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XANTHAN PROPERTIES IN AQUEOUS SOLUTION

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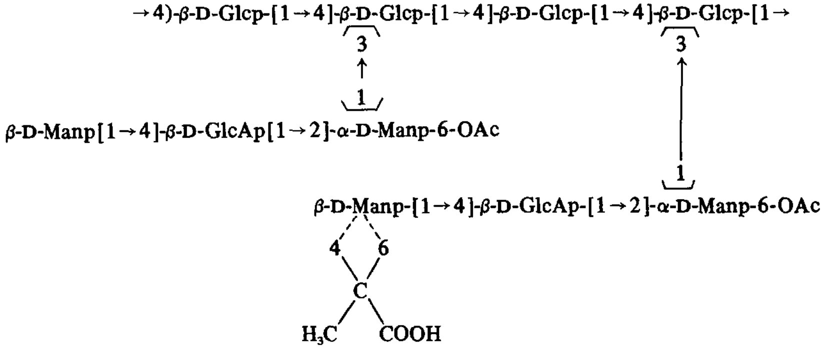
Xanthan is a polysaccharide produced by the bacterium *Xanthomonas campestris*. The molecular structure was given first by Jansson *et al.* (1975); it is a (1→4)D-glucose polymer bearing on alternate glucoses a branch with three monomers including uronic and pyruvic acids.



The polysaccharide is water soluble and possesses polyelectrolyte properties. Its use in tertiary oil recovery is well known and is due to its ability to enhance viscosity and for this to be preserved in the presence of external salt. From a variety of points of view it is a novel polymer and therefore its principal properties are of considerable interest.

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CHARACTERISATION OF THE POLYMER

The difference between commercial samples may be related to different contents of pyruvate and acetate; these groups are hydrolysed in acidic and basic media respectively. The content of each group can be determined by high resolution proton NMR as reported by Rees (Morris *et al.*, 1977) and Brant (Paradossi & Brant, 1981). ^{13}C NMR is also informative and has confirmed the chemical structure previously proposed (Vincendon *et al.*, 1982). The molecular weight is difficult to determine by light scattering due to the presence of microgels; our results, recently confirmed by J. Blackwell, show that $M_w \simeq 2 \times 10^6$ and indicate that this value is appropriate on both sides of the conformational melting temperature.

POLYELECTROLYTE PROPERTIES

The properties are those of a normal polyelectrolyte with a charge parameter $\lambda = 1{\cdot}035$ (random) or $\lambda = 1{\cdot}134$ (single 5_1 helix). The activity coefficients are $\phi_{Na} = 0{\cdot}650$ and $\phi_{Ca} = 0{\cdot}295$ for monovalent and divalent ionic forms, respectively, in the absence of external salt (Rinaudo & Milas, 1978). The ϕ_{Ca} value may indicate that the polymer is in a simple helical conformation. The only deviation was demonstrated under acidic form at a temperature lower than 40°C (Milas & Rinaudo, 1981).

LOCAL CONFORMATION

This stereoregular polysaccharide adopts a local ordered conformation in given conditions (low temperature, presence of external salt); this structure is probably a simple helix of similar structure to those observed in the solid state (Moorhouse *et al.*, 1977) (a five fold helix with a pitch of 47 Å was proposed). Evidence of this ordered local conformation is obtained from measurements of optical rotation when the conformational transition is induced by changes in temperature, pH or by addition of salt. Nevertheless, the chromophores involved in such studies are the carbonyls on the lateral chains; the modification of their neighbourhood (and mobility) does not, therefore, strictly reflect the properties of the backbone. The conformational change is characterised by a melting temperature, T_m, which depends on the chemical structure, but T_m always varies linearly with the logarithm of the total ionic strength (μ); other methods give the same information:

1. Proton NMR signals reflect mobility of acetate and pyruvate group (Morris *et al.*, 1977).
2. Circular dichroism (c.d.) measurements show the equilibrium between two extreme conformations (Milas & Rinaudo, 1979) whose specific ellipticity is independent on the polymer concentration.

3. Disappearance of birefringence on more concentrated solutions corresponds also to the same T_m value at the corresponding μ.

The question of whether it is a single or double helix is still open to discussion.

HYDRODYNAMIC BEHAVIOUR

The dependence of viscosity on temperature is still under investigation. Dilute solutions show the following features:

1. On the addition of salt (NaCl or $CaCl_2$) the reduced viscosity remains constant in concentrations up to at least 0·01 N; in the same concentration region, the ordered conformation is formed. This behaviour is opposite to that of synthetic polyelectrolytes.
2. The rheological behaviour of the solutions is highly non-Newtonian as established by Whitcomb and Macosko (Whitcomb *et al.*, 1977) and more recently by Chauveteau & Zaitoun (1981) and Rinaudo *et al.* (1979).

