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The role of side-chains in the Cr^{3+}-induced gelation of xanthan and xylinan (acetan) variants

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The effect of the length and chemical composition of the side-chains in comb-like branched polysaccharides on gelation with trivalent metal ions has been studied using xanthan and xylinan (acetan) with intact and truncated side-chains.

Partial or complete removal of the terminal β-D-mannose, or removal of up to 22% of the trisaccharide side-chains of xanthan using partial acid hydrolysis, has only small effects on the Cr^{3+}-induced gelation. In contrast, replacement of β-D-mannose by the trisaccharide α-L-Rha*p*-(1 → 6)-β-D-Glc*p*-(1 → 6)-α-D-Glc*p*-(1 → 4)- to yield the polysaccharide xylinan totally inhibits the gelation with Cr^{3+} ions. Removal of the trisaccharide by partial acid hydrolysis, which leads to a series of polymers with structures converging towards the partially hydrolysed xanthans, restores the gelling ability with Cr^{3+} ions.

These observations seem to support the gelation model where Cr^{3+}–glucuronic acid interactions are involved in the cross-linking of chains. It is further suggested that this interaction can be suppressed due to steric hindrance caused by the bulky side-chains in xylinan.

INTRODUCTION

The polysaccharide xanthan (Fig. 1a) forms gels in the presence of trivalent cations such as Cr^{3+}, Fe^{3+} and Al^{3+} (Conway *et al.*, 1983; Menjivar, 1986; Hubbard *et al.*, 1986; Lund *et al.*, 1988; Nolte *et al.*, 1992). Cr^{3+}–xanthan gels have been studied in some detail due to their potential as profile modifiers in oil production (Menjivar, 1986; Hubbard *et al.*, 1986; Hejri *et al.*, 1989).

The mechanisms which lead to the formation of the Cr^{3+}-mediated polysaccharide network are apparently complex. The chromium ions form different oleates (oligomers) in aqueous solutions which may be involved in cross-linking the polysaccharide chains. From the observed pH optimum with respect to the elastic modulus it has been suggested that the dimer or higher oligomers of chromium are required for the cross-linking (Nolte *et al.*, 1992). Since chromium ions bind ligands containing carboxylate ions strongly it is generally assumed that the carboxylate groups of the glucuronic acid and pyruvate substituents are the main groups involved in the Cr^{3+}-xanthan cross-links (Shu, 1989). Otherwise, little is known about the role of the remaining components of xanthan in the gelation process. The aim of this work is therefore to investigate the role of the polysaccharide side-chains in the gelation by studying the gelation with Cr^{3+} of xanthan variants with modified (truncated) side-chains.

The xanthan variants used in this study are produced by partial acid hydrolysis. This method leads to preferential hydrolysis of the terminal β-D-mannose (in addition to rapid removal of pyruvate and acetate substituents) (Christensen & Smidsrød, 1991; Christensen *et al.*, 1993*a*). The inner α-D-mannose is hydrolysed about 10 times slower than the β-D-mannose, leading to removal of the entire side-chain, whereas the glucuronic acid is essentially resistant to hydrolysis. These modifications can be performed without changing the basic conformational properties in terms of the chiroptically defined order–disorder transition (Christensen *et al.*, 1993*b*). Moreover, the double-stranded nature of these xanthans prevent, to a large extent, fragmentation, i.e. reduction in the measured molecular weight, when linkages in the

