On the thermal stability of xanthan gum

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(Received 21 January 1985; revised 9 April 1985)

The thermal stability of xanthan gum in dilute aqueous solutions at 90°C is considered. The relative viscosity as a function of ageing time is discussed, and it has been found to depend on the polymer concentration and conformation as well as on the salt content. The effectiveness of a quencher demonstrates the existence of a free-radical process in the degradation. During ageing, the molecular weight first decreases by rapid random hydrolysis of the main chain and loss of the pyruvate and acetate substituents. Later, oligomers are formed corresponding to a breakdown of both the side chain and the main chain. The identification of cellodextrins in the oligomer pool demonstrates the second effect.

(Keywords: xanthan; thermal stability; chemical degradation process; molecular weight variation; substituent content)

INTRODUCTION

Xanthan gum is a well-known polysaccharide whose use in tertiary oil recovery has been proposed[1-3]. However, its use for this industrial purpose is complicated by several problems including:

(1) The injectability of the polymer is impeded by the presence of microgels. To correct this we have already proposed an enzymic treatment for the clarification of polysaccharide solutions[4].

(2) In the oil-field environment stability of polysaccharide viscosity varies according to external factors including temperature, salinity of the water and rock porosity. Since long-term stability of viscosity is critical in this application we have explored three aspects of the problem. Firstly, we have examined the interrelationship between thermal and chemical stability with physicochemical aspects e.g. polymer concentration and conformation and ionic effects. Secondly, we have recovered and characterized the degradation products and thirdly, we have used these results to suggest a degradation mechanism.

The devolution of molecular structure in the polymer (loss of substituents and molecular weight) was studied by a combination of two methods: ^{1}H n.m.r. to determine the acetate and pyruvate contents[5] and gel permeation chromatography on silica gel with both refractometric and low angle laser light scattering (LALLS) detectors to measure the molecular weights of the samples[6].

The degradation was also characterized by the analysis of oligomers formed after long ageing times.

EXPERIMENTAL

Xanthan was purified as the sodium salt from a powder supplied by Rhône Poulenc as previously described[7]. This sample had a molecular weight, $\bar{M}_w$, of 2.8×10^6 and a degree of substitution per side chain of 1.0 and 0.5 for acetate and pyruvate groups, respectively.

The ^{1}H n.m.r. was performed at 85°C on a Bruker WP 100 MHz spectrometer at a polymer concentration C_p, of $5\,g\,l^{-1}$. The substituent content was determined by measuring the peak areas of the acetate ($\delta = 2.09$ ppm) and pyruvate ($\delta = 1.4$ ppm) in comparison with sodium acetate ($\delta = 1.8$ ppm) as a concentration reference (5×10^{-3} M in D_2O).

For gel permeation chromatography, columns ($l = 127$ cm, $r = 0.4$ cm) were filled with porous silica gel (Spherosil 150 to 3500 Å, Fractosil 10000 and 25000 Å). The eluant was 10^{-1} M $NaNO_3$ at a constant flow rate $d = 30$ ml/h. The molecular weight detector was a LALLS photometer (Chromatix KMX-6) and the concentration detector was a differential refractometer (Iota from Jobin-Yvon). Before injection, samples were always passed through 0.8 μm Millipore filters and the effluent was filtered through 0.45 μm filters before entry into the cell of the LALLS detector.

Stability tests were carried out at $T = 90$°C using hermetically sealed glass bottles. The polymer concentrations were 1–$0.2\,g\,l^{-1}$.

Viscosity was measured as a function of degradation time. The samples, previously cooled to 25°C, were passed through 0.8 μm Millipore filters and the ionic strength was adjusted to 10^{-1} M minimum, when necessary, to avoid electroviscous effects. Results are expressed as R, the relative viscosity, given as a percentage of the initial viscosity.

Depending upon the polymer concentration, viscosities were measured either with a capillary viscosimeter (FICA Viscomatic, $d = 0.5$ mm) or with a coaxial cylinder viscosimeter (Contraves LS 30). The latter was also used to determine the zero shear rate viscosities.

G.p.c. on Biogel P_2 and P_6 and h.p.l.c. on Sugar Pak and Radial Pak C-18 with aqueous solvents were used for the fractionation and identification of the oligomers and sugars formed as degradation products.

The optical rotatory power was determined with a FICA Spectropol 1B, equipped with a 5 cm cell thermostatted to 25°C ± 0.1°C.

