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Carboxylation of scleroglucan for controlled crosslinking by heavy metal ions

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Samples of carboxylated scleroglucan, sclerox, with a degree of carboxylation in the side-chains varying from 10 to 50% were made in order to investigate the potential of using carboxylation as a means to control subsequent gelation by heavy metal ions. The storage and loss moduli of aqueous solutions of sclerox samples as a function of time were determined at $T = 20°C$ and 30°C after addition of trivalent chromium ions. The rheological characterization showed a transition from a viscoelastic liquid to a gel with a characteristic time depending on the chromium concentration and the degree of carboxylation. For 20% carboxylation, the rate of change in the storage modulus could be controlled within nearly three orders of magnitude from 10^{-3} to 1 Pa min^{-1}, using total chromium concentrations ranging from 0·3 to 6 mM. This rate was decreased by a factor of 2–5 by reducing the degree of carboxylation to 10%. The present study indicates that carboxylation of scleroglucan can be used to control the rate of gelation mediated by heavy metal ion complexation. This finding suggests that extension of the application range of this polysaccharide from an efficient viscosifer for polymer flooding to profile modification of high temperature oil reservoirs is attainable.

INTRODUCTION

Polymer gel technology based on ionic crosslinking of polymers, in particular the bacterial polysaccharide xanthan and synthetic partially hydrolysed polyacrylamides, has recently attracted attention for oil-field applications (Conway *et al.*, 1983; Menjivar, 1986; Hubbard *et al.*, 1986; Moradi-Araghi *et al.*, 1988; Lockhart *et al.*, 1991). Aqueous polymer gels are considered both for near wellbore treatments and placement deeper in the reservoir formation. The function of a properly placed polymer gel is to modify the permeability profile of heterogeneous reservoirs and thereby divert subsequently injected fluids away from the thief-zones. Ideally, this would lead to sweeping of previously unswept, originally low-permeable regions and thereby increase the efficiency of the oil recovery process. Placement of the gel in the most permeable zones is to a large extent governed by the rheological properties of the injected gellable polymer solution. Other requirements to the polymer-crosslinker system may include the ability to control the gelation rate over a wide range, good filterability, and long term mechanical and conformational stability.

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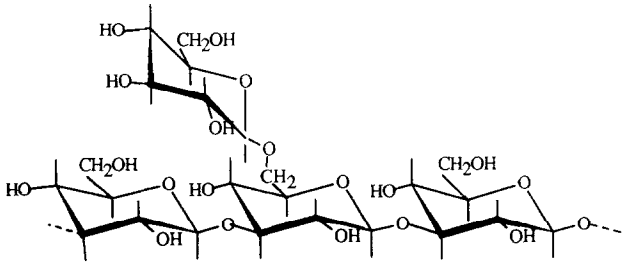
The temperature or temperature profile during the polymer gelation in the oil reservoir must be taken into account when designing a particular field application. Control of the gelation time can be achieved by controlling the concentration ratios between the crosslinking ions and polymer (Lund *et al.*, 1988; Nolte *et al.*, 1992), or by using a ligand that competes for the active crosslinking site on the polymer (Lockhart, 1991). The combination of chromium with acetate, which contains the same carboxylate functionality as the polymer, e.g. glucuronic acid in xanthan, and aluminium with citrate, are the two most commonly employed metal–ion–ligand systems. The gelation was found to be even more delayed when the competing ligand in the chromium induced crosslinking was changed from acetate to other ligands such as glycolate or malonate (Ahmed & Moradi-Araghi, 1994). In this study, an alternative method for controlling the number of crosslinking sites on the polymer and thus the gelation rate, will be illustrated using scleroglucan as an example. Controlling the number of carboxylic groups on a naturally occurring polysaccharide such as xanthan is not straightforward, but a certain decrease in the number of these groups can be invoked by acid hydrolysis while retaining a relatively high molecular weight (Christensen & Smidsrød, 1991; Christensen *et al.*, 1993, 1994).

Although the charge density of the glucuronic acid to a large extent can be controlled by altering the pH in solution, this is not a viable route when crosslinking using trivalent metal ions is of interest. This is because the metal ions like Cr(III) and Al(III), depending on pH, form different olates with different crosslinking efficiencies (Baes & Mesmer, 1976; Stunzi *et al.*, 1989). Because the relative fraction of olates depends strongly on pH, independent control of the glucuronic acid charge and the state of the metal ion crosslinker is not possible.