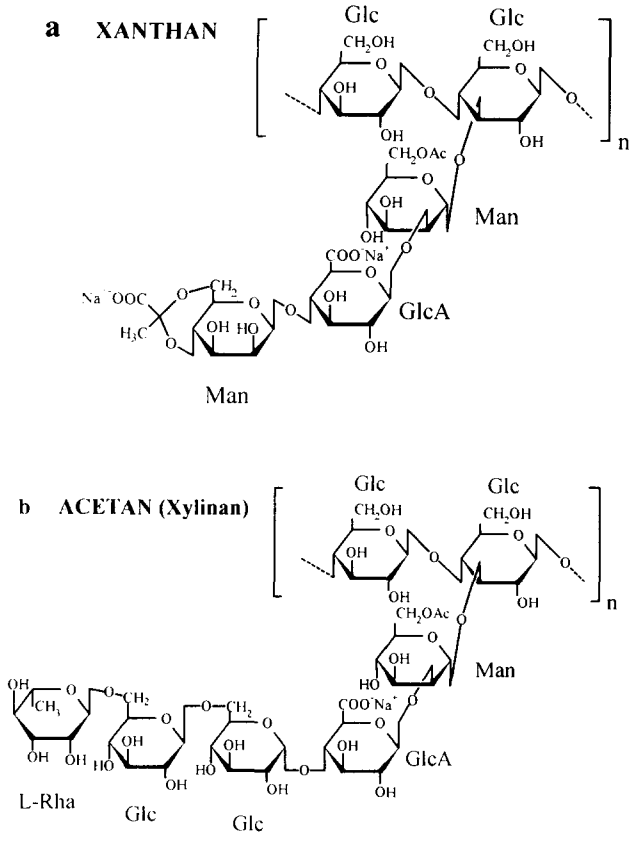

Fig. 1. Chemical structures of (a) xanthan and (b) xylinan (acetan, AM2) in their Na^+ salt form.

cellulosic backbone are hydrolysed (Stokke *et al.*, 1992). Therefore, high molecular weights are maintained when the side-chains are truncated. Typically, all of the terminal β-D-mannose may be removed while M_w is still in the region of 4×10^5 (Christensen *et al.*, 1993*a*, *c*). It should be noted that hydrolysis of sugars in the side-chains appears to follow first order kinetics with respect to the linkages involved. This will result in a statistical (random) distribution along the chains of both cellobiose residues containing side-chains and cellobiose residues without side-chains.

The hydrolysis of side-chain residues is of particular relevance when Cr–xanthan gels are used in subterranean formations in connection with oil recovery. Under slightly acidic conditions, hydrolysis will occur, particularly at elevated temperatures. For example, the half-life of the terminal β-D-mannose is approximately 1–2 weeks at 80°C and pH 3 (Christensen & Smidsrød, 1991). For long term use, hydrolysis in the side-chains must be considered. This work will therefore focus on the influence of such hydrolysis on the gel-forming properties. Further, gelation studies of samples varying in the content of glucuronic acid may provide information about the involvement of this residue in the proposed ligand exchange reaction, which is thought to be mechanistic for the gelation.

This study also includes gelation properties of partially hydrolysed xylinan. This polysaccharide, which is produced by strains of *Acetobacter xylinum* (Valla & Kjosbakken, 1981), is also named acetan (Couso *et al.*, 1987) or AM2 (Tayama *et al.*, 1985), and has the structure given in Fig. 1b (Jansson *et al.*, 1993). The chemical structure of xylinan differs from that of xanthan in that the terminal β-D-mannose is replaced by the trisaccharide α-L-Rha*p*-(1 → 6)-β-D-Glc*p*-(1 → 6)-α-D-Glc*p*-(1 → 4)-. Partial hydrolysis of xylinan (Christensen *et al.*, 1993*b*) leads to preferential hydrolysis of the trisaccharide in addition to the expected lability of the terminal α-L-rhamnose. The chemical structure of partially hydrolysed xylinans should therefore converge towards those of partially hydrolysed xanthans, and converging physical properties, including gelation with Cr^{3+}, are expected.

Table 1. Sample characteristics[a]

Sample	Hydrolysis 0·1 M HCl, 80°C (h)	M_w ($\times 10^{-6}$)	$f_{\beta\text{-Man}}$	f_{ABA}	f_{Rha}	f_{Gent}
Xan-3	3	2·9	0·92	0·99	—	—
Xan-3S (sonicated)	3	0·45	0·92	0·99	—	—
Xan-22	22	2·0	0·52	0·95	—	—
Xan-22S (sonicated)	22	0·53	0·52	0·95	—	—
Xan-62	62	0·97	0·16	0·86	—	—
Xan-100	100	0·51	0·05	0·78	—	—
Xan-100S (sonicated)	100	0·43	0·05	0·78	—	—
Xyl-0	0	2·8	—	1·00	1·00	1·00
Xyl-1	1	2·7	—	1·00	1·00	1·00
Xyl-24	24	1·2	—	0·9	0·11	0·4
Xyl-48	48	0·70	—	0·8	0·00	0·05
Xyl-72	72	0·47	—	0·8	0·00	0·00

[a] $f_{\beta\text{-Man}}$ = fraction of repeating units containing a terminal β-D-mannose; f_{ABA} = fraction of repeating units containing a side-chain (with or without a terminal β-D-mannose); f_{Rha} = fraction of repeating units containing a terminal α-L-rhamnose; f_{Gent} = fraction of repeating units containing a gentiobiose unit in side chain (with or without a terminal α-L-rhamnose).

EXPERIMENTAL

Materials

Partially hydrolysed xanthans and xylinans were obtained as described earlier (Christensen *et al.*, 1991, 1993*a*, *c*). Table 1 shows the chemical composition, intrinsic viscosity and molecular weight of the samples as determined previously (Christensen *et al.*, 1993*c*). Some of the samples were further depolymerized by ultrasonic treatment, and the molecular weights obtained were determined by HPLC combined with low angle laser light scattering earlier (Christensen *et al.*, 1993*a*).

