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Properties of the Concentrated Xanthan Gum Solutions

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Summary

Viscosity measurements have been done on concentrated aqueous solutions of the polyelectrolytic polysaccharide xanthan in the range where the solutions of xanthan exhibit a transition between isotropic and cholesteric phases. The critical volume fractions of the polymer corresponding of the both transitions (isotropic-biphasic ; biphasic-cholesteric) are discussed in term of the Flory theory for rigid rod like molecules.

INTRODUCTION

The xanthan, at least when it is partially hydrolysed by enzyme, behaves as a rigid rod like molecule in given conditions (RINAUDO et al, 1979). These conditions are that which stabilize the ordered conformation and they are controlled by optical rotation measurements. In this conformation, when the polymer concentration increases, a phase separation is observed as predicted theorically for rigid rod like molecules (FLORY 1956, ONSAGER, 1949). In the biphasic region spherolites separate from an isotropic phase and formed a more concentrated phase which has been demonstrated to be a cholesteric phase (MARET et al, 1981). In this work, we want to give the viscosity dependence in the polymer concentration range from isotropic to anisotropic phase on a well characterized xanthan fraction.

EXPERIMENTAL

The xanthan gum is purified and partially hydrolysed by enzyme as previously discussed (RINAUDO and MILAS, 1980). The sample is recovered after carefull fractionation based on the phase separation itself. The macromolecular characteristics are the following : Mw = 235 000, Mw/Mn = 1,35 (from the gel permeation chromatogramm with a refractometric and light scattering detectors (LAMBERT et al, 1982) ; the pyruvate and acetate contents from RMN ^1H spectra (RINAUDO et al, 1983) are respectively 0.89 and 1 groups per side chain. The solutions are prepared in NaCl 0.1 M for screening the long range electrostatic repulsions which play an important role in the critical concentration (RINAUDO and MILAS, 1982). The viscosity measurements are performed with a Low Shear 30 from Contraves (Switzerland) at controlled temperature. The viscosity is determined as a function of the rate of shear $\dot{\gamma}$ but the curves are drawn at a constant $\dot{\gamma}$ value. The two critical concentrations of the phase diagram are obtained from the determination of the birefringence between crossed nicols. The volume fraction ϕ of the anisotropic domain in the biphasic region is determined directly at the equilibrium in a spectroscopic cell (1 mm optical path).

RESULTS AND DISCUSSION

On figure 1, the volume fraction Ø of the cholesteric phase is given as a function of the overall polymer concentration. The dependence is linear in the biphasic region as usually for polymer with low polydispersity. On the same figure, the reduced viscosity is drawn ; it is low at the small concentrations of Xanthan, but increases with the polymer concentration up to a maximum which corresponds to the transition between isotropic and biphasic phases. Then, the viscosity decreases and reaches a plateau at the transition of the biphasic-anisotropic phase In the anisotropic phase, the reduced viscosity is nearly identical to the lower polymer concentration one in the isotropic region. The values of the viscosity η are taken at a shear rate of 1. s^{-1}. The dependence of η with γ will be discussed later.

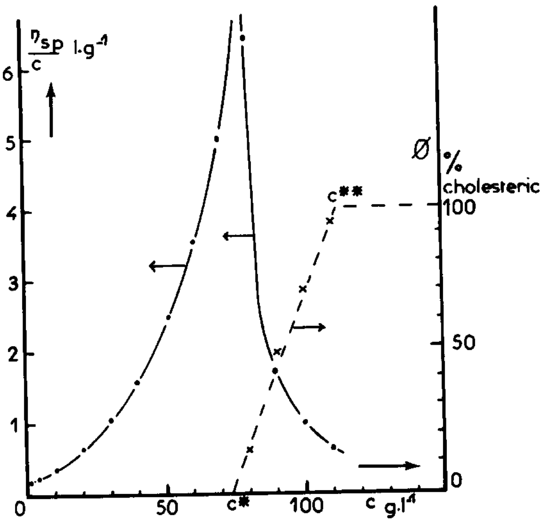

Figure 1 : Reduced viscosity and volume fraction of the cholesteric phase as a function of xanthan concentration (NaCl 0.1 N ; Mw = 235 000 ; T = 25° C ; $\dot{\gamma} = 1\ s^{-1}$).

