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# Degradation of starch by polarised light

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**Abstract**

Aqueous suspensions of either original corn starch (30%, w/w), or starch heated for 2 h at 120°C in water, were illuminated by linearly polarised visible (>500 nm) light for 5–25 h. Molecular weights ($\bar{M}_w$) and radii of gyration ($\bar{R}_g$) for amylopectin, intermediate and amylose fractions of illuminated starches were measured by high-pressure size exclusion chromatography, coupled with multi-angle laser light scattering and refractive index detectors. Average molecular weight ($\bar{M}_w$) and radii of gyration ($\bar{R}_g$) of amylopectin fraction for original starch was $2.08 \times 10^8$ and 214 nm, respectively. Similar values were found for samples that were illuminated for 5 h ($2.14 \times 10^8$ and 211 nm). After 25 h of illumination decrease in $\bar{M}_w$ ($5.71 \times 10^7$) and $\bar{R}_g$ (122 nm) was observed. Prolonged illumination, for 50 h, led to an increase in both $\bar{M}_w$ ($9.38 \times 10^7$) and $\bar{R}_g$ (150 nm) values. The molecular weight and radius of gyration of the amylopectin fraction of the original corn starch heated for 2 h at 120°C ($7.90 \times 10^7$ and 133 nm, respectively) were lower than for the original starch. Illumination of preheated starch led, after first 5 h, to a further decrease in $\bar{M}_w$ ($4.87 \times 10^7$) and $\bar{R}_g$ (101 nm), followed by a rise in both values after 25 ($8.97 \times 10^7$; 146 nm) and 50 h ($9.69 \times 10^7$; 147) of illumination. The differences in the pasting properties of the original sample, and samples illuminated for 5 as well as 50 h were negligible; only the starch sample illuminated for 25 h produced gels of essentially different rheology. Illumination of preheated starch produced more significant changes in the rheology of corresponding pastes, regardless of the period of sample illumination. The effect of illumination upon the thermal properties of starch, could be observed solely as the decrease in the onset temperature for the sample illuminated for 50 h. 

*Keywords*: Corn starch; Starch degradation; Illuminated starch

## 1. Introduction

Degradation of starch is one among the common targets of starch processing. It provides a wide spectrum of products from white (thin-boiled) through yellow dextrins up to D-maltose and D-glucose. Degradation is a typical energy-requiring process. Application of a given energy source is a convenient way of degradation control, and it provides the required products.

Among several energy sources, thermolysis and thermolysis combined with action of chemicals were, perhaps, the first and most common method of starch degradation to dextrins (Tomasik, Wiejak & Palasinski, 1989). Apart from biotechnological (enzymatic) methods, which have recently gained priority, there are several other more or less conventional methods of starch degradation to dextrins, lower oligosaccharides and D-glucose. The sources of energy, which can be involved are: the solvent effect, mechanical energy (mechanochemistry), irradiation of starch with neutrons, X-ray, high-energy electrons, γ-rays, visible and ultraviolet light, freezing, infrared radiation, microwave radiation, ultrasounds, silent electrical discharge, and heat–moisture–pressure treatment (extrusion) (Tomasik & Zaranyika, 1995). Energy from the interaction of chemicals, particularly protons, i.e. acid catalysed starch hydrolysis, is also frequently used for the manufacture of dextrins and glucose syrups. As a matter of fact, the majority of chemical modifications to starch is accompanied by starch degradation (Tomasik & Schilling, 1999).

In this study, visible, polarised light as a source of energy has gained our attention. It was observed (Semmens, 1947) that moonlight, assumed to be a source of polarised light, decomposed starch. Recently, Hartmann and Mollwo (1998) reported that moon and starlight stimulated the germination of sensitised lettuce seeds. The effect observed could be either directly or indirectly related to the degradation of starch, playing a common role of energy reserve for plants. Although Navez and Rubenstein (1928) documented that moonlight acted via activation of starch degrading enzymes, there is also a report (Weigel & Plath, 1986) that low-intensity 460 nm light produced a photochemical

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Table 1
Melting temperatures and enthalpy for native and linear polarised visible light illuminated starch (means of three independent experiments ± standard deviation; means within columns with different indices are significantly different at $P < 0.05$

| Sample | Temperature | | | Transition enthalpy $\Delta H$ (J/g) |
|---|---|---|---|---|
| | $T_o$ (°C) | $T_p$ (°C) | $T_c$ (°C) | |
| Native | 60.5 ± 0.4 A | 66.5 ± 0.3A | 72.6 ± 0.4A | 12.25 ± 0.25B |
| PLN 5 | 60.1 ± 0.3A | 65.3 ± 0.4B | 71.2 ± 0.4B | 14.55 ± 0.64A |
| PLN 25 | 58.9 ± 0.5B | 65.8 ± 0.4A,B | 71.2 ± 0.5B | 12.67 ± 0.24B |
| PLN 50 | 50.0 ± .05A | 66.2 ± 0.6A | 71.3 ± .03B | 12.72 ± 0.25B |
| PLA 50 | 59.8 ± 0.3C | 66.1 ± 0.2A | 61.4 ± 0.4C | 11.55 ± 0.30C |

oscillating reaction a having sine-wave character. This information prompted us to re-examine the effect of polarised light on starch.

