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The Viscosity Dependence on Concentration, Molecular Weight and Shear Rate of Xanthan Solutions

M. Milas, M. Rinaudo, and B. Tinland

Centre de Recherches sur les Macromolécules Végétales, C.N.R.S., B.P. 68,
F-38402 Saint Martin D'Heres, France

Summary

This paper concerns the viscosity dependence of Xanthan as a function of polymer concentration, shear rate and molecular weight in the ordered conformation. The different samples with various molecular weights are obtained by ultrasonication. A unique curve is obtained for the reduced specific viscosity (η_{sp}/η_{sp_0}) as a function of $\gamma\cdot\gamma_r^{-1}$ for the different molecular weight samples and polymer concentrations below an overlap concentration $C\,[\eta]_0 \leqslant 1.5$. The master curve giving the relation η_{sp_0} as a function of $C\,[\eta]_0$ is drawn and compared with that of polystyrene in good solvent. The largest increase of η_{sp_0} in semidilute solution may be due to larger interchain interactions and to larger stiffness of the Xanthan molecule.

INTRODUCTION

The viscosity of polymer solutions is related with the conformation and molecular weight of the polymer or with the thermodynamic interactions with the solvent in the dilute regime. Deviation from the linear dependence of the reduced viscosity with the concentration is observed above a critical concentration C^* ; in the semidilute regime, the behaviour is then more complicated, due to interpenetration of the macromolecular domains or entanglements. They lead to viscoelastic properties observable in shear flow experiments.

An increase of the shear rate above a critical value $\dot{\gamma}_r$ leads to a decrease of the viscosity from its zero shear value. Increasing concentration or increasing the molecular weight leads to a decrease of the values of $\dot{\gamma}_r$. These dependences were recently described by Kulicke for aqueous polyacrylamide solutions (1) and polystyrene in toluene and decalin (2).

The rheology of aqueous Xanthan solutions was investigated by Chauveteau (3) on a sample with $\overline{M}_w = 1.8 \times 10^6$ assuming a rigid rod like conformation.

This paper concerns the viscosity dependence on concentration and rate of shear for a series of Xanthan samples with different molecular weights obtained by ultrasound irradiation. It seems to be important to understand the role of these parameters on the level of specific viscosity in aqueous dilute and semidilute solutions. In all the experiments the conformation of the Xanthan is ordered, using NaCl 0.1 M as solvent. In these conditions, the electrostatic interactions are screened and the polymer behaves as a worm like chain (4-5).

EXPERIMENTAL

The sample of Xanthan was kindly given by Shell Cy ; the yield in substituants was 0.75 and 0.4 respectively for the acetate and pyruvate groups per side chain. Xanthan gum was purified by the usual method (6) and isolated as the sodium form.

The native polymer was solubilized in water ; then concentrated NaCl solution was added to obtain a 0.1 N salt concentration ; in this condition the ordered conformation is stable (7). The native polymer was then degraded by ultrasound irradiation during different times from 10 mn to 6 hours with a Branson Sonifier Mod B15-150 W ; temperature was maintained around 0°C and aliquots were taken for investigations without isolation. All the experiments were done at 25°C ; the viscosity measurements were performed as a function of the shear rate with a Low Shear 30 Contraves (up to γ 128 s^{-1}) and a Rheomat 30 Contraves (up to 1770 s^{-1}).

The viscoelastic properties were tested with a Low Shear 30 sinus Contraves ($0.033\ s^{-1} < \dot{\gamma} < 8.33\ s^{-1}$; $\theta = 7{,}5°$). For very low viscosities, a Ubbelhode capillary viscosimeter FICA was used ; the inner diameter of the tube was 0.5 mm. The molecular weight distributions were established by gel permeation chromatography on 1 x 6 000 and 1 x 4 000 TSK PW (60 cm) columns using differential refractometer (IOTA from Jobin Yvon-France) and a LALLS (Chromatix CMX 100 - U.S.A.) on line. The elution was performed with $NaNO_3$ 0.1 M in the presence of 0.2 g/l NaN_3 and 1 % ethylene glycol at 25°C. The characteristics of the samples used are given in Table I ; the polydispersity index $\overline{Mw}/\overline{Mn}$ is around 1.5 and the samples are used without fractionation.