Native scleroglucan does not possess carboxylic groups (Fig. 1, I), and does, therefore, not form gels in the presence of Cr(III). Crescenzi and coworkers (1983) and Gamini *et al.* (1984) report on quantitative carboxylation of scleroglucan by first employing a periodate oxidation step, which due to the periodate resistant β1,3-linked residues in the main chain leads to selective oxidation, and hence, introduction of aldehyde groups in the side-chains. The second oxidation step using chlorite in acidic environment introduces two carboxylate groups for each converted side-chain residue (Fig. 1, II). It is important to realise that the reaction is considered to be nearly quantitative. The latter implies that scleroglucan samples with different degrees of carboxylation can readily be produced. In this study, carboxylated scleroglucans (named sclerox (Crescenzi *et al.*, 1983)) with degrees of carboxylation from 10 to 50% were made. These samples were subsequently used to study how the degree of carboxylation affects the gelation behaviour when trivalent metal ions are added to the aqueous polymer solutions.



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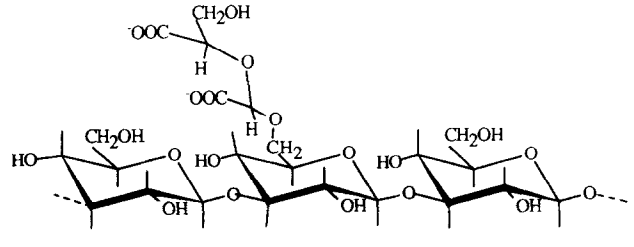

II

Fig. 1. The repeating unit of unmodified scleroglucan and carboxylated scleroglucan.

MATERIALS AND METHODS

Carboxylation of scleroglucan

750 mg of powdered scleroglucan (CS11, kindly provided by Sanofi), was added to 750 ml of Milli-Q (MQ)-water and stirred overnight. To four aliquots, each 120 ml, was added 13·3 ml n-propanol. The first oxidation step was carried out by adding 0·31, 0·62, 1·23 and 3·1 ml, respectively, of 30 mM $NaIO_4$ stock solution. The reaction proceeded in darkness for 24 h at room temperature. The four solutions were then dialysed excessively against MQ-water, and subsequently transferred to 250 ml flasks. The second oxidation step was carried out under acidic conditions by adding acetic acid to a final concentration of 0·5 M and solid $NaClO_2$ to a final concentration of 0·5 M (in a hood). The samples were then left in the dark overnight at room temperature. Each solution was subsequently adjusted to pH 6–7 by addition of NaOH, and dialysed against MQ water until they were free from chlorine. The polysaccharide concentration was determined using a colorimetric assay (Dubois *et al.*, 1956). The solution was concentrated to a final polymer concentration of 10 mg/ml under low pressure using a Rotavapor®. These samples will be referred to as sclerox-0.*X* where *X* depicts the degree of carboxylation. Analogous carboxylations were also carried out on scleroglucan obtained from a fermentation broth (kindly provided by Statoil Biosentrum).

Characterization of carboxylated scleroglucans

The degree of carboxylation was determined by measuring the amount of Mg^{2+} ions bound as counterions to carboxylic groups of the polymers. Aliquots of 4 ml (1·5 mg/ml) were first dialysed against 2 × 50 ml of 0·2 M $MgCl_2$, subsequently against 3 × 50 ml MQ-H_2O, and 3 × 20 ml 0·2 M HCl. The Mg content in the three solutions of 0·2 M HCl were determined by atomic absorption employing a Perkin Elmer 560 Atom Absorption spectrometer equipped with a Ca–Mg Intesitron lamp.

Intrinsic viscosities were determined using four or five concentrations of the sample in a low shear Cartesian Diver viscometer (Troll *et al.*, 1980) operated at 20°C, and using rotation times of the diver corresponding to average shear rates from 1 to 20 s^{-1}.

The sclerox samples were visualized by electron microscopy employing the vacuum-drying of aqueous glycerol solution–heavy metal replication preparation procedure (Tyler & Branton, 1980). Chain stiffness of the visualized polysaccharides were determined based on the decay of directional correlation, analysed by equations valid for two-dimensional chain statistics and subsequently corrected for apparent sampling dimensionality $D_{app} = 2{\cdot}6 \pm 0{\cdot}2$ as described (Stokke & Brant, 1990).