Gelation studies

Solutions of polysaccharide (0·5–2·5 mg/ml in 0·1 M NaCl) were thoroughly mixed with 2–5 mM $Cr(NO_3)_3$ and transferred to a Bohlin VOR rheometer where the gelation was monitored at 30°C.

The measurements were carried out using parallel plate geometry. The sample was sealed under a low density, low viscosity silicon oil to minimize potential problems with solvent evaporation during gelation. Gelation was monitored by repeatedly measuring the loss (G'') and storage (G') moduli at selected frequencies with intervals of 5 or 10 min. The oscillation amplitude was in the linear viscoelastic response at the start of the experiment.

RESULTS AND DISCUSSION

Table 1 gives the chemical composition and molecular weights of the partially hydrolysed xanthans and xylinans samples studied here. Some of the samples were further depolymerized by sonication.

Figure 2 shows the time dependence of the storage modulus (G') for samples Xan-22, Xan-62 and Xan-100, obtained at constant polymer concentration (2 mg/ml) and Cr^{3+} concentration (0·8 mM). Gel formation, characterized by an increase in G' of 3–4 orders of magnitude during the first 24 h, is observed for all three samples. The G' values obtained (100–300 Pa after 24 h) are somewhat higher than the values reported for unhydrolysed xanthans under similar conditions (Nolte *et al.*, 1992). Xan-100 gives slightly lower G' values (factor 2–7) than the other two, which are practically indistinguishable. The data alone suggest that the removal of the β-D-mannose and the corresponding reduction in molecular weight (factor of about 5) has a very small effect on the gel formation with Cr^{3+} within the range Cr^{3+} and polymer concentrations studied here.

The frequency dependence of G' and G'', determined 24 h after the addition of Cr^{3+} (Fig. 2), is shown in Fig. 3. Both G' and G'' are essentially independent of the frequency. Furthermore, G' is 7–40 times larger than G''. Both features correspond closely to data obtained earlier with unmodified xanthans (Lund *et al.*, 1988).

Depolymerization of Xan-3 by ultrasonic irradiation

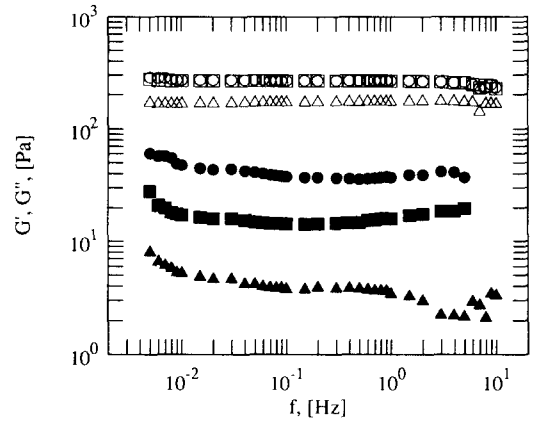

Fig. 3. Frequency dependence of G' (open symbols) and G'' (filled symbols) for partially hydrolysed xanthans Xan-22 (○ ●), Xan-62 (□ ■) and Xan-100 (△ ▲), obtained after 24 h of gelation at c_p = 2 mg/ml and $[Cr^{3+}]$ = 0·8 mM.

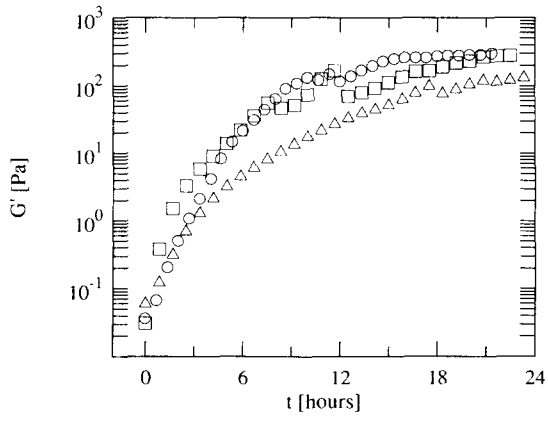

Fig. 2. Time dependence of the storage modulus (G') for partially hydrolysed xanthans Xan-22 (○), Xan-62 (□) and Xan-100 (△), obtained at constant concentration of polymer (c_p = 2 mg.ml) and chromium ions ($[Cr^{3+}]$ = 0·8 mM).

