

Polyelectrolytic Behaviour of Photodegradable Xanthan Solutions

Part I. Viscosity Change in Aqueous Solution

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ABSTRACT

Photodegradation curve of xanthan gum in aqueous solution has been reported. Solution viscosities for xanthan in aqueous solution have been measured before and after UV-irradiation. UV-irradiation decreases the values of relative, specific, reduced and intrinsic viscosities, molar mass, hydrodynamic volume, Fuoss & Strauss constant and solute-solute contact in the aqueous solution of xanthan gum. It increases the solute-solvent interaction.

Key Words: Ultraviolet radiation; Solution viscosity; Fuoss and Strauss equation.

INTRODUCTION

Chemistry of polysaccharides such as xanthan polymer and others is described in Zaikov book (Zaikov, 2005); while photodegradation details for these polymers are given in the literature (Geuskens, 1975; Rabek, 1975,1996; McNeill, 1992; Wach, Mitomo, Kudoh, Muroya, Kasumura, & Yoshi, 2005; Abo-Eisa, 2006).

Polysaccharides such as the polyelectrolyte of xanthan undergo photo-rheological change when exposed to ultraviolet (UV) radiation (Geuskens, 1975; Rabek, 1975,1996; McNeill, 1992; Wach, Mitomo, Kudoh, Muroya, Kasumura, & Yoshi, 2005; Abo-Eisa, 2006). A major cause of such change is the main chain scission. As a result, the molar mass and related parameters (McNeill, 1992; Rabek, 1996; Wach, et al., 2005 Abo-Eisa, 2006).

In our present investigation we report the effect of UV-radiation on structure-viscosity relationship for dilute xanthan in aqueous salt solutions, in terms of viscosity, molar mass and hydrodynamic parameters.

EXPERIMENTAL

Material and Mother Solution:

The powder material of xanthan was supplied by a local Libyan company (JOWF) and used without further purification. Three mother solutions (M, Muv & MPuv) each of 1 kg m^{-3} concentration were prepared by adding a known weight of the polymer to fixed volume of a double distilled water and dissolving with magnetic stirring. Some extra double distilled water was, then, added up to the required volume (Abo-Eisa, 2006).

UV- Irradiation:

The two mother solutions (M_{uv} & M_{puv}) were irradiated for 5 hours in air at room temperature by a Low Pressure Mercury Lamp, Type 93110, E27 of spectral lamp company, $\lambda = 185$ nm and $P = 6W$. Further details are described elsewhere (Rabek, 1996; Abo-Eisa, 2006).

Dilute Solutions:

The native and irradiated mother solutions (M , M_{uv} , M_{puv}), were each divided into ten parts. Then some extra double distilled water was added up to the required volume (Abo-Eisa, 2006).

Viscosity Measurements:

The accuracy of the viscosity measurements was ± 0.015 . The measured values were expressed in terms of relative (η_r) and, accordingly, in specific (η_{sp}) viscosities as follows (Kulicke, 2004):

$$t_{xanthan} / t_{solvent} = \eta_{xanthan} / \eta_{solvent} = \eta_r ; \eta_{sp} = \eta_r - 1,$$

where $t_{xanthan}$ = the solution efflux time of dilute xanthan in aqueous solution, $t_{solvent}$ = the solvent efflux time of aqueous solution, $\eta_{xanthan}$ = the solution viscosity of dilute xanthan in aqueous solution, $\eta_{solvent}$ = the solvent viscosity of aqueous solution, η_r = the relative solution viscosity of dilute xanthan in aqueous solutions, η_{sp} = the specific solution viscosity of dilute xanthan in aqueous solutions.

RESULTS AND DISCUSSION

The measured and calculated results are given in Figs 1, 2, 3 and 4, and Table 1.

Fig.1 demonstrates the progress of UV scission on the chain of xanthan in water. It suggests that the UV-irradiation had a very marked scission-in effect up to 270 min, for the upper plot, while the lower plot represents the post-irradiation effect (Geuskens, 1975; Rabek, 1975,1996; McNeill, 1992; Abo-Eisa, 2006).

Plots in Figs. 2 and 3 represent the native (higher) plots, irradiated (medialer) plots and post-irradiated (lower) plots of relative and specific viscosity values against concentration, respectively; all being increasing exponentially over the dilute concentration range involved, due to the cross-over and probably chains entanglement behaviour for the xanthan polymer (Berry, 1996; Fujita, 1997). On the other hand, the rate of increment in the viscosity values after UV-irradiation is less than those before UV-irradiation. This would accord with the calculated results, in Table 1, show that the values of intrinsic viscosity ($[\eta]$), Fuoss and Strauss constant (B), relative molar mass ($\langle M_v \rangle_r$), and hydrodynamic volume (V_h) of native dilute xanthan solution are greater than those of irradiated one. This could be attributed to the marked scission effect on the polymer chain.