RESULTS AND DISCUSSION

I. CONCENTRATION DEPENDENCE ON THE FLOW CURVES

Polymers in solution exhibit a shear rate dependent viscosity above a critical shear rate $\dot{\gamma}_r$ and above a polymer concentration which depends on the molecular weight (Table I). The value of $\dot{\gamma}_r$ decreases as the concentration or the molecular weight increases. The figure 1 gives the curves $\eta(\dot{\gamma})$ as a function of concentration from 2 to 0.0625 g/l for a Xanthan with $\bar{M}_w = 7 \times 10^6$. The results are in good concordance with those of Chauveteau on Xanthan (3) and Kulicke on polystyrene (2).
In dilute solution, the intrinsic viscosity $[\eta]_0$ and k' values are determined from specific viscosity in the newtonian regime (η_{sp_0}) ; when $\bar{M}_w < 5 \times 10^5$ the capillary viscosimeter may be used for better precision as no shear rate effect exists in this range of molecular weights. The values of $[\eta]_0$ are given in Table I from which the overlap concentration $C^* = 0.77\ [\eta]_0^{-1}$ can be estimated (8).

Tableau I : Characteristics of the samples investigated.

Ref	$\overline{M}_n \times 10^{-6}$	$\overline{M}_w \times 10^{-6}$	$[\eta]_0$ ml/g *	$C^* = \frac{0.77}{[\eta]_0}$ (g/l)	Limit concentration for newtonian regim (g/l) **
Native form	-	7.	10500	0.073	
F_1	-	5.3	6150	0.125	0.0625
F_2	1.5	2.3	2900	0.266	0.25
F_3	0.51	1.0	1340	0.575	1
F_4	0.28	0.45	476	1.62	-
F_5	0.23	0.31	320	2.41	-

* Intrinsic viscosity at zero shear rate. ** In the range of $\dot{\gamma} < 2000\ s^{-1}$

II. MOLECULAR WEIGHT DEPENDENCE ON THE FLOW CURVES

At a given weight concentration (2 g/l) of the different samples, the shear rate curves were established (Figure 2). From this set of results the figure 3 is drawn showing the viscosity as a function of the molecular weight ($\overline{M}_w$) at given shear rates. This curve is different from that obtained and discussed by Kulicke of polystyrene (2) and the viscosity never becomes independent on the molecular weight. These results (Figure 3) demonstrate the difficulties to use the viscosity measurements to follow degradation of the polymer (9) even at constant shear rate.

From the experimental results obtained for different $\overline{M}_w$ samples at different concentrations, it is easy to determine $\dot{\gamma}_r$ on each curve and to consider the reduced specific viscosity (η_{sp} / η_{sp_0}) as a function of the reduced shear rate $\dot{\gamma}.\dot{\gamma}_r^{-1}$ (Figure 4). A master curve is obtained up to an overlap parameter $C\,[\eta]_\rho \leqslant 1.5$; this result is in good agreement with the previous result obtained by Chauveteau who finds $C\,[\eta]_\rho \leq 1.9$. The new information here is that the values for the different $\overline{M}_w$ and concentrations are on the same master curve.

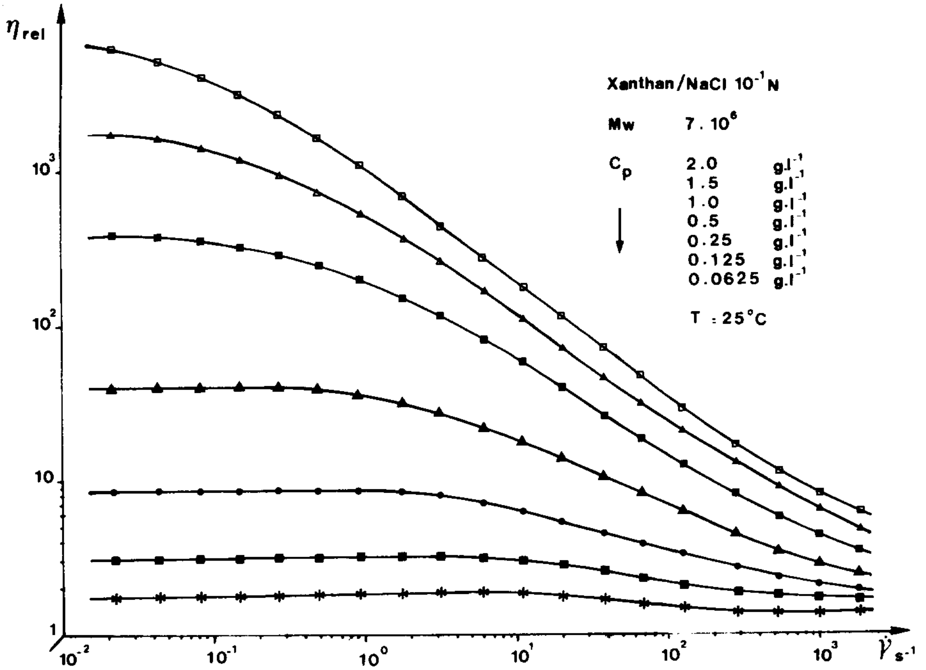


FIGURE 1 : Relative viscosity shear rate curves for various Xanthan concentrations.