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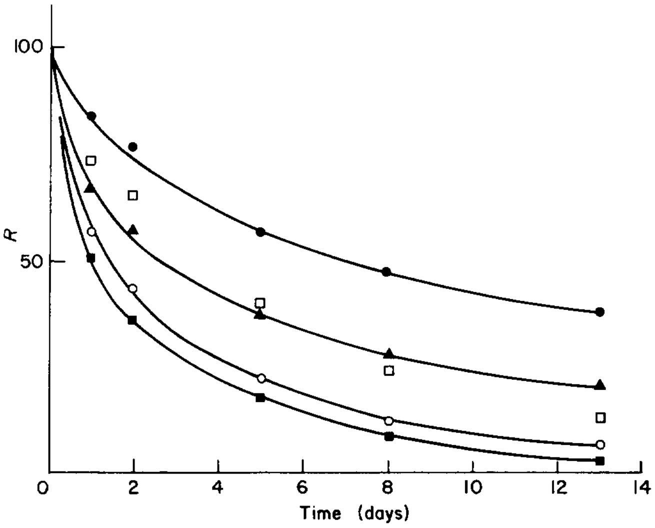

Figure 1 Time dependence of relative viscosity: 1 N NaCl, $\dot{\gamma}_{mes} \to 0$, (■) 1 g/l, (○) 0.8 g/l, (▲) 0.6 g/l, (□) 0.4 g/l, (●) 0.2 g/l. Viscosity measured at 0.2 g/l

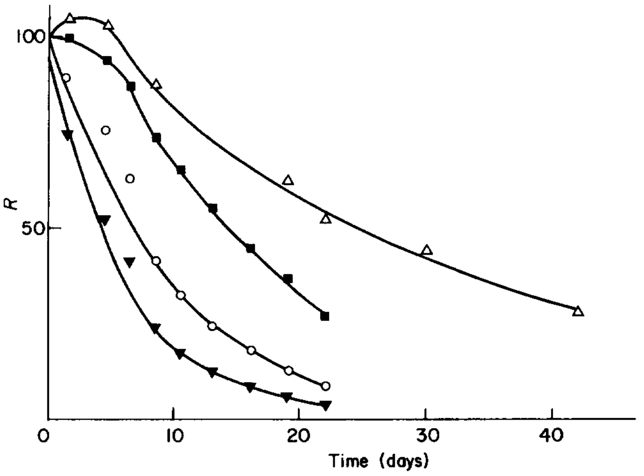

Figure 2 Effect of the shear rate on the relative viscosity measurements for the xanthan degradation at $C_p = 1$ g/l in 1 N NaCl, (▼) $\dot{\gamma} \to 0$, (○) 5.96 s^{-1}, (■) 69.5 s^{-1}, (△) $\dot{\gamma} = 700$ s^{-1}. Viscosity measured $C_p = 0.2$ g/l

RESULTS AND DISCUSSION

Relative viscosity of xanthan solution

Dependence on polymer concentration. The viscosities of the samples were determined as a function of ageing time in 1 N NaCl over a concentration range 0.2–1.0 g/l (*Figure 1*). It can be seen that the decrease in relative viscosity becomes larger with increasing polymer concentration.

As shown in *Figure 2* the rate of shear significantly influences the relative viscosity measurement. Since the relative viscosity is affected by many parameters including molecular weight, conformation, ionic-strength as well as intermolecular interactions, it is clear from these data that the probe is not a reliable indicator of ageing effects. However if it is to be used in this capacity it is more instructive to make measurements in concentration and shear rate domains approximating actual field conditions.

Dependence upon polymer conformation and specific counterions. Divalent counterions induce a coil→helix transition in xanthan gum when their concentration in solution reaches 10^{-3} eq/l.[8] Divalent counterions, even in trace quantities increase the conformational melting temperature.

In *Figure 3*, the relative viscosity is shown to be independent of the choice of counterion (Na^+ or Ca^{2+}) under conditions where the ordered conformation is stable at 90°C as established by optical rotation measurements[9].

In oil-field flooding operations the fluids used often have seawater as the major component. Typically this highly variable solvent has sodium as the major cation with dilvant cations (mostly calcium and magnesium). To simulate these conditions we used a 'model sea water' whose composition was 9.4 g/l NaCl, 10 g/l $CaCl_2$, 6 g/l $MgCl_2$. The stability of xanthan in this medium is lower than with the single salt solutions[9].