Gelation of carboxylated scleroglucans

Solutions of sclerox (10 mg/ml in MQ-water) were thoroughly mixed with aliquots of 1–10 mM $Cr(NO_3)_3$ and rapidly transferred to the sample stage of a Bohlin VOR rheometer. A serrated, parallel plate geometry with diameter 25 mm and set at a gap distance of 0·8–0·9 mm was used. The sample was sealed employing a low density, low viscosity silicon oil to minimize potential problems associated with evaporation of the solvent during the gelation experiment. Gelation was determined by measuring the storage (G') and loss (G'') moduli at intervals of 5 or 10 min using one selected frequency and temperature.

RESULTS AND DISCUSSION

Table 1 shows the experimentally determined degree of carboxylation of the sclerox samples compared with what is expected from the amount of $NaIO_4$ used in the first oxidation step and assuming full conversion. The data showed good agreement between the experimental data and that expected from the amount of periodate used. The rather small deviation between the experimental result from Mg^{2+} binding and that calculated from periodate consumption for the unsubstituted sample could arise from methodological limitations, in particular nonspecific binding of Mg^{2+} to the dialysis tubing and not to the polysaccharide. Sclerox-0·1, sclerox-0·2 and sclerox-0·5 depict the 10, 20 and 50% carboxylated samples, respectively (Table 1).

Table 1. Characterization of carboxylated scleroglucans

Sample	Degree of carboxylation	
	Calculated from $NaIO_4$ concentration	Determined from binding of Mg^{2+}
Sclerox-0	0	0·045
Sclerox-0·1	0·1	0·122
Sclerox-0·2	0·2	0·172
Sclerox-0·5	0·5	0·50

The electron micrographs of sclerox-0·1 (Fig. 2a) and sclerox-0·5 (Fig. 2b) show polymer chain trajectories characteristic of high molecular weight polydisperse, and rather stiff polysaccharides. The persistence length of sclerox-0·5 was determined from the electron micrographs as 62 ± 10 nm. This value is corrected for apparent sampling dimensionality of $2{\cdot}6 \pm 0{\cdot}2$ in the electron micrographs (Stokke & Brant, 1990). Comparison with the previously reported electron micrographs of the unmodified scleroglucan and the numerical values of the persistance length (Stokke & Brant, 1990) suggests that sclerox-0·5 is more flexible than the unmodified scleroglucan.