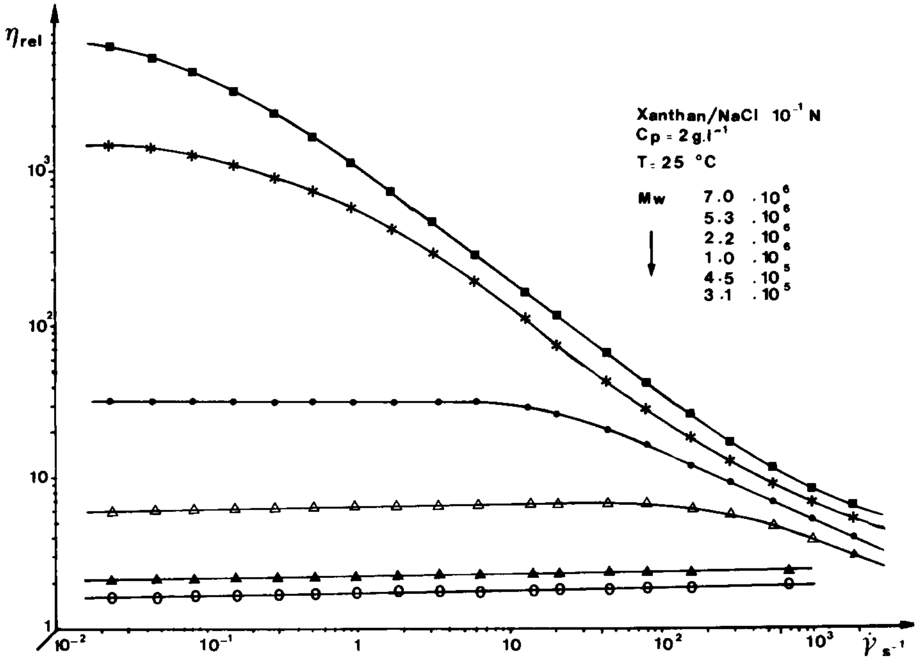


FIGURE 2 : Relative viscosity shear rate curves for various Xanthan molecular weights.

