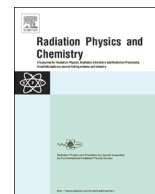




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# Influence of gamma-irradiation on thermally-induced mesoscopic gelation of degalactosylated xyloglucans

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## HIGHLIGHTS

- Influence of  $\gamma$ -irradiation on a partially degalactosylated xyloglucan is investigated.
- Molecular weight reduction is observed in the investigated dose range.
- Modification of the temperature-induced mesoscopic gelation kinetics is evidenced.

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## ABSTRACT

Thermoresponsive degalactosylated xyloglucans have been already proposed as in situ gelling scaffolds for tissue engineering, due to their reversible macroscopic thermal gelation at body temperature and biodegradability. The highly branched, hydroxyl group-rich molecular structure renders xyloglucans interesting raw materials also in the form of micro/nanoparticles for application as nanoscale drug delivery devices in cosmetic and pharmaceutical formulations. Owing to their natural source, xyloglucans show high average molecular weight, broad molecular weight distribution and poor water solubility, as large and compact aggregates usually form via inter-molecular hydrogen bonding. <sup>60</sup>Co  $\gamma$ -irradiation has been here applied to reduce the molecular weight. The aqueous solutions of irradiated xyloglucan were characterized by dynamic light scattering measurements and gel filtration chromatography. The aggregation kinetics at 37 °C were studied by dynamic light scattering measurements to confirm the temperature-responsive behavior of this polymer even when dispersed in water at low concentration after  $\gamma$ -irradiation. Irradiation dose–molecular properties relationship has been sought.

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## 1. Introduction

Xyloglucan derived from tamarind seeds is a polysaccharide composed of a (1–4)- $\beta$ -D-glucan backbone chain with (1–6)- $\alpha$ -D-xylose branches partially substituted by (1–2)- $\beta$ -D-galactoxylose. Due to its ability to act as thickener and stabilizing agent (Dea, 1989; Mishra and Malhotra, 2009), xyloglucan has a large number of commercial and industrial applications as food and cosmetic additive. Xyloglucan from tamarind seeds is also known for its biological activity as hypolipidemic and antidiabetic agent. Similarly to other hydrocolloids, xyloglucan is capable of altering the physiology of the intestinal tract and reducing the absorption of nutrients (Yamatoya et al., 1997).

Xyloglucan properties are dependent on the average molecular weight, as often observed with other polysaccharides. When xyloglucan is partially degraded by fungal  $\beta$ -galactosidase to remove more than 35% of the galactose residues, it exhibits a thermally reversible transition from sol to gel in aqueous solutions at concentration above 1–2 wt%. At 44% galactose removal ratio, a sol–gel transition occurs at about 20 °C with a large thermal hysteresis. This property makes xyloglucan particularly attractive for biomedical applications (Shirakawa et al., 1998).

Differently from other natural biopolymers, such as cellulose (Charlesby, 2003), starch (Michel et al., 1980) and chitosan (Choi et al., 2002), there are fewer studies on the application of irradiative methods on xyloglucans to reduce the molecular weight (Vodenicarova et al., 2006; Patel et al., 2008). A comparative investigation on the effects of different radiation sources, namely ultrasound,  $\gamma$ -irradiation and microwave heating, on xyloglucan structural and molecular properties, had shown that ultrasonication and relatively low dose  $\gamma$ -irradiation in air are the

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most convenient methods of reducing the molecular weight without altering the chemical structure and thermal responsiveness. When  $\gamma$ -irradiation was performed at doses higher than 40 kGy, unsaturated structures of higher molecular mass were observed (Vodenicarova et al., 2006).

More recently, xyloglucans were subjected to  $\gamma$ -irradiation in the 10–70 kGy dose range. It was observed that doses up to 50 kGy caused no significant change in the degree of branching of the residual polymer chains, while a small increase of branching was detected at doses above 50 kGy (Patel et al., 2008).

In present paper the influence of  $\gamma$ -irradiation in air and in the 10–60 kGy dose range on water-solubility of a partially degalactosylated xyloglucan was evaluated for the first time. Thermally induced aggregation kinetics of dispersions prepared with either irradiated or non-irradiated polymer were also investigated.

## 2. Experimental

### 2.1. Materials and irradiation experiments

Xyloglucan with a galactose removal ratio of 44% (Deg-XG) was kindly provided by DSP Gokyo, Food and Chemical Co, Japan. Measurements were performed on the “untreated”, as received polymer (NP) and on the same material after application of an extensive purification method consisting in (i) dissolution at low concentration (0.1 wt%) in deionized water followed by homogenization at 5 °C for 5 h at 13,500 rpm, (ii) autoclaving at 120 °C for 20 min, (iii) centrifugation at 8000 rpm for 15 min, (iv) extensive dialysis against deionised water and (v) freeze drying. The polymer recovered after this procedure is named as “P”. Aqueous Deg-XG dispersions at 0.1, 0.25 and 0.5 wt% were prepared through homogenization of the powder in water at 5 °C for 5 h at 13,500 rpm. Samples were always stored at 5 °C. The effects of centrifugation at 8000 rpm for 45 min on the “untreated” material (NP-C) and of autoclaving at 120 °C for 20 min on both the “untreated” (NP-A) and “purified” polymer (P-A) were also investigated.