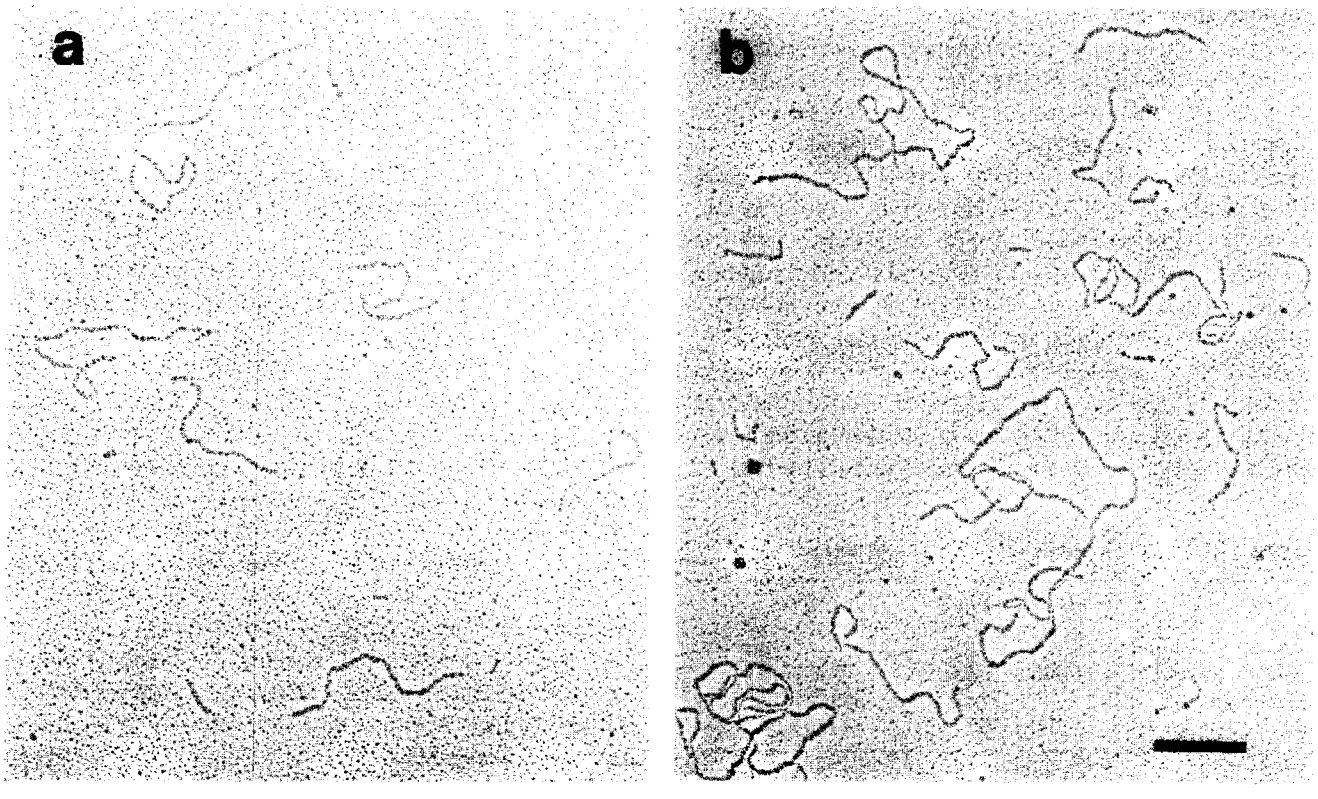

Fig. 2. Electron micrographs of (a) sclerox-0·1; (b) sclerox-0·5. Preparation started from 10 μg/ml polysaccharide in 0·1 M NH_4Ac in 50% w/v of aq. glycerol, pH = 6·5. Scale bar = 200 nm.

The experimentally determined values of the intrinsic viscosity, $[\eta]$, reveal that the introduction of carboxylic groups in scleroglucan makes the molecule sensitive to the ionic strength, I, of the solution, as is expected for a polyelectrolyte. The experimentally determined chain expansion of the sclerox-0·5 sample as a result of lowered ionic strength was further used to estimate the chain stiffness employing Smidsrød and Haug's (1971) B-parameter. This parameter equals $S/[\eta]_{I=0.1}^{1.3}$, where $S = [\eta]/\Delta I^{-0.5} = 2{\cdot}0$, and $[\eta]_{I=0.1}$ is the intrinsic viscosity at an ionic strength I of 0·1 M. The numerical values require that the units of $[\eta]$ are in dl g^{-1}. For the sclerox-0·5, B is determined to be 0·017, which suggests that the persistence length is about 61 nm using the relation $BL_{pe} = 1{\cdot}04$ (Morris & Ross-Murphy, 1981) when the persistence length, L_{pe}, is given in nanometres, and B as specified. This is consistent with that determined from the micrographs and less than the values of 120–200 nm estimated from hydrodynamic data of the unmodified scleroglucan in aqueous solution (Yanaki *et al.*, 1981; Carriere *et al.*, 1985).

The experimentally determined $[\eta]$ of sclerox-0·5 (Table 2) is reduced with about 37% in distilled water and 70% in synthetic seawater compared to the unmodified scleroglucan. At least part of this reduction can be attributed to the reduced persistence length, but chain depolymerization during the carboxylation cannot be excluded. The important point in this respect is that it is possible to carry out the carboxylation of scleroglucan and obtain high molecular weight samples for subsequent ionic crosslinking.

Figure 3 shows the experimentally determined time dependence of storage modulus G' (a) and phase angle $\delta = \arctan(G''/G')$ (b) at $T = 20°C$ for sample sclerox-0·2 at a concentration of 3 mg/ml and using Cr^{3+} concentrations from 0·35 to 4·9 mM. The rate of gelation depends strongly on the chromium concentration. For a Cr^{3+} concentration of 0·35 mM, there is only a very small increase in G' (0·1 Hz) and a corresponding decrease in δ from 20° to 10° within the first 24 h after addition of chromium to the aqueous solution of sclerox-0·2. Increasing the chromium concentration increases the gelation rate significantly and for 4·9 mM Cr^{3+}, the average rate of change of the storage modulus, $\Delta G'/\Delta t$, during the first 5 h is found to be 10·6 Pa h^{-1}.