## 2. Materials and methods

### 2.1. Materials

Normal corn starch (approximately 25% of amylose) was purchased from Samyang Genex (Seoul, Korea). Bovine serum albumin (BSA), pullulan (P-100), and dextrans (D-580 and D-2000) of known molecular weights were purchased from Sigma Chemical Co.(St. Louis, MO, USA). In some pasting experiments (HPSEC-MALLS-RI) before illumination, solid starch was heated for 2 h at 120°C in a convection oven.

### 2.2. Illuminations

Aqueous corn starch slurry (250 ml, 30% w/w) was illuminated from a distance of 30 cm, with the slit illuminator KB 502 (Kabid, Chorzow, Poland) equipped with a 150 W xenon arc lamp XBO 150 (Oriel, England). The HN 22 linear polarising filter (Polaroid, USA), with glass filter cutting out wavelengths below 500 nm was mounted between the slit illuminator and sample. Illumination was carried out, on agitation, under nitrogen (5 ml/min) for 5, 15, 25 and 50 h at 25°C. For comparison, suspensions were illuminated in air for 50 h (5 ml/min). Illuminated starch was filtered (Whatman 41, England) under reduced pressure, then dried at 50°C for 24 h.

The light source emitted continuous intensity in the visible range. Its energy flux at the place of the samples was 8 mW/cm$^2$ as checked by a YSI radiometer (Yellow Springs, USA).

### 2.3. Thermal properties

Thermal properties of original and illuminated corn starch were determined using a differential scanning calorimeter DSC 6100 (Seiko Instruments, Osaka, Japan). The starch (1.5–2.0 mg) was sealed in an aluminium pan with water in the ratio of 1:4 (starch/water, w/w ratio). Samples were heated at 10°C/min, the rate of temperature increase was from 25 to 125°C. An empty pan was used as reference.

### 2.4. Pasting properties

Pasting curves of original and illuminated corn starch (8%, w/w) were measured with a Rapid Viscoanalyzer (RVA, Newport Scientific, Newport, Australia). The starch suspensions were heated at the rate of 3.5°C/min up to 95°C, were maintained at this temperature for 10 min, cooled to 50°C at the rate of 4.5°C/min, and held for 10 min.

#### 2.4.1. HPSEC-MALLS-RI

High performance size exclusion column chromatography (HPSEC) system consisted of a pump (P2000, Spectra System, Palo Alto, USA), an injection valve (model 7021, Rheodyne, Palo Alto, USA), a guard column (TSK PWH, Tosoh Corporation, Tokyo, Japan), and an SEC column TSK Gel 5000 PW (7.8 × 300 mm, Tosoh Corporation, Tokyo, Japan). A multi-angle laser light scattering (MALLS) detector Dawn-DSP-F (Wyatt Technology, Santa Barbara CA, USA) and a differential refractive index (RI) detector (Model SE71, Shodex, Tokyo, Japan) were connected to the columns. Columns were maintained at 50°C, and the RI detector at 35°C. The mobile phase (0.15 M $NaNO_3$ with 0.02% sodium azide in water) was filtered off, first through 0.2 μm and then through 0.1 μm cellulose acetate filters (Whatman, England). The flow rate of the mobile phase and sample injection volume was 0.5 ml/min and 500 μL, respectively. The output voltage of the RI and light scattering (LS), at 18 angles, was used for calculating the weight-average molecular weight ($\bar{M}_w$) and radius of gyration ($\bar{R}_g$) using Astra 4.50 software (Wyatt Technology, Santa Barbara, CA, USA). A Berry plot with third-order polynomial fit was used to calculate ($\bar{M}_w$) and ($\bar{R}_g$) values (Aberle, Burchard, Vorwerg & Radosta, 1994; Bello-Perez, Paredes-Lopez, Roger & Colonna, 1996a; Hanselmann, Ehrat & Widmer, 1995)

### 2.5. Calibration of the detector

The calibration constant for the RI detector was determined by the injection into the detector, of five (0.05 ~ 0.50 mg/ml) aqueous NaCl solutions of known concentration. The output voltage from the detector was

Table 2
Weight average molecular weight ($M_w$), radius of gyration ($R_g$) and peak viscosity of original and illuminated corn starch (means of three independent experiments ± standard deviation; means within columns with different indices are significantly different at $P < 0.05$)