Deg-XG powder was  $\gamma$ -irradiated in air at room temperature using a  $^{60}\text{Co}$  source (Gamma Chamber 5000, Institute of Nuclear Chemistry and Technology, Warsaw, Poland) at 8 kGy/h and irradiation doses of 10, 20, 40 and 60 kGy. Samples of irradiated Deg-XG were prepared by dissolving the powder in cold water, homogenizing as described before and centrifuging at 8000 rpm for 45 min.

### 2.2. Dynamic light scattering measurements

The hydrodynamic radius ( $R_h$ ) of the particles in dispersion was measured by dynamic light scattering (DLS) using a Brookhaven Instrument BI200-SM goniometer. Samples were put in the thermostated cell compartment of the instrument and the effect of temperature was investigated in the range 15–37 °C. Average scattered light intensity and intensity autocorrelation function were measured at 90° scattering angle by using a Brookhaven BI-9000 correlator and a 100 mW solid-state laser (Quantum-Ventus MPC 6000) tuned at  $\lambda=532$  nm. The correlator was operated in the multi- $\tau$  mode and the experimental duration was set to have at least 2000 counts on the last channel of the correlation function. All samples were filtered through 5  $\mu\text{m}$  cellulose acetate (Millipore) syringe filters to remove gross contaminants. DLS data were analyzed by the method of cumulants. According to this method, the logarithm of the field-correlation function is expressed in terms of a polynomial in the delay time  $\tau$ , with the first and second cumulant providing information on the mean value and standard deviation of the distribution of particles hydrodynamic size (Koppel, 1972).

### 2.3. Gel filtration chromatography

The chromatographic profile was obtained by using two Shodex SB HQ columns in series (806 and 804) thermostated at 15 °C with a Knauer oven and connected to a HPLC device (LC-2010 AT Prominence, Shimadzu, Kyoto, Japan) equipped with a 50  $\mu\text{l}$  sample loop. All samples were eluted with 0.02% sodium azide solution at 0.5 ml/min and the refractive index was recorded with a Smartline RI detector 2300 Knauer.

## 3. Results and discussion

### 3.1. Influence of preparation protocol on Deg-XG solubility

The preparation of homogenous aqueous solutions of Deg-XG is a difficult task due to the strong intermolecular interactions that prevent a full solubilization of the individual polymer chains (Lang et al., 1993). We observed that polymer aggregates were present in solution even after a prolonged homogenization at sub-ambient temperature (5 °C) and tended to precipitate upon storage at 5 °C. Centrifugation at 8000 rpm for 45 min was found effective in inducing the phase separation of a solid deposit, that was estimated to be about 4 wt% of the initial polymer content. Centrifuged samples remained stable against deposit formation even after a prolonged storage at 5 °C. DLS measurements at 15 °C were done to evaluate the average hydrodynamic size of Deg-XG in water at three concentrations. The measurements on non-centrifuged samples were done immediately after cold homogenization (5 °C) for 5 h. Table 1 reports the average value and standard deviation of the diameter distribution of Deg-XG in water before centrifuging (NP) and in the supernatant solution after centrifuging (NP-C). The hydrodynamic diameter increases significantly with polymer concentration, and it is always much smaller in centrifuged samples even though the percentage reduction is minor at larger concentration.

A purification protocol was developed to remove the impurities present in the feedstock material and evidenced by transmission microscopy studies on thin films (unpublished data). The purification process yields 70–75% of recovered product. Aqueous dispersion of purified polymer proved more stable since the sediment formation was no longer observed. The hydrodynamic size of the purified polymer was found slightly smaller than that of the untreated polymer, as shown in Table 2. This suggests that the large value of the hydrodynamic size mainly reflects the strong inter-chain interactions that establish in the dry state and cannot be easily reverted by water addition. As next step, we checked if very high temperatures have some effect in reducing the average size, as suggested by the existence of an UCST at  $\sim 100$  °C in the phase diagram of Deg-XG aqueous solutions at 44% galactose removal ratio (Shirakawa et al., 1998). Solutions of both un-treated and purified variants were autoclaved at 120 °C and the average diameter was determined at 15 °C by DLS measurements. Data reported in Table 2 show that autoclaving always caused a significant reduction of the particles' size for both the purified and non-purified systems, even though the effect was lower than

**Table 1**  
Dependence on the average hydrodynamic diameter on polymer concentration before (b.c.) and after centrifuging (a.c.).

Concentration [wt%]	Dh [nm] (std. dev. [%]) b.c.	Dh [nm] (std. dev. [%]) a.c.	$-(Dh_f - Dh_i)/Dh_i$ (%)
0.1	407 (36.8)	204 (33.7)	49.9
0.25	704 (44.9)	516 (48.4)	26.7
0.5	2192 (40.1)	1791 (46.9)	18.3

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