Table 2. Intrinsic viscosities[a] of scleroglucan and sclerox-0·5

Solvent	$[\eta]$ of scleroglucan CS11 ml/g	$[\eta]$ of sclerox-0·5 ml/g
Synthetic sweater[b]	11,900 ± 1500	3650 ± 200
0·03 M NaCl		4600 ± 300
H_2O	12,200 ± 500	7800 ± 1400

[a] Determined at $T = 20°C$, shear rate 2 s^{-1} in a Cartesian diver viscometer.
[b] Composition of synthetic sweater given by Stokke *et al.* (1992), ionic strength $I = 0{\cdot}72$ M.

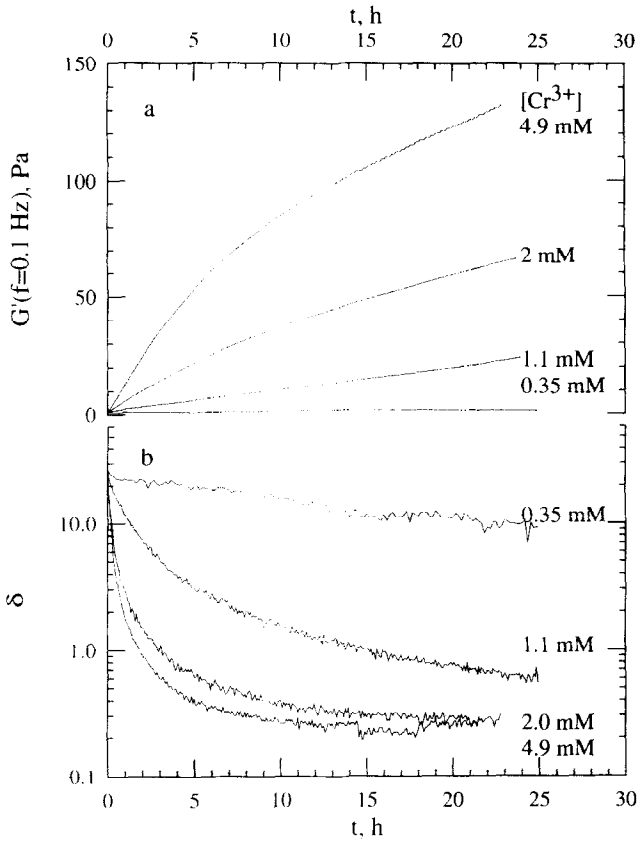

Fig. 3. (a) Time dependence of the storage modulus G' (0.1 Hz); and (b) phase angle $\delta = \arctan(G''/G')$ at $T = 20°C$ for 3 mg/ml sclerox-0·2 in 0·35, 1·1, 2·0 and 4·9 mM $Cr(NO_3)_3$.

The initial increase is fast and the time needed for the initial increase of 10 Pa in G', $t_{\Delta G'=10\,Pa}$, is only 45 min.

The kinetic parameters for the gelation reaction, $\Delta G'/\Delta t$, and the inverse of the time needed to yield the initial 10 Pa increase in G', $1/t_{\Delta G'=10\,Pa}$, is reported for Cr-crosslinking of the sclerox samples because it is important to distinguish between the two approaches when estimating activation energies is of interest (Nolte *et al.*, 1992). Figure 4 shows the effect of Cr^{3+} concentration on the kinetic parameters $\Delta G'/\Delta t$ (a) and $1/t_{\Delta G'=10\,Pa}$ (b) at $T = 20°C$ for chromium induced crosslinking of sclerox-0·2 at polymer concentrations of 1·7, 3·0 and 4·5 mg/ml. The parameter $\Delta G'/\Delta t$ shows a strong dependence on the chromium concentration, and fitting a power law to the experimental data, $\Delta G'/\Delta t = K\{[Cr^{3+}]/mM\}^{\alpha}$, yields coefficients $\alpha = 2{\cdot}3$, 2·3 and 2·2 for polymer concentrations 1·7, 3·0 and 4·7 mg/ml, respectively. Changing the polymer concentration appears mainly to affect the value of the front factor K in the power law of $\Delta G'/\Delta t$ vs $[Cr^{3+}]$, and not the coefficient α (Fig. 4a).