| Sample (recovery from SEC columns (%)) | $M_w \times 10^7$ Whole peak | $M_w \times 10^7$ Amylopectin | $M_w \times 10^7$ Intermediate | $M_w \times 10^6$ Amylose | $R_g$ Amylopectin (nm) | $R_g$ Intermediate (nm) | $R_g$ Amylose (nm) | Peak viscosity, (RVI units) |
|---|---|---|---|---|---|---|---|---|
| Native (65) | 13.40 ± 0.25A | 20.82 ± 0.40B | 2.00 ± 0.10A | 6.20 ± 0.20A | 214.4 ± 5.6A | 98.3 ± 4.0A | 113.0 ± 4.9C | 82.3 ± 1.2A |
| PLN 5 (65) | 12.30 ± 0.30B | 21.43 ± 0.50A | 1.03 ± 0.09B,C | 3.87 ± 0.35B | 211.3 ± 6.0A | 92.0 ± 5.2A | 152.5 ± 5.6A | 82.9 ± 3.5A |
| PLN 25 (73) | 2.80 ± 0.15D | 5.71 ± 0.20F | 0.33 ± 0.05F | 1.33 ± 0.20E | 122.1 ± 4.2D | 47.4 ± 3.6C | 69.2 ± 4.0E | 58.1 ± 2.3B |
| PLN 50 (70) | 12.40 ± 0.30B | 9.38 ± 0.15C,D | 0.94 ± 0.09C,D | 2.71 ± 0.32C | 150.2 ± 3.6B | 62.8 ± 4.0B | 91.1 ± 3.5D | 83.4 ± 2.3A |
| PLA 50 (68) | 12.30 ± 0.45B | 21.30 ± 0.23A | 1.90 ± 0.08A | 5.90 ± 0.40A | 207.0 ± 5.2A | 94.5 ± 5.0A | 123.7 ± 4.5B | 83.7 ± 3.0A |
| HN (75) | 2.99 ± 0.30D | 7.90 ± 0.15E | 0.87 ± 0.06D,E | 1.43 ± 0.35D,E | 132.9 ± 6.7C | 60.2 ± 5.5B | 88.5 ± 2.5D | 11.8 ± 1.2D |
| HPLN 5 (75) | 1.87 ± 0.20E | 4.87 ± 0.10G | 0.87 ± 0.05D,E | 2.47 ± 0.40C | 101.5 ± 5.5E | 49.0 ± 3.5C | 89.4 ± 3.0D | 7.9 ± 1.5E |
| HPLN 25 (69) | 4.30 ± 0.40C | 8.97 ± 0.15D | 1.12 ± 0.06B | 1.11 ± 0.15E | 146.6 ± 5.8B | 59.6 ± 4.0B | 41.4 ± 3.0F | 38.3 ± 2.0C |
| HPLN 50 (72) | 3.87 ± 0.35C | 9.69 ± 0.10C | 0.78 ± 0.05E | 1.87 ± 0.20D | 147.1 ± 6.0B | 58.6 ± 3.6B | 91.9 ± 3.5D | 36.7 ± 1.8C |

collected by Rical 2 software (Wyatt Technology, Santa Barbara, CA, USA) and the calibration constant was calculated from the slope of the graph of $n = c\ \mathrm{d}n/\mathrm{d}c$ vs voltage. The following values of $\mathrm{d}n/\mathrm{d}c$ (the change in refractive index with concentration) were used in calculating ($\bar{M}_w$) and ($\bar{R}_g$): pullulan 0.148, dextran 0.142, and starch 0.146. The LS calibration constant for the diode at 90° was obtained measuring the LS intensity of toluene. Normalisation of the response of the photodiodes, arranged around the scattering cell to the diode at 90°, was carried out using BSA. One pullulan and two dextran standards were applied for testing the accuracy of the calibration.

All the injected standards are recovered, over 95%. The determined $M_w$ were $9.9 \times 10^5$, $6.2 \times 10^5$, $2.0 \times 10^6$ for pullulan P-100, dextrans D-580, and D-2000, respectively. These estimations were a good match with those given by the manufacturer ($9.8 \times 10^5$, $5.8 \times 10^5$, and $2.0 \times 10^6$, respectively). Recovery of the starch samples was in the range 65–75% (Table 2).

Calculations were made using the Berry equation with the third-order polynomial.

### 2.6. Sample preparation for HPSEC

Moisturised starch (1 g) with 10 ml of water was suspended in dimethylsulfoxide (DMSO, 90 ml), boiled for 2 h, and stirred in an after bath. Then, the starch solution was stirred for 24 h at 25°C, followed by the addition of abs. alcohol (500 ml) for precipitation of the starch. The precipitate was centrifuged (2500 rpm, 20 min), washed three times with ethanol, and dried overnight under vacuum, at room temperature. The purified starch (~5 mg) was moistened with abs. ethanol (200 μL) and dissolved in 2 M NaOH (1 ml) by stirring at 70°C for 1 h. An aliquot of 0.15 M $NaNO_3$ (17 ml) was then added. The starch solution, after neutralisation with 2 M HCl (1 ml), was diluted with 0.15 M $NaNO_3$ to obtain a final concentration of about 0.24 mg/ml. Prior to the HPSEC injection, the solution was filtered through 0.8 μm cellulose acetate filter Duncan's new multiple range test was used for comparing the sample means.