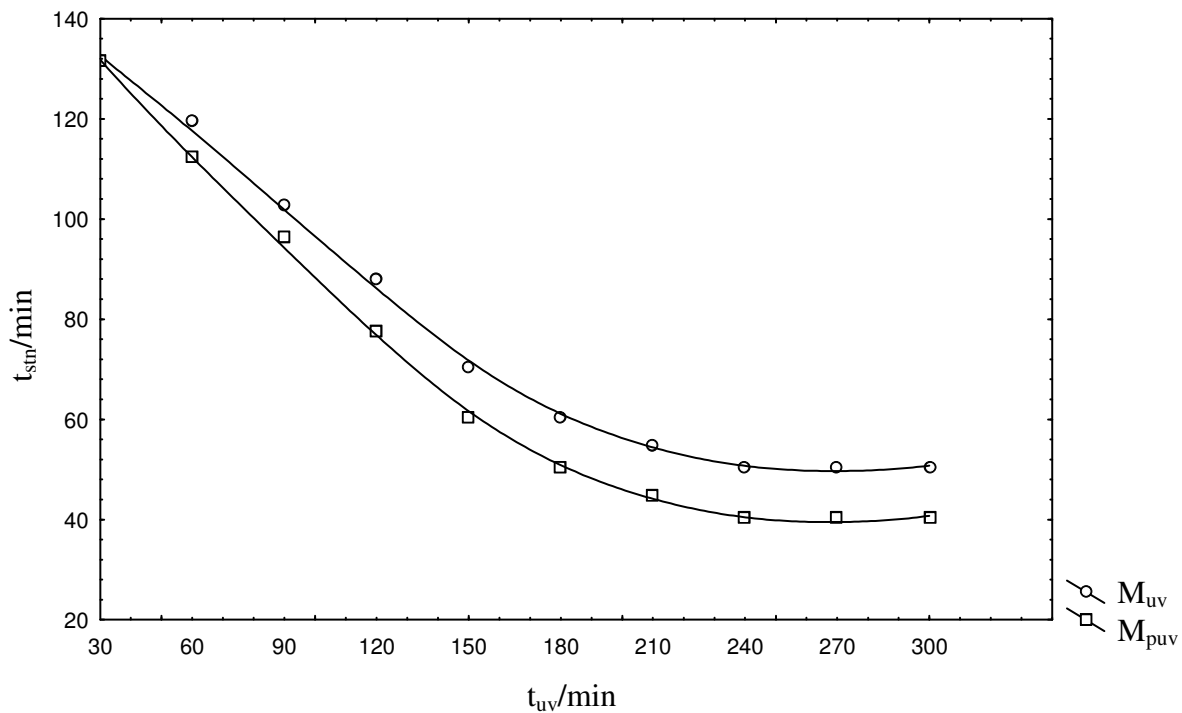


Fig. 1. UV-Exposure time vs efflux time for xanthan aqueous solution at 25 °C.