Since xanthan gum in water at 90°C has been shown to exist in the disordered form, results in *Figure 3* also indicate the greater stability of the polysaccharide ordered form. This point has already been discussed in terms of enzymic degradation[10] and thermal stability[11-12].

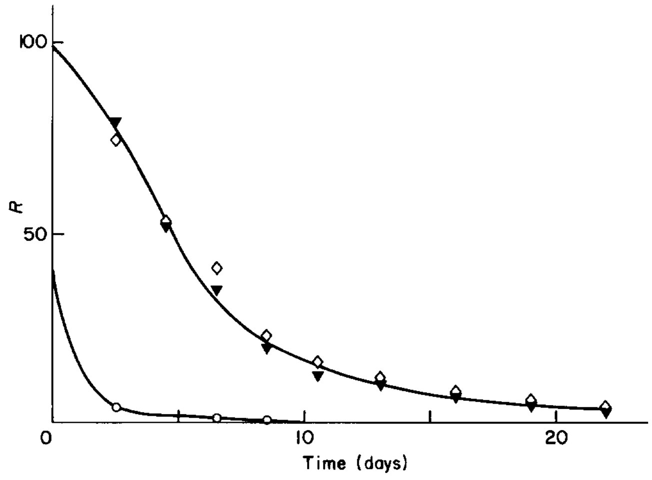

Figure 3 Effect of the nature of the counterion on the xanthan thermal stability: $\dot{\gamma}_{mes} \to 0$, $C_p = 1$ g/l, (○) H_2O, (◇) 1 N NaCl, (▼) 1 N $CaCl_2$. Viscosity measured at $C_p = 0.2$ g/l

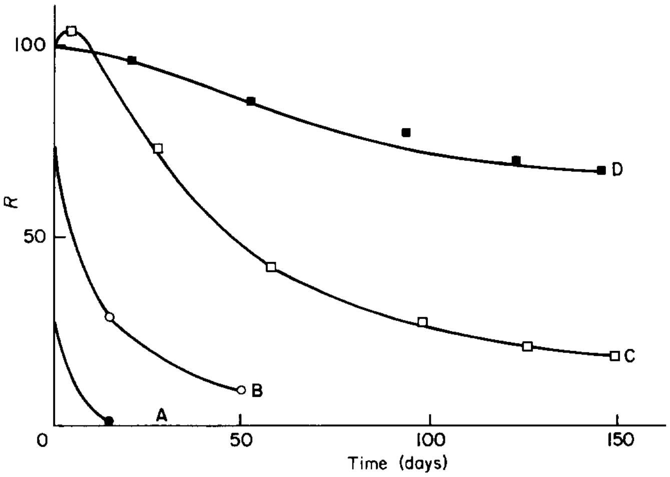

Figure 4 Influence of sodium dimethyldithiocarbamate (S) at a concentration $C_s = 1$ g/l on the stability of xanthan solutions at $C_p = 0.2$ g/l. Curves A and B in H_2O, (●) without S, (○) with S. Curves C and D in 'sea water', (□) without S, (■) with S

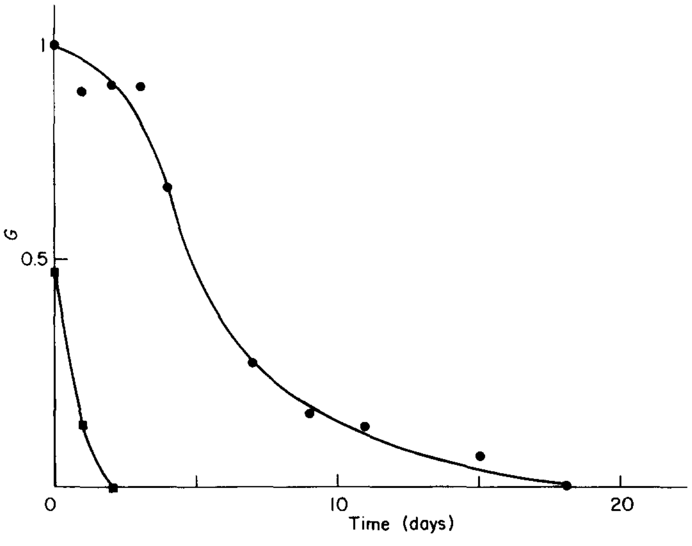

Figure 5 Degradation of xanthan in H_2O at $C_p = 1$ g/l: time dependence of the substituents content (G); (●) acetate, (■) pyruvate