Figure 1 shows the dependence of the relative viscosity ($\eta_{\text{polymer}}/\eta_{\text{NaCl}}$) as a function of the rate of shear $\dot{\gamma}$ for both conformations. On each curve, a critical $\dot{\gamma}$ separates the Newtonian and non-Newtonian regimes; this value depends on the conformation just as the slopes in the non-Newtonian domain. For the polymer with $M_w \simeq 3{\cdot}6 \times 10^6$ and at a concentration of 1 g litre^{-1}, the reduced viscosities obtained from extrapolation to $\dot{\gamma} \to 0$ are:

ordered conformation (15°C): 190 700 ml/g
unordered conformation (70°C): 159 500 ml/g

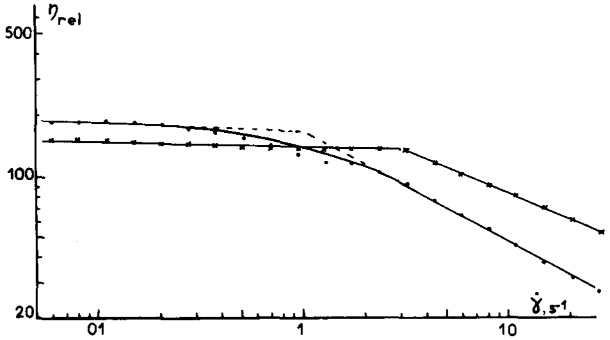

Fig. 1. Relative viscosity of xanthan as a function of the rate of shear, $\dot{\gamma}$. Polymer concentration = 1 g litre^{-1}; solvent, NaCl $1{\cdot}2 \times 10^{-2}$ N. ●, Temperature 15°C (ordered conformation); ×, temperature 70°C (unordered conformation).

corresponding only to a 15% increase when the ordered conformation is stabilised; this means that there is only a fairly small increase in molecular rigidity.

All the experimental results agree with a rigid rod like molecule behaviour with a length of between 6000 and 10 000 Å. More recent results from Holzwarth (1981) and Brant (Paradossi & Brant, 1981) point to a rigid wormlike chain. In our opinion, it is impossible to draw firm conclusions about the morphology in dilute solution before measurements are obtained on a well defined sample and thereby avoid the effects of contribution arising from aggregation and polydispersity.

It is also necessary to control the rate of shear, $\dot{\gamma}$, during experiments investigating the effects of temperature and ionic strength dependence since there is clear evidence that the transition observed in the curve of viscosity-temperature depends on $\dot{\gamma}$ (Rinaudo *et al.*, 1979).

MESOPHASE FORMATION

As previously mentioned, birefringence appears when an ordered conformation exists, and when the polymer concentration is larger than 2·5 g/litre the critical concentration C^* depends on the molecular weight ($C^* \sim 1/M$) just as predicted in the Flory theory.

In partially hydrolysed polymers (thereby reducing the molecular weight and the viscosity) we have observed the formation of a cholesteric phase.

Figure 2 represents the volume fraction of the cholesteric phase as a function of the polymer concentration in water and 0·1 M NaCl. These results demonstrate that the electrostatic interchain repulsions which exist in water favoured the organisation of the cholesteric phase. We have also investigated the dependence of the pitch (p) of the cholesteric phase on polymer concentration, ionic strength and molecular weight.

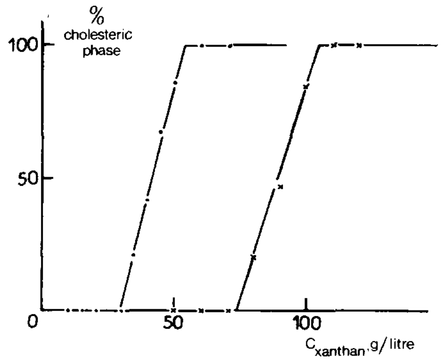

Fig. 2. Volume fraction of the cholesteric phase as a function of the polymer concentration. ●, In H_2O; ×, in 0·1 N NaCl.

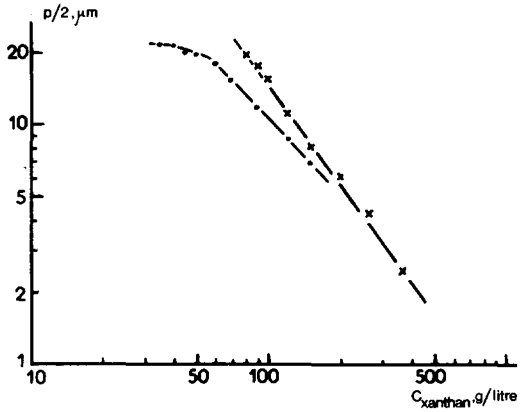

Fig. 3. Half pitch of the cholesteric phase as a function of the polymer concentration. ●, In H_2O; ×, in 0·1 N NaCl.

In Fig. 3, the dependence of the half pitch of the cholesteric phase ($p/2$ expressed in μm) is given in two solvents. In NaCl the slope is −1. This result is in agreement with previous data of Jizuka (1978) who found −1·1 but in contradiction with Senechal *et al.* (1980) and Robinson *et al.* (1958) who gave values of −0·5 and −2, respectively. The interpretation of the behaviour in water is still under discussion. The negative birefringence and the cholesteric rotatory power allow us to describe the cholesteric phase as a left-handed, cholesteric form with the right-handed, helical structure of the polymer (Maret *et al.*, 1981).

CONCLUSION

Some important questions remain unsolved:

1. In dilute solution, does the molecule occur as a single or a double helix?
2. The hydrodynamic behaviour and dependence of viscosity on temperature is complex. Likewise, is the ordered conformation a rigid rod- or wormlike chain?

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