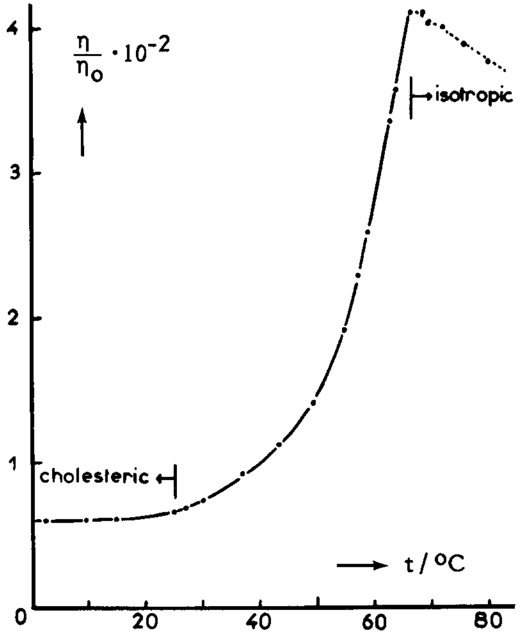

Figure 2 : Relative viscosity of a xanthan solution as a function of the temperature (NaCl = 0.1 N ; Cp = 110 g/l Mw = 235 000 ; $\dot{\gamma} = 2.37\ s^{-1}$)

On figure 2, the relative viscosity is given at constant polymer concentration and shear rate as a function of the temperature in a range where the ordered conformation is stable. At the lower temperatures, in the anisotropic phase, the viscosity remains constant. Then, at a given temperature T_1= 27°C, the viscosity increases up to T_2=65°C. This increasing corresponds to the biphasic region. Above T_2, the viscosity begins to decrease slowly, but the measurements become imprecise, and the solution is isotropic. We can calculated from the experimental critical concentrations (figure 1) the critical volume fractions of the polymer corresponding to the both transitions, with the assumption that the specific volume $\bar{v}$=0.62 as usually in polysaccharides. These values, given in table I, can be compared with the theorical ones from the first Flory's theory (FLORY 1956) for monodisperse rods.

Critical Volume fractions	Experimental values	Calculated values with X = 121	
v*	0.043	8/X	0.066
v**	0.067	12.5/X	0.103

TABLE 1 : Critical volume fractions : comparison between experimental and theoritical values from Flory.
(C*=70 g/l ; C**=107 g/l ; M=235 000 ; M_{dimer}=960 ; l_{dimer}=0.94 nm ; d=1.9 nm ; MOORHOUSE et al. 1977)

In fact, the calculated values are questionnable because the value of the axial ratio X is difficult to choose. Assuming that the diameter is 1.9 nm (MOORHOUSE et al. 1977) and the length of the single helix L=230 nm, it comes X=121. But the experimental values fit very well if one assumes an axial ratio equal to 186 corresponding to d=1.14 nm. So, the agreement between the experimental and calculated values is fairly good and seems to confirm that the xanthan is a single helix as a dimer formation should much decrease the X value.

In addition, one has to take into account the polydispersity of the sample which decreases the critical concentration for isotropic to biphasic transition (MOSCICKI and WILLIAMS 1982).

CONCLUSION

This work gives the first quantitative results obtained on concentrated solutions of Xanthan gum in the range of the phase separation. The general behaviour looks like the other liquid cristalline systems. The results allow to conclude that the partially hydrolyzed Xanthan behaves as a rigid rod like molecule ; this behaviour confirms previous data on the original high viscosity of the solutions of the native polysaccharides and agrees with a single helix conformation in solution.

REFERENCES

P.J. FLORY : Proc. Roy. Soc. 234 73 (1956)
F. LAMBERT, M.MILAS and M.RINAUDO : Polymer Bulletin 7, 185 (1982)
G. MARET, M.MILAS and M.RINAUDO : Polymer Bulletin 4 291 (1981)
R. MOORHOUSE, M.D.WALKINSHAW and S.ARNOTT : in "Extracellular Microbial Polysaccharides" ACS Symposium Series (Eds P.A. Sandford and A.Laskin) 45 90 (1977)
J.K.MOSCICKI and G.WILLIAMS : Polymer 23 558 (1982)
L.ONSAGER : Ann. N.Y. Acad. Sci. 51 627 (1949)
M. RINAUDO, M. MILAS and R. DUPLESSIX 26th Int. Symp. on Macromolecules, Preprints C2-12 p. 800 Mainz 17-21 Sept (1979).
M.RINAUDO and M.MILAS : Int. J.Biol. Macromol. 2 45 (1980)
M.RINAUDO and M.MILAS : Carbohydrate Polymers 2 264 (1982)
M.RINAUDO, M.MILAS, F.LAMBERT and M.VINCENDON Macromolecules in press (1983)

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