## 3. Results and discussion

### 3.1. Thermal properties

Table 1 gives the onset ($T_o$), peak ($T_p$), conclusion ($T_c$) and transition enthalpy ($\Delta H$) for the melting of native and visible polarised light irradiated starches. Transition enthalpy and melting temperatures for native starch and samples irradiated for 5 (PLN 5), and 25 h (PLN 25), were almost identical. The samples irradiated for 50 h (PLN 50) showed lower onset temperature (50.04°C) than the native samples (60.50°C). These data indicated that polarised light did not affect the crystalline structure of the starch granule.

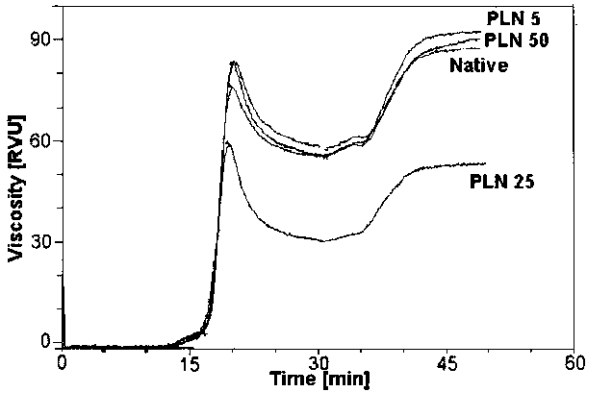


Fig. 1. Viscosity profiles obtained by Rapid Viscoanalyzer for original corn starch (native) and the starch illuminated for 5 (PLN5), 25 (PLN25) and 50 h (PLN50) under nitrogen.

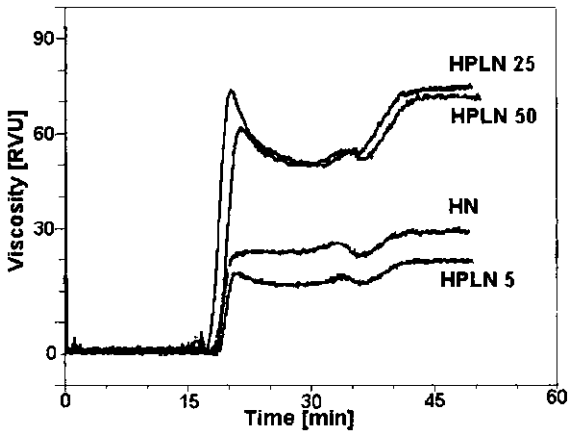


Fig. 2. Viscosity profiles obtained by Rapid Viscoanalyzer for preheated original corn starch (HN) and preheated starch illuminated for 5 (HPLN5), 25 (HPLN25) and 50 h (HPLN50) under nitrogen.

### 3.2. Pasting properties

Pasting properties were determined for illuminated and non-illuminated original starch, the latter was soaked in water for the same time period as that of illumination. Paste viscosity of the samples, illuminated for 5 (PLN 5) and 50 h (PLN 50), were similar to that of the original starch. The decrease in paste viscosity for the sample illuminated for 25 h (PLN 25), was observed. Viscosity profiles for the original starch and PLN 25 and PLN 50 samples are given in Fig. 1.

For preheated (120°C, 2 h) original starch, (HN) a significant decrease in paste viscosity was observed. Further, a decrease in paste viscosity was noted for the preheated original starch illuminated with polarised light for 5 h (HPLN 5). Samples illuminated for 25 and 50 h (HPLN 25 and HPLN 50, respectively) showed noticeably higher viscosity than the heated original starch. Pasting profiles for samples HN, HPLN 5, HPLN 25, and HPLN 50 are presented in Fig. 2.

### 3.3. Molecular weight distribution

Superimposed chromatograms of original corn starch taken with the RI detector and LS detector diode at a 90° angle, are given in Fig. 3. Based on the pattern, the peak was arbitrarily divided into three regions attributed to amylopectin, intermediate and amylose fractions. Chromatograms of illuminated samples resembled that of the native starch. Therefore, the same approach was applied for all-illuminated samples. The ($\bar{M}_w$) and ($\bar{R}_g$) were calculated for the whole complex peak of eluate and for each of its regions. The ($\bar{M}_w$) and ($\bar{R}_g$) for the original and illuminated samples are given in Table 2. The absolute molecular weights of particles above $10^8$, and with a radii of above 300 nm are determined with the Berry plot with an error exceeding 20% (Hanselman et al., 1995). Therefore, $M_W$ and $R_g$ values within such regions, should be understood as estimations or apparent values of molecular weight and radius of gyration (Bello-Perez, Colonna, Roger and Paredes-Lopez, 1998).

Molecular weight patterns of starch illuminated on aeration did not change, even after 50 h of illumination (PLA50). The sample illuminated under nitrogen for 5 h (PLN 5) had a slightly lower molecular weight calculated for the whole peak ($1.23 \times 10^8$), than the original starch ($1.34 \times 10^8$). Significantly lower $M_w$ and $R_g$ for all regions established on the chromatogram, were observed for samples illuminated for 25 h (PLN25). Amylopectin, intermediate and amylose fractions, in samples illuminated for 50 h (PLN 50), had higher molecular weights than the fractions in sample PLN 25.