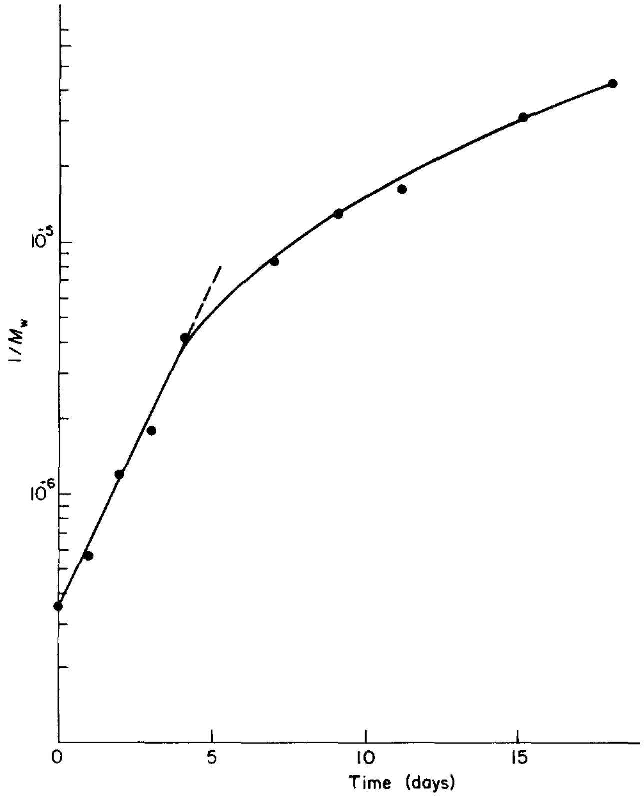

Figure 6 Degradation of xanthan in H_2O at $C_p = 1$ g/l: evolution of the reciprocal average molecular weight with ageing time

Use of a chemical additive. A literature review suggests that in oilfield conditions, the most important chemical degradation reaction should be thermal oxidation. This mechanism involves the formation of free-radical species by dissolved oxygen and redox couples involving transition metals such as Fe which are present in the water. Recently, a radical degradation mechanism for charged polysaccharides was proposed from e.s.r. measurements[13]. To minimize such degradation, an antioxidant, sodium dimethyldithiocarbamate was added to polymer solutions at a concentration, C_s, of 1 g/l.[14]

In pure water, *Figure 4*, the antioxidant slightly improves the xanthan thermal stability. Yet, optical rotation measurements establish that this improvement is not due to a conformational change as the antioxidant does not induce formation of the xanthan ordered form in these test conditions.

In the presence of external salts, the additive efficiency is much greater. This may be related to its ionic character

Table 1

Time (days)	M_w
0	2.8×10^6
1	1.7×10^6
2	821 000
3	552 000
4	236 700
7	116 590
9	75 000
11	69 000
15	29 960
18	21 680
20	18 900
30	6 000
60	4 800