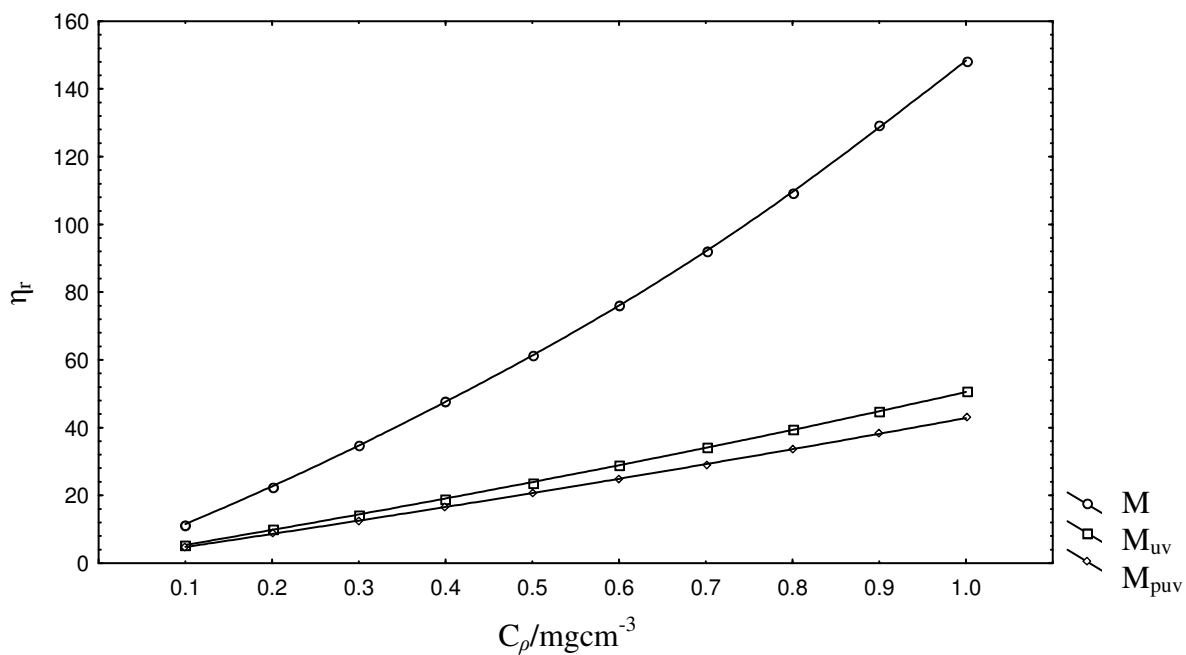


Fig. 2. Concentration vs relative viscosity for dilute xanthan salt-free aqueous solution before and after UV-irradiation at 25 °C.

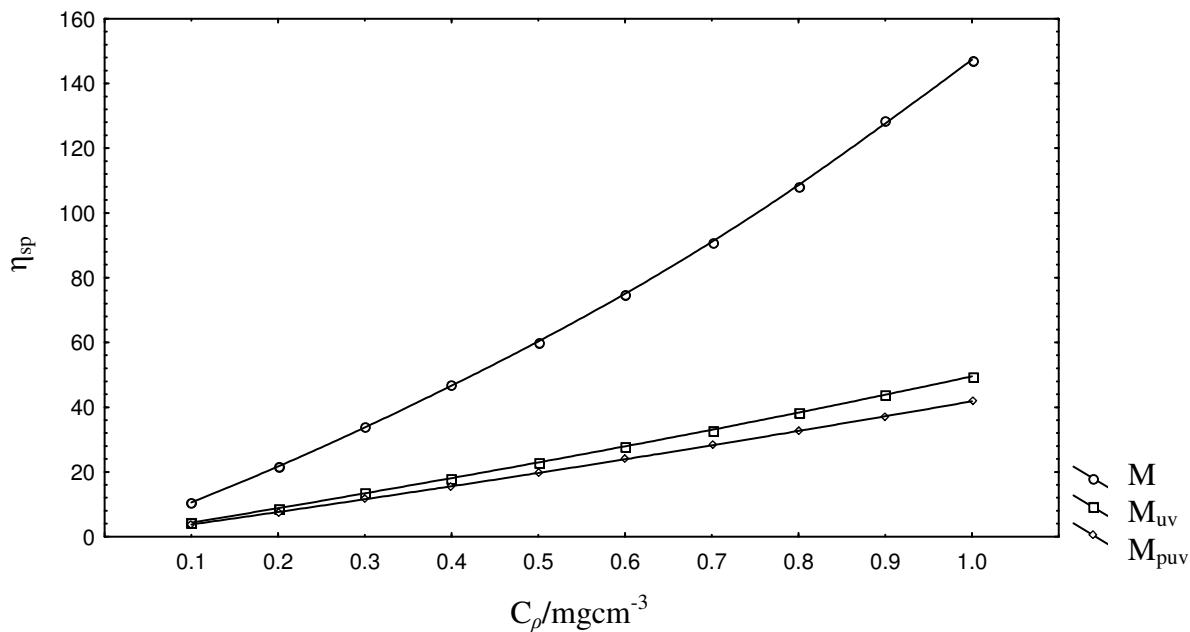


Fig. 3. Concentration vs specific viscosity for dilute xanthan salt- free aqueous solution before and after UV-irradiation at 25 °C.