The inverse of the time needed for the initial 10 Pa increase in G', shows likewise a strong dependence on the chromium concentration (Fig. 4b). The parameters β in

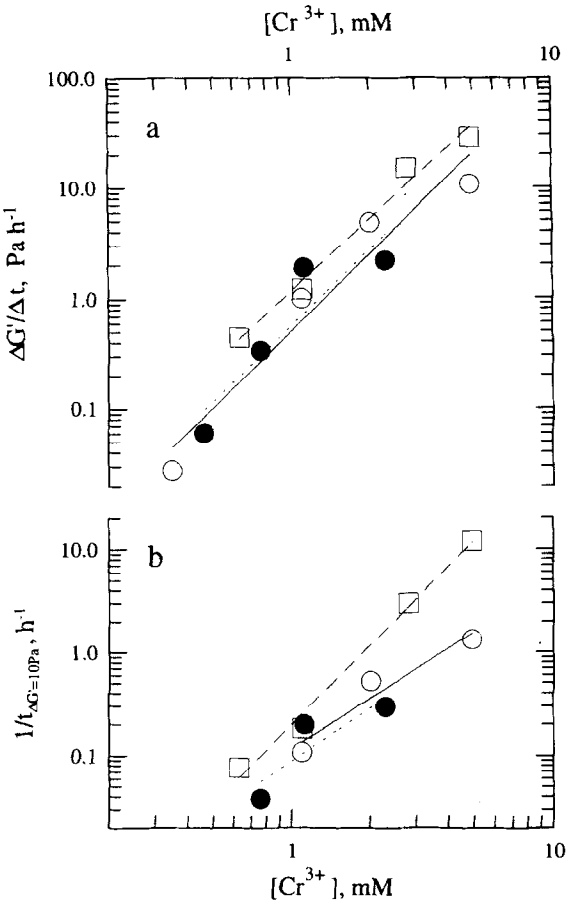

Fig. 4. (a) Average increase of the storage modulus during the first 5 h, $\Delta G'/\Delta t$; and (b) $T = 20°C$ vs $[Cr^{3+}]$ for chromium induced crosslinking of sclerox-0·2 at concentrations of 1·7 (●, – – –), 3·0 (○, ——) and 4·5 mg/ml (□, — — —). The lines depict least square fits of a power law.

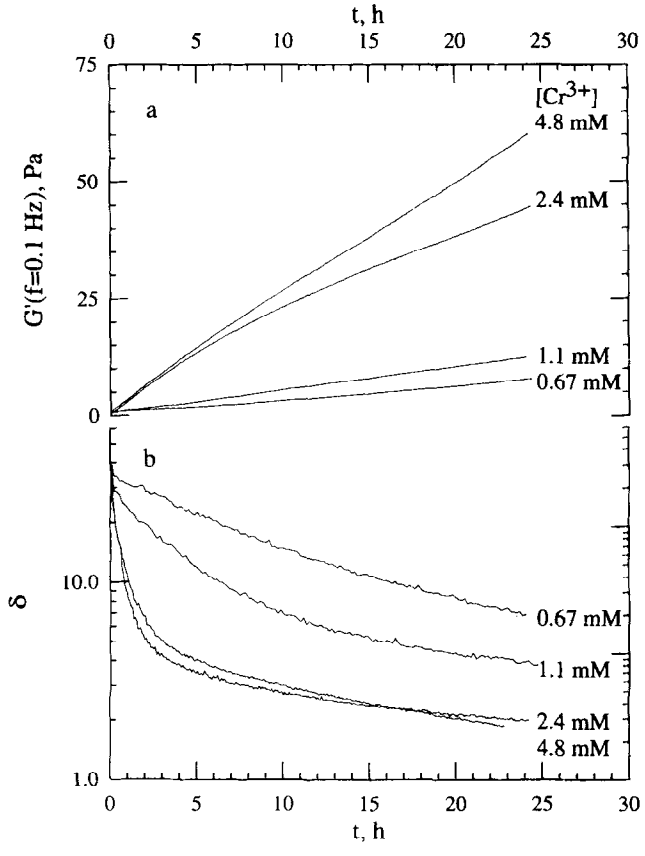

Fig. 5. (a) Time dependence of the storage modulus G' (0·1 Hz); (b) phase angle $\delta = \arctan(G''/G')$ at $T = 20°C$ for 4·7 mg/ml sclerox-0·1 in 0·67, 1·1, 2·4 and 4·8 mM $Cr(NO_3)_3$.

