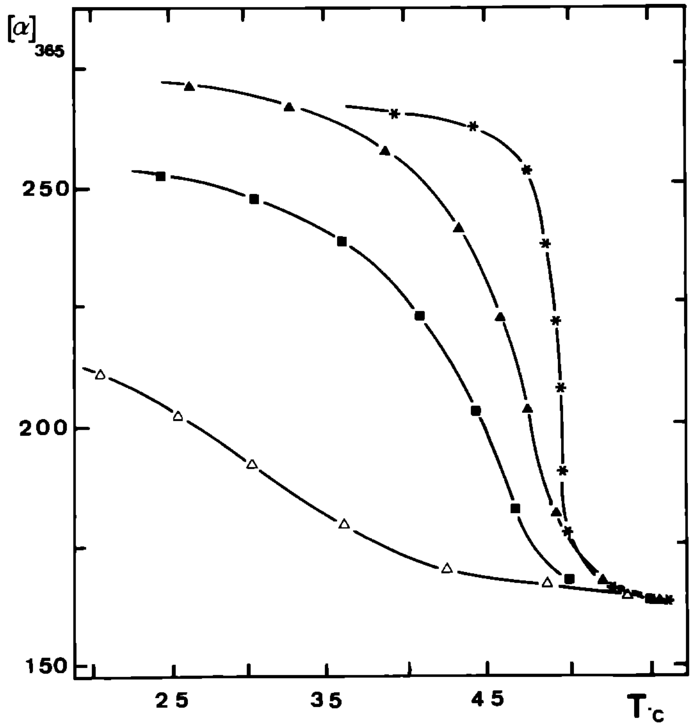

Fig. 3. Optical rotation temperature dependence (cooling, 25°C/h) of different hydrolyzed fractions of kappa carrageenan in 0·1 M KCl, $C_p = 0{\cdot}5$ g/litre, *, ▲, ■, △, fractions 10, 21, 22, 23 respectively.

approximation even if during the onset of the gelation a fraction of the polymer is in the stiffer helical conformation.

The yield stress presents a different correlation with the molecular weight (Fig. 6). We find a linear correlation between the yield stress and the molecular weight. This correlation is similar to the correlation postulated for polysaccharide gels in general by Mitchell (1980). It is not possible to detect a critical molecular weight M_c as can be done from the elastic modulus data. The yield stress continuously increases with molecular weight.

The dependence of the elastic modulus on the molecular weight at different salt concentrations (Fig. 5) obtained at a polymer concentration of 10 g/litre is consistent with the results found for sample 0 for a large concentration range, 2–50 g/litre (Rochas & Landry, 1988). The shape of the curves are similar to the curve obtained on Fig. 4 and it is also possible to obtain the same critical molecular weight M_c.

The dependence of the yield stress on molecular weight and salt concentration (Fig. 7) obtained at a polymer concentration of 10 g/litre