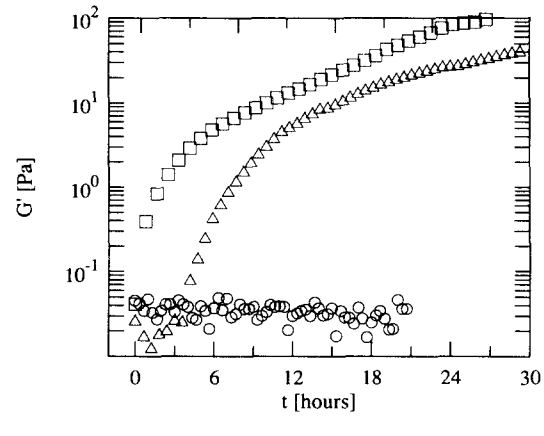

Fig. 4. Time dependence of the storage modulus (G') for partially hydrolysed xanthans Xan-3 (0·67 mg/ml, $[Cr^{3+}]$ = 0·5 mM) (□); Xan-3S (1·6 mg/ml, $[Cr^{3+}]$ = 0·5 mM) (○); Xan-3S (2·7 mg/ml, $[Cr^{3+}]$ = 1·7 mM) (△).

(resulting in sample Xan-3S) showed that the gelation is much more strongly influenced by molecular weight reduction than by removing side-chain residues. This is illustrated by Fig. 4. Xan-3 shows the expected gel formation at a polymer concentration of 0·67 mg/ml and a Cr^{3+} concentration of 0·5 mM. In contrast, the sonicated Xan-3S shows no increase in G' in the presence of 0·5 mM Cr^{3+}, even though the polymer concentration (1·6 mg/ml) had been increased. This is attributed to an increase in the critical overlap concentration (c^*, reported to be $c = 0{\cdot}7\text{–}1{\cdot}4/[\eta]$, where $[\eta]$ is the intrinsic viscosity), accompanying the depolymerization. In this case c^* (estimated to be 0·4 and 2 mg/ml for Xan-3 and Xan-3S, respectively) exceeds the actual polymer concentration, and gelation does not take place at a measurable rate. It has previously been shown that the gelation rate of xanthan with Cr^{3+} is substantially reduced when the polymer concentration is approaching c^* (Nolte *et al.*, 1992). In line with this explanation, a further increase in both the polymer concentration (2·7 mg/ml) and the Cr^{3+} concentration (1·7 mM) allows gel formation of Xan-3S (Fig. 4).

Figure 5 shows the effect of the Cr^{3+} concentration on the rate of gelation, defined as $\Delta G'/\Delta t$, for samples Xan-3 to Xan-100. As with unhydrolysed xanthans, a strong dependence on the Cr^{3+} concentration is generally observed. Despite some scatter in the data, the influence of the degree of hydrolysis in the side-chains is generally small. The data also suggest that extrapolation of the gelation rate to zero yields a critical Cr^{3+} concentration of 0·37 mM needed necessary for gelation.

Gelation data for partially hydrolysed xylinans (2·0 mg/ml) in the presence of Cr^{3+} (1·7 mM) are shown in Fig. 6. In contrast of xanthan, unhydrolysed xylinan does not form gels with Cr^{3+}, as illustrated by a low and constant value of G'. However, partial hydrolysis induces gelling ability, although the G' values obtained are somewhat lower than for the partially hydrolysed xanthans. According to Fig. 6 a maximum gel forming ability is obtained for sample Xyl-48. The decrease in gelling ability upon further hydrolysis is attributed to

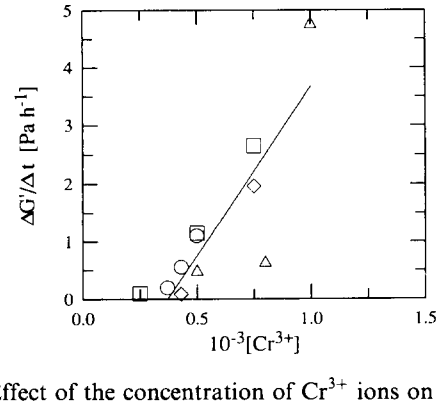

Fig. 5. Effect of the concentration of Cr^{3+} ions on the rate of gelation ($\Delta G'/\Delta t$), for samples Xan-3 (○), Xan-22 (◇), Xan-62 (□) and Xan-100 (△).