the power law $t_{\Delta G'=10\,Pa} = K_2\{[Cr^{3+}]/mM\}^{-\beta}$, are observed to be 1·7, 1·6 and 2·6 for the concentrations 1·7, 3·0 and 4·7 mg/ml of sclerox-0·2, respectively. The relative uncertainties in the numerical values of β are larger than in α for polymer concentrations of 1·7 and 3·0 mg/ml because G' did not increase by 10 Pa within the 24 h duration of the gelation experiments for the lowest concentration of chromium. Chromium(III) induced gelation of xanthan is reported to yield a coefficient $\alpha = 2·7 \pm 0·2$ (Nolte *et al.*, 1992), and 2·7 for hydrolysed polyacrylamide (HPAM) crosslinked with Cr(VI) (Prud'homme *et al.*, 1983). The present finding of the average of the α and β being close to 2 is consistent with the experimental data for xanthan and HPAM indicating that the crosslinking in the carboxylated scleroglucans is analogous to that of these two polymers.

Changing the degree of carboxylation of scleroglucan influences the kinetics of gelation. Figure 5 shows the experimentally determined time dependence G' (a) and δ (b) at $T = 20°C$ for solutions containing 4·7 mg/ml sclerox-0·1 and Cr^{3+} concentrations from 0·67 to 4·8 mM. The rate of gelation depends strongly on the chromium concentration as found above for the sclerox-0·2 sample (Fig. 3a). The observed increase in the storage modulus $\Delta G'/\Delta t$ changes from 0·18 Pa h^{-1} at a chromium concentration of 0·67 mM to 2·8 Pa h^{-1} at 4·8 mM Cr^{3+}. These results for the sclerox-0·1 sample are significantly lower than for the sclerox-0·2 sample at comparable Cr^{3+} concentrations. This shows that the kinetics of Cr^{3+} induced gelation can be controlled by altering the degree of carboxylation.

The concentration of chromium influences the kinetics of gelation for sclerox-0·1 (Fig. 6) analogously to what was found for sclerox-0·2. The determined values of coefficients α and β for sclerox-0·1 at $T = 20°C$ are 1·48 and 1·16, respectively. These results are lower than the values found for the sclerox-0·2 sample. The reason for this is unknown, but it appears very unlikely that different degrees of carboxylation should affect the mode of crosslinking with chromium ions. It is noted, however, that there is an unexpectedly small difference in the gelation kinetics between the samples at 2·4 and 4·8 mM Cr^{3+}, and omitting the latter chromium concentration in the estimation of α and β yields an increase in these parameters. Figure 6 shows furthermore that increasing the temperature yields an increased gelation rate, whereas the effect of chromium concentration can be described by a power law dependence