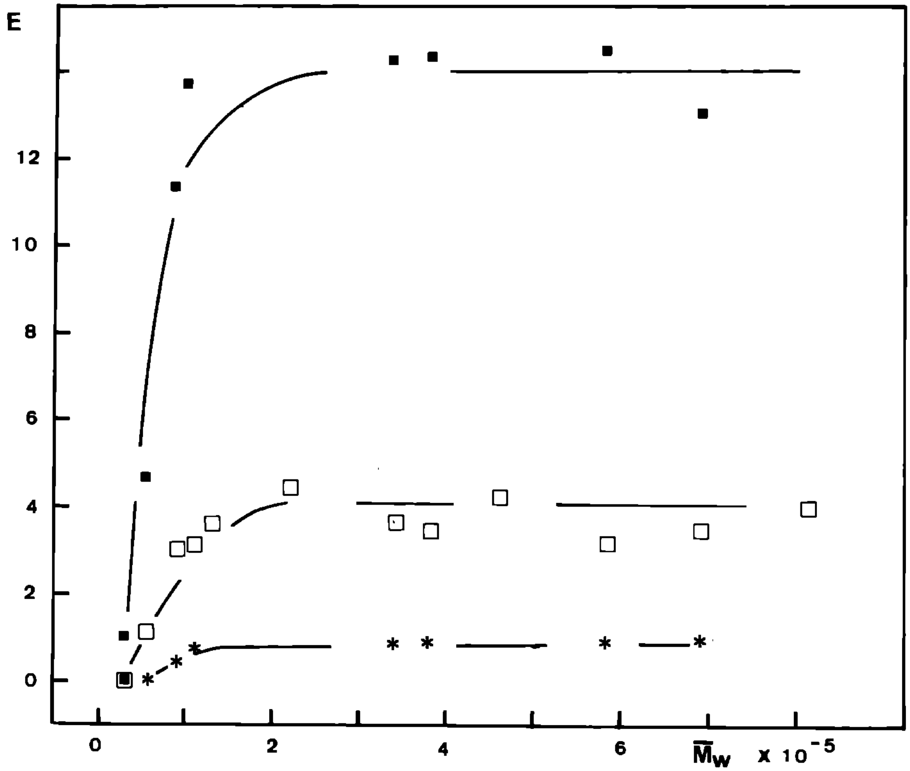

Fig. 4. Elastic modulus E (10^5 dyne/cm^2) versus molecular weight of different fractions of kappa carrageenan in 0·1 M KCl *, □, ■, polymer concentration 5, 10, 20 g/litre respectively.

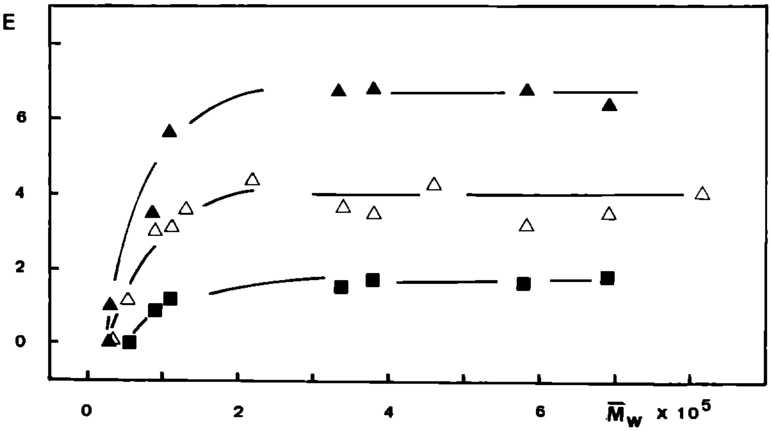

Fig. 5. Elastic modulus E (10^5 dyne/cm^2) versus molecular weight of different fractions of kappa carrageenan at a concentration of 10 g/litre with different salt concentration: ■, △, ▲ KCl concentration 0·05 M, 0·1 M, 0·5 M respectively.

is also consistent with the results obtained for sample 0 (Rochas & Landry, 1988). An almost linear correlation is obtained between the yield stress and the molecular weight over the critical value M_c (Fig. 7). While the elastic modulus is strongly dependent on salt concentration, the yield stress is independent of KCl concentration in the range 0·1–0·05 M (Fig. 8) as previously shown for the sample 0 over a large concentration range of polysaccharide (Rochas & Landry, 1988). The yield stress obtained at 0·5 KCl is lower. This is a consequence of the yield stress–salt dependence which shows a maximum near 0·05 M but the elastic modulus increases continuously with salt concentration.

CONCLUSIONS

Two parameters are required to characterize a gel: the elastic modulus and the yield stress, because these parameters give complementary