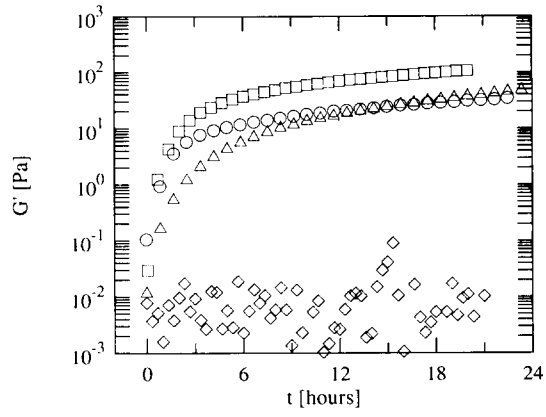

Fig. 6. Time dependence of the storage modulus (G') for partially hydrolysed xylinans Xyl-0 (◇), Xyl-24 (△), Xyl-48 (□) and Xyl-72 (○), obtained at constant concentration of polymer ($c_p = 2{\cdot}0$ mg/ml) and chromium ions ($[Cr^{3+}] = 1{\cdot}7$ mM).

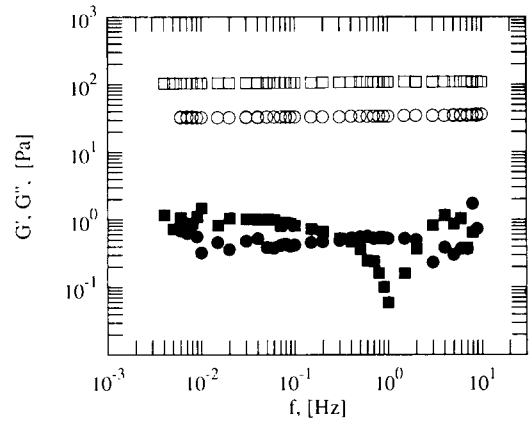

Fig. 7. Frequency dependence of G' (open symbols) and G'' (filled symbols) for gels obtained with partially hydrolysed xylinans Xyl-48 (□ ■) and Xyl-72 (○ ●).

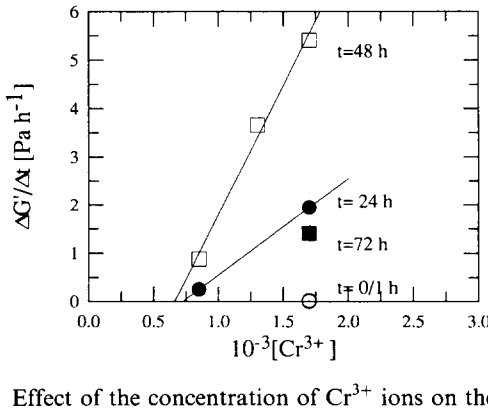

Fig. 8. Effect of the concentration of Cr^{3+} ions on the rate of gelation ($\Delta G'/\Delta t$) for partially hydrolysed xylinans Xyl-0 (○), Xyl-24 (●), Xyl-48 (□) and Xyl-72 (■).

the effects caused by the reduction in M_w, corresponding to that also seen for the sonicated xanthans (Fig. 4).

The frequency dependence of G' and G'' for gels obtained with samples Xyl-48 and Xyl-72 are shown in

Fig. 7. These gel characteristics correspond closely to those obtained with partially hydrolysed xanthans, except that the G' values are somewhat lower.

Finally, some data on the rate of gelation as a function of the Cr^{3+} concentration for the partially hydrolysed xylinans are shown in Fig. 8. The figure demonstrates that the gelation rate increases from zero for unmodified xylinan to a maximum for sample Xyl-48. Compared to the partially hydrolysed xanthans, the curves are shifted towards somewhat higher Cr^{3+} concentrations, with zero gelation rates below Cr^{3+} concentrations of 0·5–0·7 mM.

It should be noted that the gelation results presented here are all obtained with the xanthan and xylinan variants in their chiroptically detected ordered conformations (Christensen *et al.*, 1993*b*), and that the role of the conformational state on the gelation properties remains unknown so far.

CONCLUSIONS

Partial hydrolysis of the terminal β-D-mannose of the side-chains in xanthan has almost no effect on the gelation ability with Cr^{3+} ions. Only when the hydrolysis proceeds to give low molecular weights and thus increases c^* above the actual polymer concentration is the ability to form gels affected. In contrast, a longer side-chain such as that found in xylinan totally inhibits gelation. However, partial acid hydrolysis, which leads to removal of the outer trisaccharide yielding polymers similar to the partially hydrolysed xanthans, also restores the gelling ability. This indicates that the structure of the side-chains indeed influences the interaction with Cr^{3+} ions. One tentative explanation may be that the terminal trisaccharide of xylinan sterically prevents the formation of a Cr^{3+}-induced cross-link involving the glucuronic acid residues in two different polysaccharide chains.

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