It could be assumed, at first, that polarised light depolymerised polysaccharide chains, followed by crosslinking when higher doses of energy were absorbed. An analysis of the molar mass distribution supported this assumption, although Praznik and Huber (1998) considered this kind of phenomenon as an artefact, resulting from the strong interactions between lower molecular-weight components. Data from both RI and LS detectors provided calculations of cumulative and differential molar mass distribution using Astra 4.50 software. The Cumulative distribution $W(M)$ was a weight fraction of the sample of molar mass, less than M. The differential molar mass distribution gave the amount of material (differential weight fraction) in a given molar mass interval. Differential molar mass distribution $x(M)$ was calculated using the following equation (Schrott, 1993):

$$x(M) = \frac{dW(M)}{d(\log M)} = \frac{-h(V)}{f(V)}$$

where $h(V)$ was the normalised concentration at volume of $V$, and $f(v) = d(\log M)/dV$ was the slope of the calibration curve determined by the light scattering measurements. Normalised concentrations $h(V)$ were given by

$$h(V) = c_i/\Sigma c_i \Delta V$$

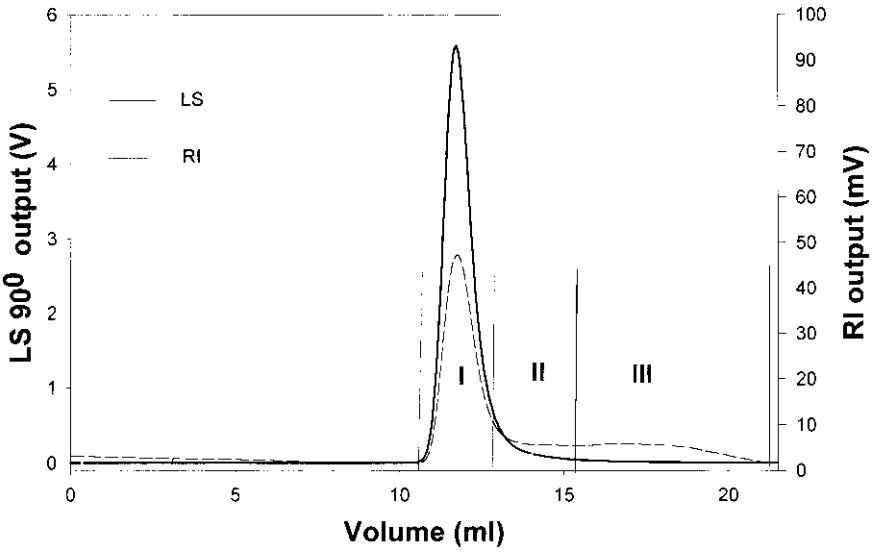


Fig. 3. Superimposed chromatograms of RI and LS at 90° detector outputs for original corn starch eluted from size exclusion columns. Regions I, II and III were established for amylopectin, intermediate and amylose fractions, respectively.

where $c_i$ was concentration of eluate (slice) i at 500 μl volume, and $\delta V$ was the volume per slice.

The plots of cumulative and differential molar mass distribution for original starch and samples illuminated with polarised light for 5 (PLN 5), 25 (PLN 25) and 50 h (PLN50) are given in Figs. 4 and 5, respectively. In the sample illuminated for 25 h (PLN 25), fragmentation of amylopectin chains took place, and low molecular weight ($<5\times10^5$) molecules resulting from such fragmentation constituted the essential fraction of the sample. Prolonged illumination led to apparent crosslinking. In PLN 50, the number of highest molecular weight molecules increased in the amylopectin region, as compared to PLN 25. A comparison of molecular distribution for PLN 50 and 25 showed that the sample illuminated for 50 h did not contain molecules of low molecular weight. It was not clear whether smaller chains combined with each other to form larger molecules, or they combined with existing amylopectin chains (Praznik & Huber, 1998). The heating of starch granules led to the depolymerisation of the polysaccharide chains. Molecular weights calculated for the entire eluted peak and three fractions of preheated original corn starch (HN), were much lower than for the original corn starch (see Fig. 3). A further decrease in molecular weights, indicating