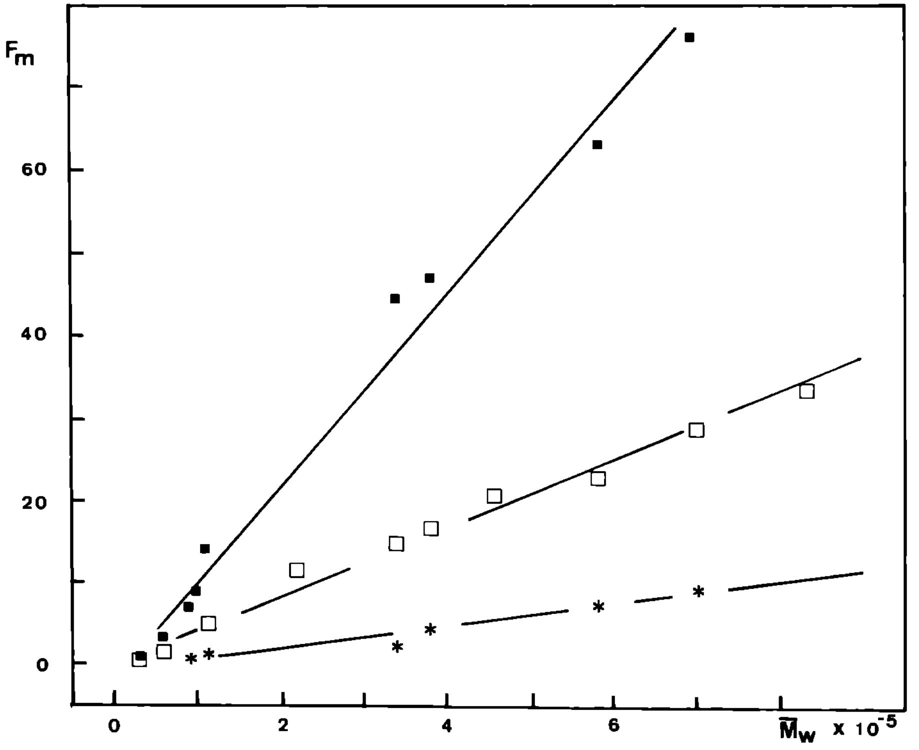

Fig. 6. Yield stress F_m(N) versus molecular weight of different fractions of kappa carrageenan in 0·1 M KCl, *, □, ■, polymer concentration 5, 10, 20 g/litre respectively.

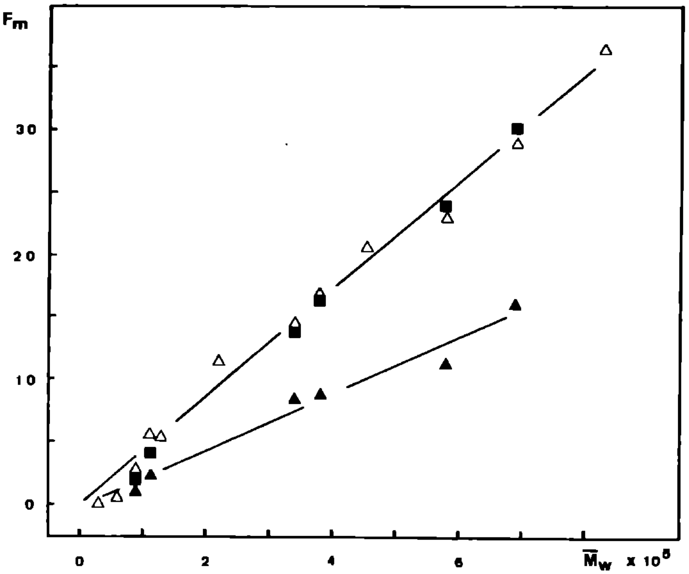

Fig. 7. Yield stress F_m(N) versus molecular weight of different fractions of kappa carrageenan at a concentration of 10 g/litre with different salt concentration: ■, △, ▲ KCl concentration 0·05 M, 0·1 M, 0·5 M respectively.