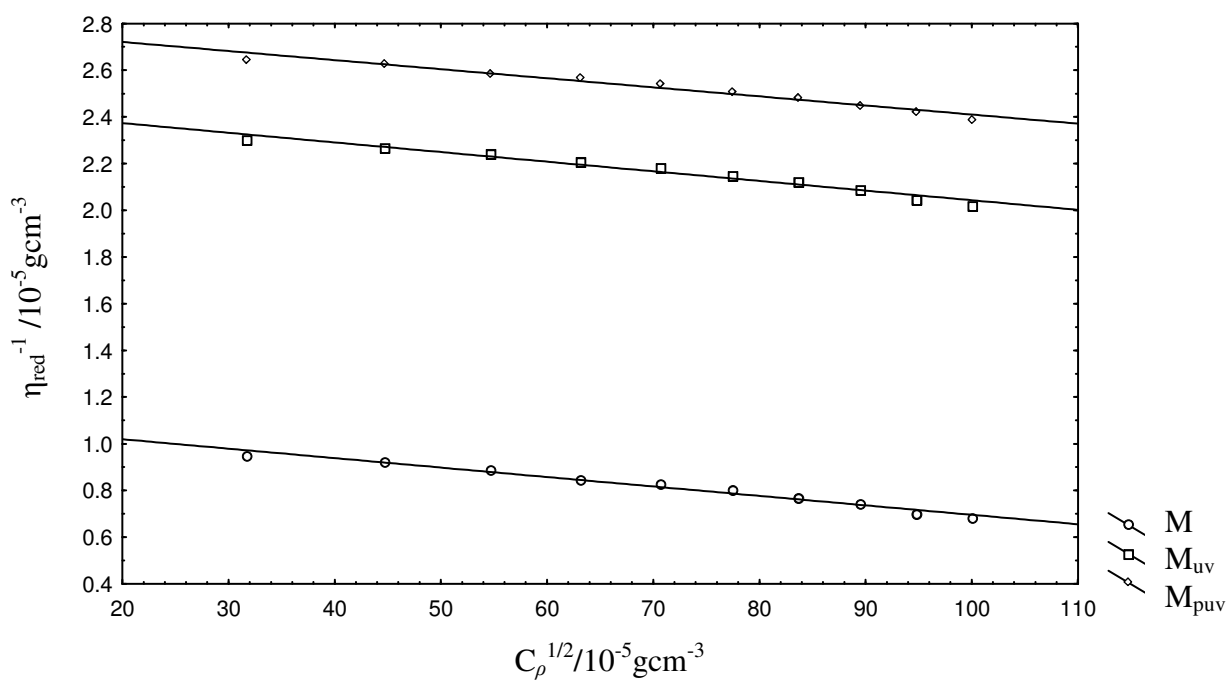


Fig. 4. Root square of mass concentration vs reciprocal of reduced viscosity for dilute xanthan salt- free aqueous solution before and after UV- irradiation at 25 °C.

Table 1. Intrinsic viscosity and related parameters for dilute xanthan salt-free aqueous solution before and after UV-irradiation at 25 °C.

Sample	$[\eta]/\text{cm}^3\text{g}^{-1}$	$B/10^{-4}\text{cm}^3\text{g}^{-1}$	$\langle M_v \rangle_r$	$V_h/10^{-18}\text{cm}^3$
M	90909.09	27.27	982042.01	349077.40
M_{uv}	40816.32	12.65	542650.42	86604.08
M_{puv}	35971.22	10.43	494161.88	69504.03

Furthermore, the values of intrinsic viscosity and Fuoss and Strauss constant in Table 1, were estimated from the typical linear plots of Fuoss and Strauss, in Fig. 4, according to the following equation (Fuoss & Strauss, 1943) :

$$\eta_{red} = A / (1 + B C_p^{1/2}), \quad (1)$$

where, η_{red} , is reduced viscosity, A, is represents the intrinsic viscosity.

In addition, the values of molar mass in Table 1, were calculated according to the following form of Mark-Houwink equation for helical conformation (Kim, Choi, Kim, & John, 1998):

$$[\eta] = 0.74 \times 10^{-3} \text{ g}^{-1} \text{ cm}^3 \langle M_v \rangle_r^{1.35}, \quad (2)$$

while, the values of hydrodynamic volume, V_h , for native and irradiated xanthan in aqueous solution in Table 1, were calculated according to the following expression (Kurata & Tsunashima, 1999; Kulicke, 2004; Abo-Eisa, 2006):

$$V_h = (2/5) [\eta] \langle M_v \rangle / N_A, \quad (3)$$

CONCLUSION

Xanthan in water undergoes chain scission in presence of ultraviolet radiation in air. The period of exposure time and post-irradiation effect have considerable influence on the amount of scission and consequently on the length of xanthan in water. Characterization of viscosities at 25 °C of the polymer in dilute salt-free aqueous solution before and after ultraviolet irradiation reveals the fact that UV-irradiation of xanthan induces degradation which in turn decreases the mass, size, extension configuration, solute-solute contact and increase the solute- solvent interpretation.

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