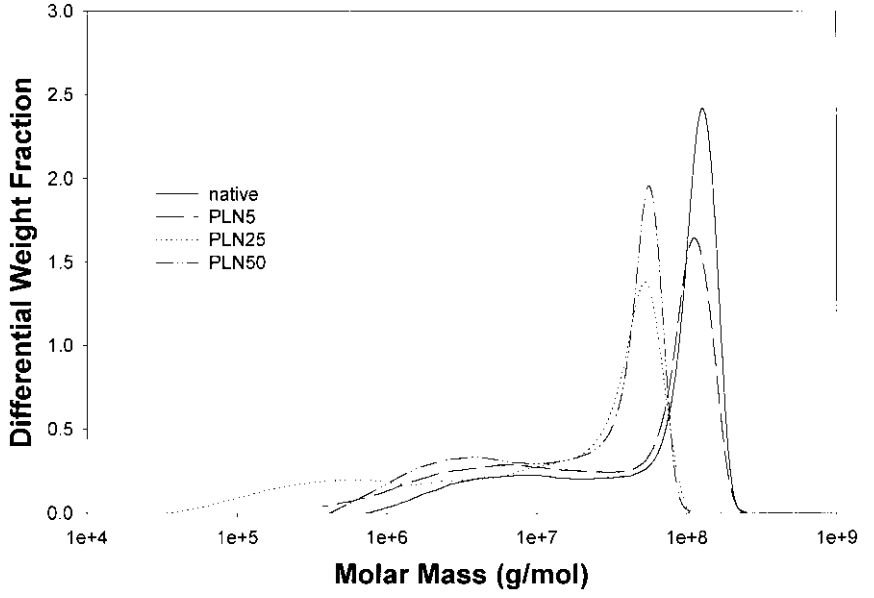


Fig. 4. Plots of differential weight fraction vs elution volume for original corn starch (native) and starch illuminated for 5 (PLN5), 25 (PLN25) and 50 h (PLN50).

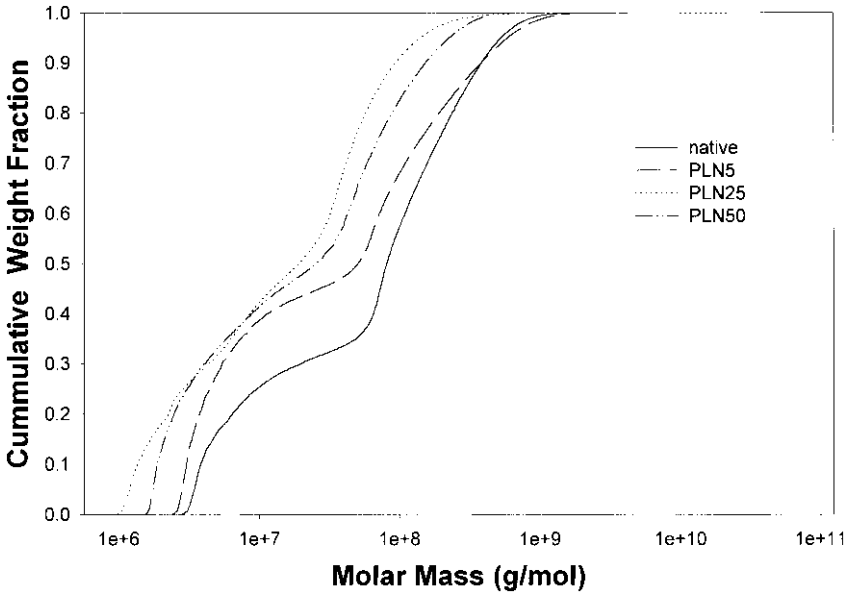


Fig. 5. Plots of cumulative weight fraction vs elution volume for original corn starch (native) and starch illuminated for 5 (PLN5), 25 (PLN25) and 50 h (PLN50).

depolymerisation on illumination of polysaccharide chains, was observed for sample HPLN 5 in all regions of the chromatogram. Further illumination led to crosslinking taking place, mainly in amylopectin chains. Molecular weights calculated for the entire eluted peak for HPLN 25 ($4.3 \times 10^7$) and HPLN 50 ($3.9 \times 10^7$) were similar, but molecular weight of amylopectin fraction calculated for HPLN 50 ($9.7 \times 10^7$) was significantly higher than for HPLN 25 ($8.9 \times 10^7$). However, plots of cumulative (Fig. 6) and differential (Fig. 7) weight fractions vs molar mass for HN, HPLN 5, HPLN 25 and HPLN 50, revealed that the amylose fraction of HPLN 50 contained much higher molecular weight molecules than the HPLN 25 sample. It indicated that the apparent crosslinking involved not only the amylopectin chains.

Changes in $\bar{R}_g$ values of illuminated starches match up with the changes in $\bar{M}_w$, described above. Additional information, about fractal dimensions of the particles could be derived from the double logarithmic plot of radius of gyration vs. molecular weight, of particular molecules. A straight line would indicate particle fractal dimensions which do not change in the observed size region. Its corresponding slope is defined as $\nu = 1/D_{frac}$ where $D_{fract}$ denotes the fractal dimension. According to fractal theory