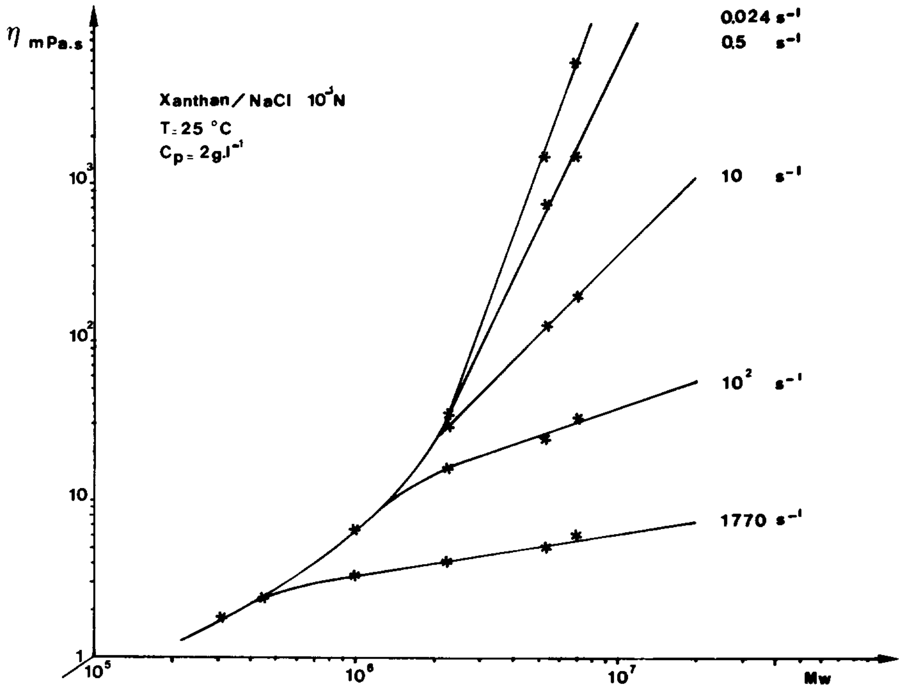
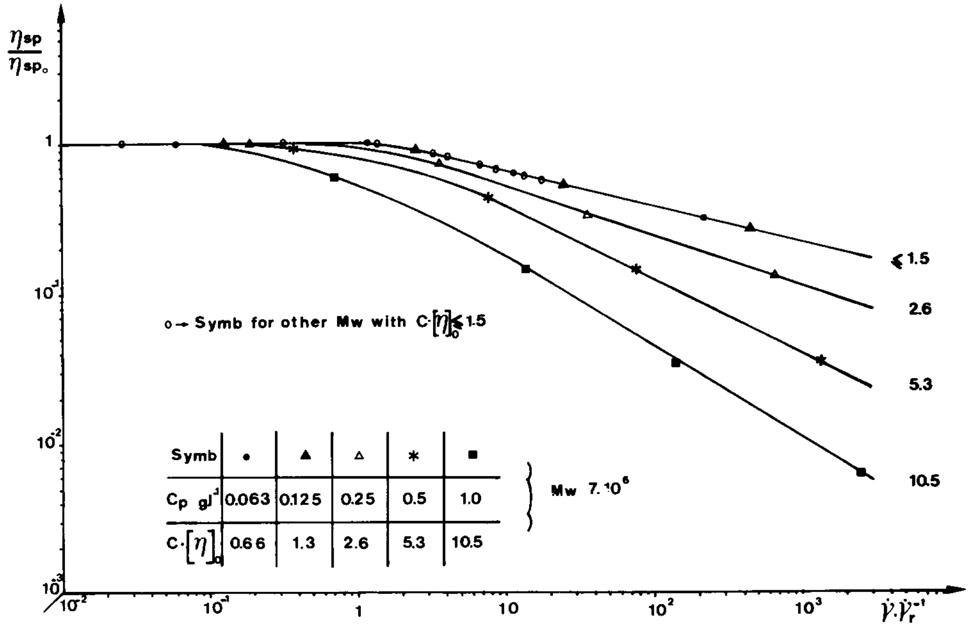


FIGURE 3 : Viscosity as a function of the molecular weight at different shear rates.



Symb	•	▲	△	*	■
C_p gl^{-1}	0.063	0.125	0.25	0.5	1.0
$C\cdot[\eta]_0$	0.66	1.3	2.6	5.3	10.5

FIGURE 4 : Specific viscosity shear rate curves in a reduced form for various molecular weights and Xanthan concentrations.

III. RELATION η_{sp_o} - $\overline{M_w}$ - C

Considering the specific viscosity in the newtonian regime, it is important to point out its dependence with $\overline{M_w}$ and the polymer concentration in given thermodynamic conditions. Different modes of representation were proposed as master curve for log η_{sp_o} as a function of log k'C $[\eta]_o$ (10), log C.$\overline{M_w}$ (11) or log C $[\eta]_o$ (2).

The most general parameter used as overlap parameter is C $[\eta]_o \alpha$ CM^a (in which "a" is the exponent of the Mark-Houwink relation). Indeed, the zero shear rate values of specific viscosities are well described by a single master curve for a given polymer-solvent system.

As the specific viscosity is given by :

$$\eta_{sp_o} = C\,[\eta]_o + \sum_{i=1}^{\infty} (k_i\, C\, [\eta]_o)^i$$

or

$$\eta_{sp_o} = C\,[\eta]_o + k_H\,(C\,[\eta]_o)^2 + B_n\,(C\,[\eta]_o)^n$$

taking into account the Huggins equation (k_H = Huggins constant) and collecting all the terms having exponents higher than 2 in one term.