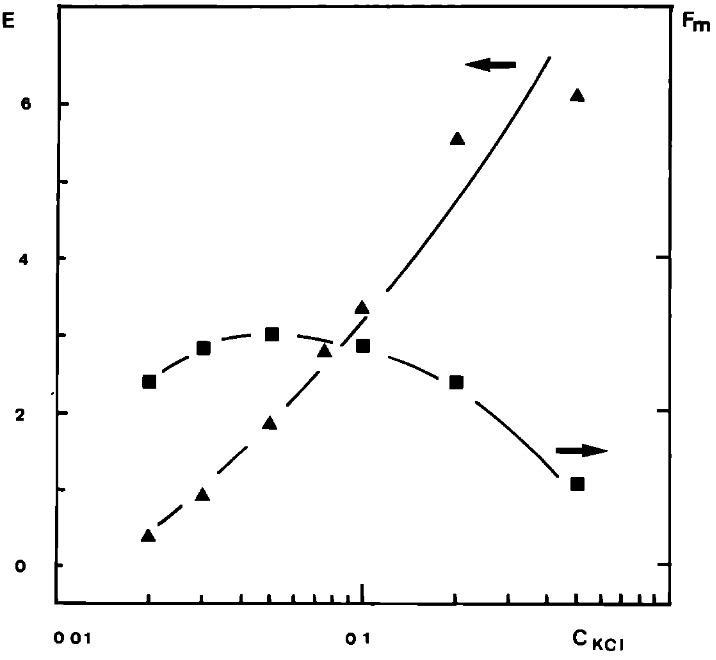

Fig. 8. Elastic modulus E (10^5 dyne/cm^2) and yield stress F_m(N) of fractions 0 of kappa carrageenan at a concentration of 10 g/litre with different KCl concentration.

information about the sample tested. The yield stress is directly proportional to the molecular weight but is not very sensitive to salt concentration. In contrast the elastic modulus is very sensitive to salt concentration and is not sensitive to the molecular weight above a critical molecular weight M_c of 180·000 for kappa carrageenan. It is obvious that more information is required to understand the meaning of the value of M_c and its possible relation to the mesh size of the gel.

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REFERENCES

Ainsworth, P. A. & Blanshard, J. M. V. (1980). Effect of thermal processing on structure and rheological properties of carrageenan carob gum gels. *J. Texture Studies*, **11**, 149–62.

Clark, A. H. & Ross-Murphy, S. B. (1987). Structural and mechanical properties of biopolymers gels. *Advances in Polymer Science*, **83**, 57–92.

Eliot, J. H. & Ganz, A. J. (1975). Gel characterization with the Weissenberg rheogoniometer: application to carrageenan gels. *J. Food Science*, **40**, 394–8.

Graessley, W. W. (1980). Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power. *Polymer*, **21**, 258–62.

Guiseley, K. B., Stanley, N. F. & Witehouse, P. A. (1980). Carrageenan. In *Handbook of water-soluble gums and resins*, ed. R. L. Davidson. McGraw-Hill, New York, p. 1.

Lecacheux, D., Panaras, R., Brigand, G. & Martin, G. (1985) Molecular weight distribution of carrageenan by size exclusion chromatography and low angle laser light scattering. *Carbohydr. Polym.*, **5**, 423–40.

Milas, M., Rinaudo, M. & Tinland, B. (1986). Comparative depolymerisation of xanthan gum by ultrasonic and enzymic treatments. Rheological and structural properties. *Carbohydr. Polym.*, **6**, 95–107.

Mitchell, J. R. (1976). Rheology of gels. *J. Texture Studies*, **7**, 313–39.

Mitchell, J. R. (1980). The rheology of gels. *J. Texture Studies*, **11**, 315–37.

Rees, D. A. (1969). Structure, conformation and mechanism in the formation of polysaccharide gels and networks. *Adv. Carbohydr. Chem.*, **24**, 267–32.

Rees, D. A., Morris, E. R., Thom, D. & Madden, S. K. (1982). Shapes and interactions of carbohydrate chains. In *The Polysaccharides*, ed. G. O. Aspinall. Academic Press, Orlando, Chapter 5, 195–290.

Rochas, C. & Rinaudo, M. (1984). Mechanism of gel formation in κ-carrageenan. *Biopolymers*, **23**, 735–45.

Rochas, C. & Landry, S. (1987). Molecular organization of kappa carrageenan in aqueous solution. *Carbohydr. Polym.*, **7**, 435–47.

Rochas, C. & Landry, S. (1988). Rheological characterization of kappa carrageenan gels. In *Gums and stabilisers for the food industry 4*, ed. G. O. Phillips, D. J. Wedlock & P. A. Williams. IRL Press, 445–51.

Smidsrod, O. & Haug, A. (1972). Properties of poly(1,4-hexuronates) in the gel state. *Acta Chem. Scand.*, **26**, 79–88.

Smidsrod, O. (1974). Molecular basis for some physical properties of alginates in the gel state. *Faraday Disc. Chem. Soc.*, **57**, 263–74.

Snoeren, T. H. M. (1976). Kappa-carrageenan. A study on its physicochemical properties, sol-gel transition and interaction with milk proteins. Thesis. Nederlands Instituut woor Zuivelonderzoek, Ede, Nederlands.