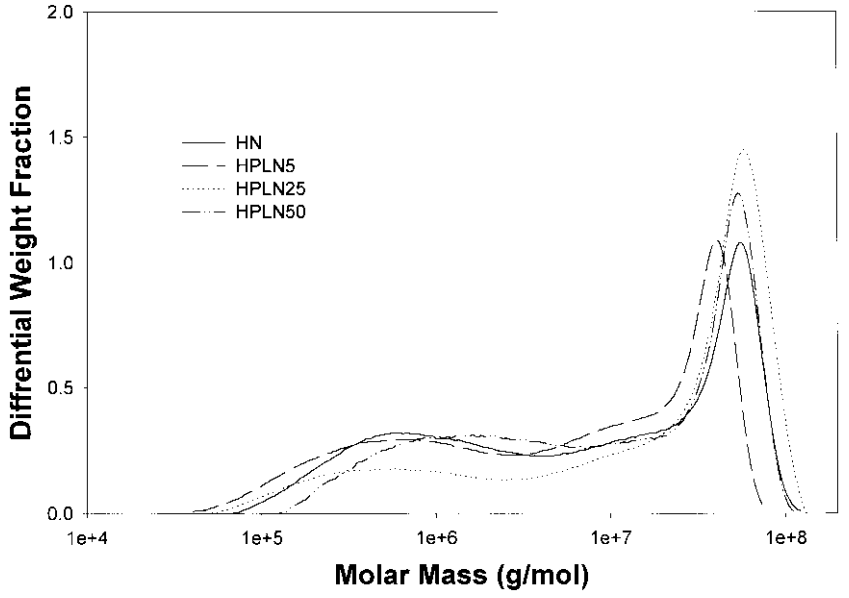


Fig. 6. Plots of differential weight fraction vs elution volume for preheated original corn starch (HN) and preheated starch illuminated for 5 (HPLN5), 25 (HPLN25) and 50 h (HPLN50).

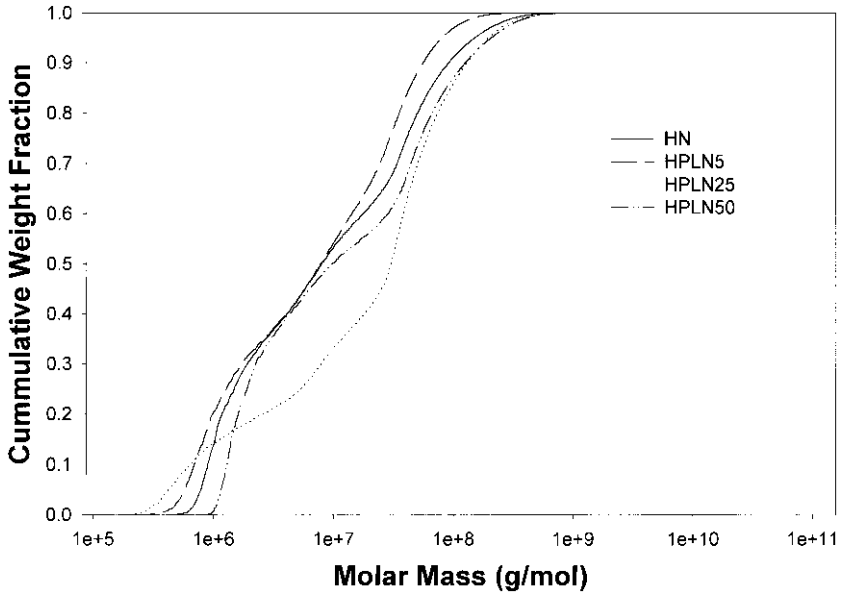


Fig. 7. Plots of cumulative weight fraction vs elution volume for preheated original corn starch (HN) and starch illuminated for 5 (HPLN5), 25 (HPLN25) and 50 h (HPLN50).

$D_{frac} = 2.0$ defines a fully swollen, randomly branched molecule in a thermodynamically good solvent and $D_{fract} = 3.0$ defines the globular structure (Hanselman et al., 1995; Hanselmann, Burchard, Ehrat & Widmer, 1996). The double logarithmic plots of $R_G$ vs. $M_W$ for the amylopectin region of native starch, and samples PLN 5, PLN25 and PLN 50 are presented in Fig. 8.

The slope for the native corn starch and starch illuminated for 5 h (PLN 5) was 0.34, whereas the slope for samples PLN 25 and 50 was 0.37. Such a slope for the amylopectin fraction of native corn starch is lower than that for waxy corn starch dissolved in water, estimated by Hanselmann et al. (1995) (0.41), and that reported for processed amylopectin in 90% DMSO-$H_2O$ by Millard, Dintzis, Willet and Klavons (1997) (0.42). Thus, it seems likely that the postulated degradation of starch polysaccharide followed by crosslinking, led to a less compact amylopectin molecule. The analogous analysis for starch heated prior to illumination, then illuminated, gave the following slopes: 0.42, 0.40, 0.38, and 0.36 for samples prior to illumination and illuminated for 5, 25 and 50 h, respectively.