The figure 5 gives the dependence of log η_{sp_o} as a function of log C $[\eta]_o$ for the different samples of Xanthan. A unique curve is obtained as

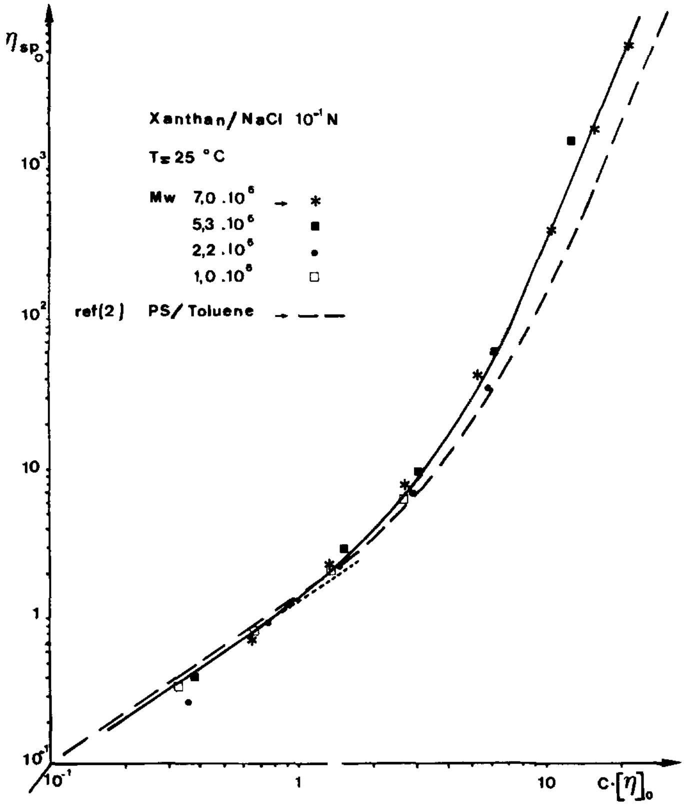


FIGURE 5 : Specific viscosity as a function of the overlap parameter C . $[\eta]_o$ for various Xanthan molecular weights.

master curve ; in addition the experimental curve is the same as the theoritical one drawn with $k_H = 0.44$ (3), $B_n = 1.73 \times 10^{-2}$ and $n = 4.24$ taken on the experimental curve.

This curve looks like that obtained by Kulicke for polystyrene in a good solvent (2). The departure from slope 1, corresponds to $C\,[\eta]_o$ around 0.8 and the linearity for large $C\,[\eta]_o$ occurs for $C\,[\eta]_o = 6$; simultaneously, i.e over $C.[\eta]_o > 5$, viscoelastic behaviour is observed on the solution from dynamic viscosity measurements. For large $C\,[\eta]_o$ values, η_{sp_o} varies as $C^{4.24}$ and $M^{4.83}$ taking into account the following relations :

- $[\eta]_o = 1.7 \times 10^{-4}\ M_w^{\ 1.14}$ (from values of Table I)
- $C\,[\eta]_o = KCM^a$(K,a = parameters of the Mark Houwink relation)
- $\eta_{sp_o} \alpha B_n C^n\ K^n\ M^{na}$

The main difference with the curve obtained with polystyrene in good solvent (2) occurs over $C\,[\eta]_o = 1$; it is shown that for a given $C\,[\eta]_o$ value, the specific viscosity is larger, due to the more rigid conformation of the polysaccharide but also to the larger interchain interactions in this regime. At end, as the value of the exponent "a" is near 1, it is impossible from our results to choose the better representation of specific viscosity dependence with $C\,[\eta]_o$ or $C.\overline{M}_w$ as discussed in the litterature (12).

CONCLUSION

The experimental results allow to relate the specific viscosity at zero shear rate as a function of the molecular weight $\overline{M}w$ of Xanthan and the polymer concentration in its ordered conformation (at 25°C in 0.1 M NaCl). The different samples were obtained by ultrasound irradiation for different times. The viscosities were measured as a function of the shear rate $\dot{\gamma}$; the viscosity decreases over a critical $\dot{\gamma}_r$ value which depends on the polymer concentration and $\overline{M}_w$ values.

It is clear from the experimental results given in figure 3 that viscosity measurement variations are difficult to interpret in terms of molecular weight dependence by exemple in aging experiments. The figure 5 summarizes the most important results ; it establishes a master curve relating the zero shear rate specific viscosity with the overlap parameter $C\,[\eta]_o$; deviation from linearisation in low range of $C\,[\eta]_o$ values is located around the critical overlap conditions for the transition from dilute to semidilute regime. In addition, the linearisation in the range of large $C\,[\eta]_o$ values corresponds also with the appearance of viscoelastic behaviour in dynamic experiments.

At end, this behaviour is very similar with that of polystyrene in a good solvent (2) ; the difference comes from larger increase of the viscosity for large $C\,[\eta]_o$ due to the increase of the interchain interactions and chain rigidity of the Xanthan.

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