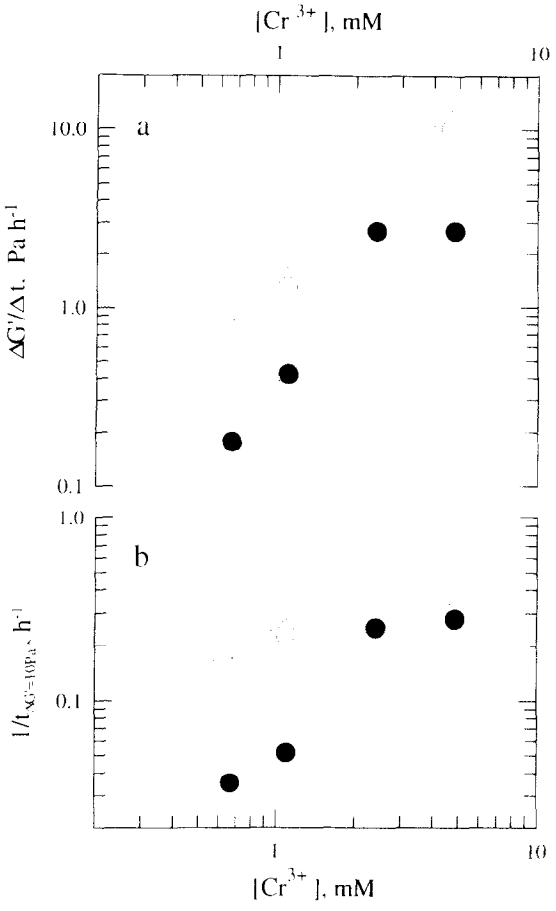

Fig. 6. (a) The average increase of the storage modulus during the first 5 h, $\Delta G'/\Delta t$; and (b) inverse of time needed to get the initial 10 Pa increase in the storage modulus $1/t_{\Delta G'\ 10\,Pa}$ vs $[Cr^{3+}]$ for chromium induced crosslinking of 4·7 mg/ml sclerox-0·1 at $T = 20$°C (●, - - -) and $T = 30$°C (○, ——). The lines depict least square fit of a power law.

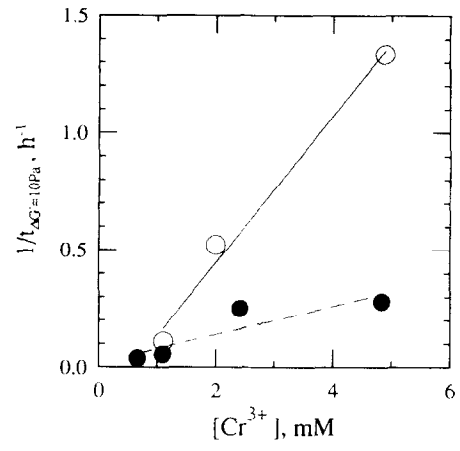

Fig. 7. The inverse of time needed for the initial 10 Pa increase in the storage modulus $1/t_{\Delta G'=10\,Pa}$ vs $[Cr^{3+}]$ for chromium induced crosslinking of 4·7 mg/ml sclerox-0·1 at $T = 20$°C (●, - - -), 3·0 mg/ml sclerox-0·2 at $T = 20$°C (○, ——). The lines depict least square fits of a linear dependence.

with almost identical coefficients α and β as for the observations at 20°C.

Increasing the degree of carboxylation of scleroglucan to 50%, sclerox-0·5 yielded precipitous structures upon addition of the chromium to a final concentration of 2 mM. This is a clear indication that an even further increase of the degree of carboxylation increases the reaction rate. However, the quantitative determination of kinetic parameters for gelation is not possible because of the inhomogeneous structures (precipitates) formed.

Direct comparison of the time needed to obtain the initial 10 Pa increase (Fig. 7) shows that the degree of carboxylation strongly influences the gelation kinetics. For instance, at a chromium concentration of about 2 mM, reduction of the degree of carboxylation from 20 to 10% yields an increase in $t_{\Delta G'=10\,Pa}$ from 115 to 200 min. These data may suggest an inverse proportionality between $t_{\Delta G'=10\,Pa}$ and the degree of carboxylation of scleroglucan, but it should be noted that the range of carboxylation for which quantitative parameters has been determined is very limited. This quantitative relationship between the kinetic parameters of the gelation and the degree of carboxylation should, therefore, be viewed with some caution.

This study shows that carboxylation can be used to extend the application range of scleroglucan from providing highly viscous solutions at low polymer concentration to also providing aqueous gels induced by heavy metal ion crosslinking. Analysis of the rheological data of the chromium induced gelation shows that the effect of varying the chromium concentration is analogous to that reported for the xanthan–chromium system. The fact that introduction of carboxylic groups is necessary for gelation shows that this group is involved in the crosslinking reaction. It is furthermore shown that the extent of carboxylation affects the gelation rate, and hence can be used to control the rate of gelation. This possibility of controlling the gelation rate arises in addition to those already established based on competing ligands to the carboxylic groups on the polymer. Another important point is that native scleroglucan is reported to show better long-term structural and chemical stability than xanthan (Davison & Mentzer, 1982; Kaplakci *et al.*, 1990). The stability of the carboxylated scleroglucan gels may, therefore, be superior to that of xanthan gels. This latter point has not yet been experimentally established, but the long-term stability of the new scleroglucan gels can be expected to depend also on the extent of the scleroglucan carboxylation as well as the degree of purification of the sample after the derivatization process.

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