A similar analysis for the fractions of lower molecular

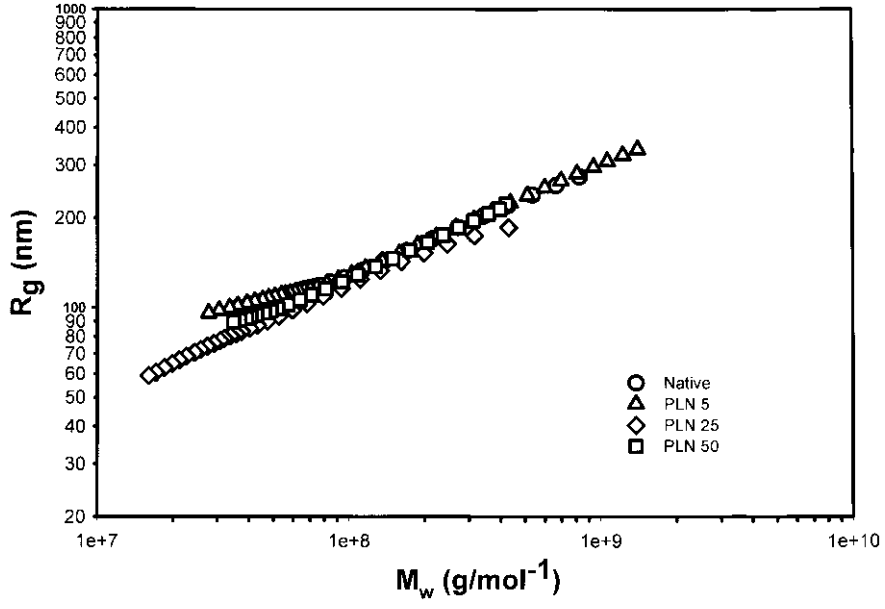


Fig. 8. Molecular weight–radius relationship for amylopectin fraction of native starch and starch illuminated for 5 (PLN5), 25 (PLN25) and 50 h (PLN50), eluted from the size exclusion column.

molecules could not produce credible results. In our size exclusion separations, the radius of eluted molecules did not decrease with time of elution, in fact it increased slightly.

Recovery of the polysaccharide material from the SEC columns was relatively low as compared to the recovery of pullulan and dextran standards. Other authors (Fishman & Hoagland, 1994; Fishman, Rodriguez & Chau, 1996) reported either similar or lower values of recovery, for the starch samples solubilised by microwave heating in water. Recoveries in the range 85–96% depending on the botanical origin of starches treated with 95% DMSO and than dissolved by microwave heating in a high-pressure vessel, were reported by Bello-Perez, Roger, Baud and Colonna (1996b). The same authors found the lower molecular weight component of the sample to be more susceptible to solubilisation and elution. Similar conclusions could be drawn from results reported by You, Fiedorowicz and Lim (1999). They found the recovery from SEC columns for isolated wheat amylopectins to be in the range of 36.3–82.3, while recovery of the debranched wheat amylopectin of low molecular weight was over 95%. Incomplete elution from SEC columns could affect the accuracy of determination of $\bar{M}_w$ and $\bar{R}_G$ of the high molecular weight component of the starch sample. In our case, the observed formation of high molecular weight polymers via crosslinking of smaller molecules after prolonged illumination could be underestimated.

Pasting profiles for non-illuminated and illuminated preheated starch were in full accordance with molecular weight data. Particularly, higher paste viscosity for HPLN 25 and 50 compared to HN confirmed crosslinking leading to the formation of chains of higher molecular weight. In preheated starch, polysaccharide chains in all fractions underwent degradation. The degradation of amylopectin was the most pronounced. Apparently, it facilitated the action of polarised light on starch polysaccharide chains.

The effect of polarised light upon observed starch degradation could be interpreted in terms of activation of enzymes present in starch. It was found (Akatsuka & Nelson, 1966; Frydan & Cardini, 1967; Macdonald & Preiss, 1983, 1985; Mu-Forster et al., 1996) that the process of isolation did not completely remove the enzymes from the starch. However, starch thermally conditioned at a temperature that should deactivate starch enzymes (120°C), was also depolymerised by polarised light. It was striking that the sensitivity of amylopectin to illumination exceeded that of amylose.

It is known that UV light induces the degradation of D-glucose in aqueous solutions (Phillips & Rickards,1969). These authors proved that UV radiation is first absorbed by acetal chromophore at C-1 atom of D-glucose molecule, followed by subsequent photoreaction. Merlin and Fouassier (1981) described starch fragmentation by UV radiation. As in the former case, the site of primary photochemical action is the chromophore at the C-1 position of D-glucose moiety. Oxygen enhanced the yield of chain scissions probably by the formation of peroxide function at the C-1 position. Under anaerobic conditions, the UV-irradiated starch underwent gradual depolymerisation resulting in diminishing molecular weight, reduction in paste viscosity, and melting enthalpy of irradiated samples (Fiedorowicz, Tomasik, You & Lim, 1999). The 5 h irradiation of aerated starch resulted in a sharp drop in molecular weight, melting enthalpy, and viscosity. Prolonged irradiation caused crosslinking leading to the increase in molecular weight, viscosity and melting enthalpy. As proposed by Merlin and Fouassier (1981), the formation of highly reactive peroxide at the C-1 position of D-glucose moiety of polysaccharide chain induced by UV radiation, explains the mechanism of observed crosslinking.

D-Glucose and polysaccharide molecules constituting starch granules do not absorb visible light. Therefore, the action of linearly polarised visible light on starch cannot be explained by the mechanism proposed for UV induced starch reactions. On the other hand, starch granules absorb polarised light (Starzyk, Lii & Tomasik, 1999). Thus, one can assume that the interaction between polarised light and crystalline fragments of starch granules leading to the excitation of crystalline structures, could rupture glycosidic bonds and cause a gradual depolymerisation.

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