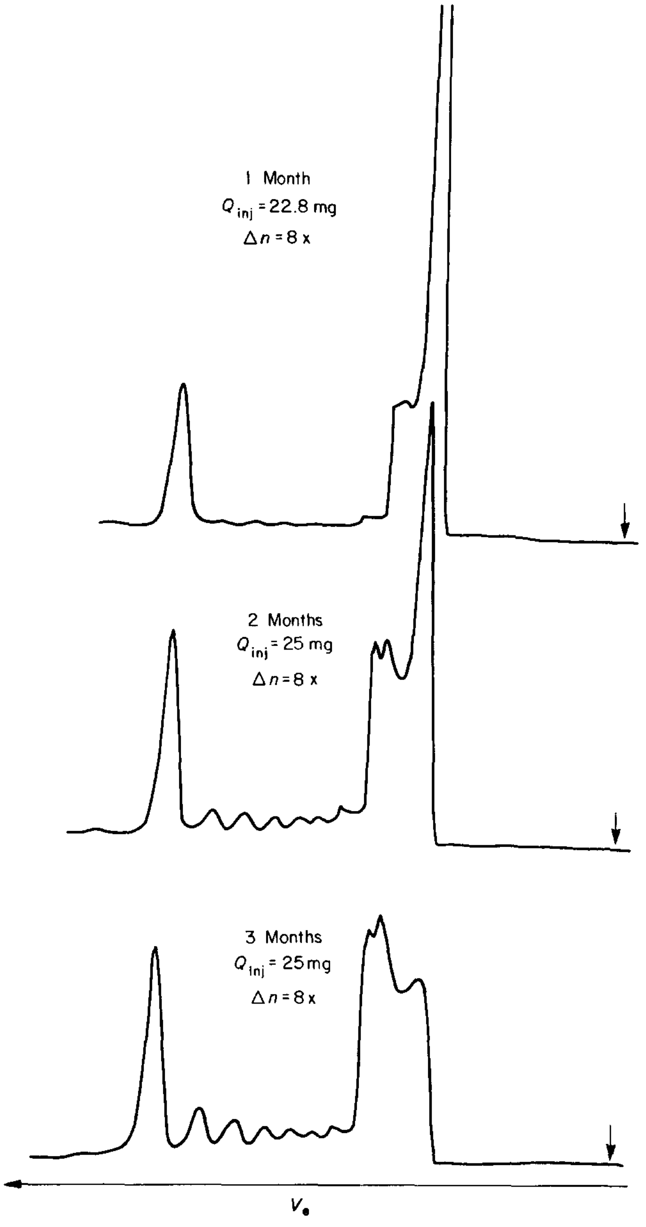

Figure 7 Degradation of xanthan in H_2O at $C_p = 1$ g/l: chromatograms obtained on Biogel P_2 with H_2O as eluant for the most degraded samples

and to the suppression by added salts of ionic repulsions between the polymer and the antioxidant.

These results agree with those previously obtained using other chemical additives[15,16]: thiourea, MgO, TEPA (tetraethylenepentamine) and show that a long-term stabilization of xanthan solutions must retard the radical degradation process.

Polymer evolution during thermal degradation

In order to determine the effect of thermal degradation on the polymer structure, the molecular characteristics were followed during experiments performed at a polymer concentration $C_p = 1$ g/l in the absence of external salts and other additives. In these conditions xanthan assumes its disordered form and degrades more rapidly. After time intervals ranging from one day to three months, the polymer was recovered by ethanol precipitation or direct freeze drying. The relative viscosity fell in the same way as seen in *Figures 3* and *4*.

Acetate and pyruvate contents. The relative number of substituents (G), measured by ^{1}H n.m.r., is given in *Figure 5*. This shows that pyruvate substituents are very labile, probably because of the ketol linkage to the polymer, and disappear after two days at 90°C. The acetate substituents, although more resistant, are fully hydrolysed after 18 days at 90°C.

Molecular weight. The LALLS determined weight-average molecular weight values for different ageing times are given in *Table 1*. The molecular weight decreases rapidly in the first stage (5 days), although no low molecular-weight carbohydrate species are formed. Therefore, this initial degradation must proceed by a random scission of the main chain (*Figure 6*).

Chromatographic analysis. The most degraded products, obtained after 1, 2 and 3 months at 90°C, were fractionated on Biogel P_2. The chromatograms are shown in *Figure 7* and can be decomposed with increasing elution volume into three discrete regions.

First, there is an excluded fraction, coinciding with the void volume of the column, and corresponding to residual polymer ($M > 6000$ for this Biogel); secondly there is a non-symmetric peak arising from mixtures of charged oligomers.

Finally there are a series of neutral oligomers with DP decreasing from 6 to 1. These oligomers were isolated on preparative scale and analysed by h.p.l.c.

The DP_1 peak corresponds to a glucose and mannose monomer mixture and the proportion of glucose increases with ageing time.

Ageing time (months)	1	2	3
Glc/Man	0.034	0.17	0.22

These results mean that the terminal mannose of the side chain is the more labile unit and that glucose is produced by the hydrolysis of the main chain.

The h.p.l.c. analysis of the other peaks shows a series of oligosaccharides and, except for cellodextrins, the components were not identified due to a lack of standards. Using the charged oligomers fraction, a g.p.c. analysis performed on Biogel P_4 with $NaNO_3$ as eluant shows that the aldobiouronic acid, glucuronic acid-mannose, was predominant after two months.

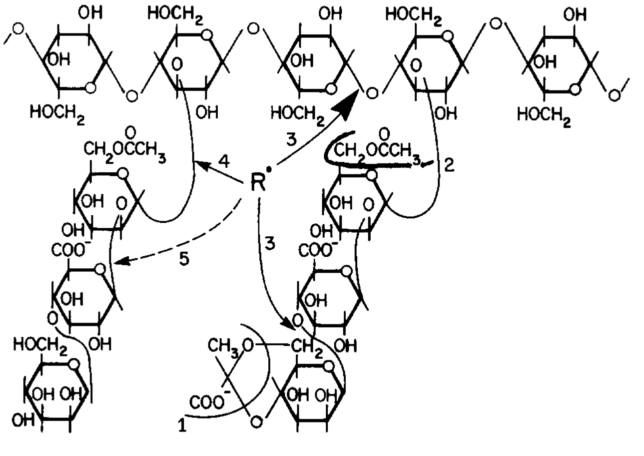

Figure 8 Mechanism proposed for the degradation of the xanthan gum in H_2O in the case of a radical process. The numbers (1–5) indicate the relative ease and rapidity of the degradative reactions with 1 > 2, etc.

Mechanism. This is illustrated in *Figure 8*. For the conditions studied, radical degradation is the predominant process but the different linkages vary in their susceptibility. After the loss of first pyruvate and then acetate substituents, breaking of the main chain results in a pronounced molecular weight decrease and hydrolysis of the other β 1→4 linkage concurrently induces the production of mannose, from the end unit of the side chain, and glucose.

Then the α 1→3 linkage is hydrolysed as confirmed by the presence of cellodextrins while the β 1→2 linkage between glucuronic acid and mannose seems to be the most stable. Such stability has been reported previously for this type of linkage[17].

CONCLUSION

The experimental results given in this paper allow a determination of the main parameters affecting the thermal degradation of aqueous xanthan solutions. By following the time dependent decrease of viscosity, it has been demonstrated that the relative viscosity is directly related to polymer concentration, to the presence of monovalent and divalent counterions separately or in mixtures and to the polymer conformation.

Oxygen is known to have an important role in polysaccharide degradation and we have shown by demonstrating the stabilizing influence of a free-radical quencher that radical induced degradation is the predominant mechanism.

The process begins with hydrolysis of acetate and pyruvate substituents accompanied by scission of β 1→4 linkages in both the main and side chains. Scission of the main chain leads an early rapid decrease in $\bar{M}_w$ and is followed by further breakdown in which aldobiouronic acid remnants of the side chain are cleaved from the cellulose main chain. Because of the combined chemical and thermal instabilities of the glycosidic linkages it seems unlikely that one can prevent xanthan degradation at a level desirable for its application in enhanced oil recovery.

ACKNOWLEDGEMENTS

The authors thank the Society ELF for its financial assistance and Mrs Vio and Heyraud for their helpful discussions.

REFERENCES

1 Holzwarth, G. *Biochemistry* 1976, **15**, 4333

2 Morris, E. R., Rees, D. A., Young, G., Walkinshaw, M. H. and Darke, A. *J. Mol. Biol.* 1977, **110**, 1

3 'Extracellular Microbial Polysaccharides' (Ed. P. A. Sandford and A. Laskin), **45**, American Chemical Society, Washington, 1977

4 Rinaudo, M., Milas, M. and Kohler, N. French Patent Applications 80/21395, 1980 and 81/10403, 1981

5 Rinaudo, M., Milas, M., Lambert, F. and Vincendon, M. *Macromolecules* 1983, **16**, 816

6 Lambert, F., Milas, M. and Rinaudo, M. *Polym. Bull.* 1982, **7**, 185

7 Rinaudo, M. and Milas, M. *Biopolymers* 1978, **17**, 2663

8 Lambert, F., Milas, M. and Rinaudo, M. *Int. J. Biol. Macromol.* 1985, **7**, 49

9 Lambert, F. Thesis, 1983, Grenoble (France)

10 Rinaudo, M. and Milas, M. *Int. J. Biol. Macromol.* 1980, **2**, 45–48

11 Lambert, F., Milas, M. and Rinaudo, M. Second European Symposium on E.O.R. (Ed. Technip), 1982, 79

12 Glass, J. E., Soules, D. A. and Ahmed, H. SPE Paper No. 11691 presented at the 1983 California Regional Meeting, Ventura, USA

13 Gilbert, B. C., King, D. M. and Thomas, B. *Carbohydr. Res.* 1984, **125**, 217

14 Vio, L. and Meunier, G. Brevet Français 83, 408

15 Wellington, S. L. SPE Paper No. 9296 presented at the 55th Annual SPE Fall Meeting, Dallas (1980), USA

16 Ash, S. G., Clarke-Sturman, A. J., Calvert, R. and Tisbet, T. M. SPE Paper No. 12085 presented at the 58th Annual SPE Technical Conference, San Francisco (1983), USA

17 Aspinall, O. 'Polysaccharides' (Ed. O. Aspinall). First Edition, Pergamon Press, 1970, 20