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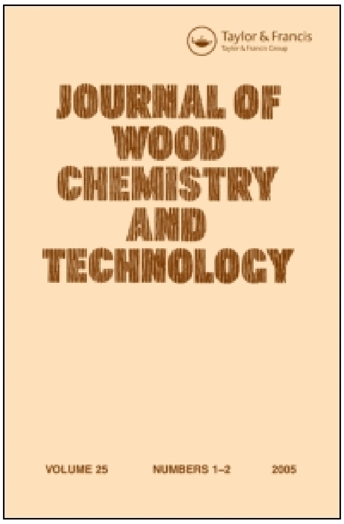

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# The Influence of Light on the Molecular Mass of Lignin

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# THE INFLUENCE OF LIGHT ON THE MOLECULAR MASS OF LIGNIN

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## ABSTRACT

Lignin is cleaved by light to a noticeable extent. In the beginning of the process secondary reactions give substances with high molecular weight.

## INTRODUCTION

In account of low costs and the possibility of alleviating potential pollution problems, interest in the use of high yield pulp for production of paper is growing worldwide. The use of such pulp is, however, hampered by its susceptibility to photoyellowing. This behaviour is caused by light-induced reactions of lignin.

Until recently, numerous investigations have been conducted on the chemical reactions of lignins and related model substances upon irradiation of light, mostly in the presence of oxygen. It has been well established that ß-O-4 linkages[1], resorcinol structures[2] and free phenolic -OH groups[3-6] are the most reactive sites of the lignin molecule after activation under the reaction conditions[3,4].

In addition, it has been demonstrated that radical species play an important role in the reaction[7-8]. After long periods of irradiations, the lignin content decreases appreciably[10].

In spite of the progress made in this field, the mechanism of light-induced yellowing of paper has not been clearly established. This is particularly true for the direct involvement of photolysis in the photoyellowing. Such photolysis is well documented in experiments with model substances[11-14].

If photolytic cleavage of bonds in lignin plays an important role in the photoyellowing, the molecular mass of lignin is expected to decrease under the effect of light. No comprehensive investigation has been conducted on this aspect of the yellowing process. This is also true for the related chemical reactions.

For these reasons, we studied the effect of light on molecular mass distribution of milled wood lignin (MWL)[15], which was isolated from normal and irradiated samples of TMP from pine. In this communication, we will report about changes in the polymer matrix of lignin under irradiation of light.

## RESULTS AND DISCUSSION

Fig. 1 shows the molecular mass distribution of (acetylated) MWL from irradiated and original TMP. Table 1 shows the analytical data. In

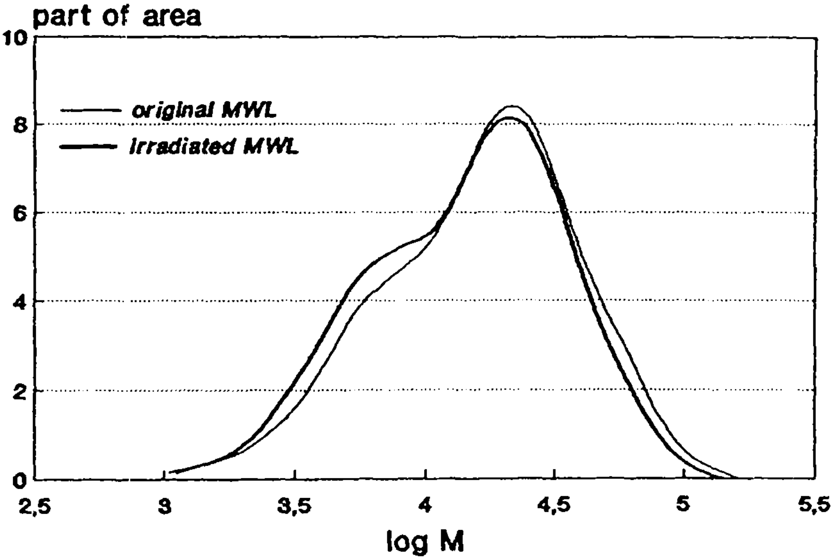

Fig. 1 Distribution of molecular masses in irradiated and original samples of MWL

Figure 1, the areas before the first (relative molecular mass, $M_r \geq 64.000$ Dalton) and after the second ($M_r \leq 10.000$ Dalton) inflection points correspond to the high and low molecular mass fractions, respectively.

The results demonstrate, that a part of the lignin undergoes cleavage under the reaction conditions. The shoulder in the low molecular mass side of the maximum is higher in the irradiated sample than that of the original sample. By contrast, the original sample shows a weak shoulder in the high molecular mass side, but not the irradiated sample.

The analytical data in Table 1 show clearly that the average molecular mass of the MWL decreases slightly on irradiation with light. It can be observed that change in $M_w$ is slightly larger than change in

TABLE 1
Distribution of molecular Masses in irradiated and original Samples of MWL

| type of sample | original | irradiated |
|---|---|---|
| high molecular mass part, % | 6.9 | 4.6 |
| low molecular mass part, % | 22.4 | 24.1 |
| $M_n$ | 11,900 | 10,900 |
| $M_w$ | 24,100 | 22,100 |

*High and low molecular part:* the portion of area (Fig. 1) before the first and behind the second inflection point, respectively

$M_n$. This indicates that high molecular mass fraction of the MWL is slightly more susceptible to degradation by light.

Although there is a slight change in the average molecular mass of the MWL from pine TMP on irradiation with light, no appreciable change in molecular mass distribution has been observed. For example, a shift of $M_{max}$ is not clearly shown. In addition, the difference in the integral under the shoulders is rather small. This ambiguity is probably caused by the method of isolation. In the course of purification of MWL, portions of substances in both end of extreme molecular mass fraction are lost. To avoid these shortcomings, we used isolated MWL sample for irradiation.

Figure 2 shows the molecular mass distribution of the MWL after different exposure times. Numerical data are summarized in Table 2. Compared to Figure 1, Figure 2 shows clearly that lignin undergoes

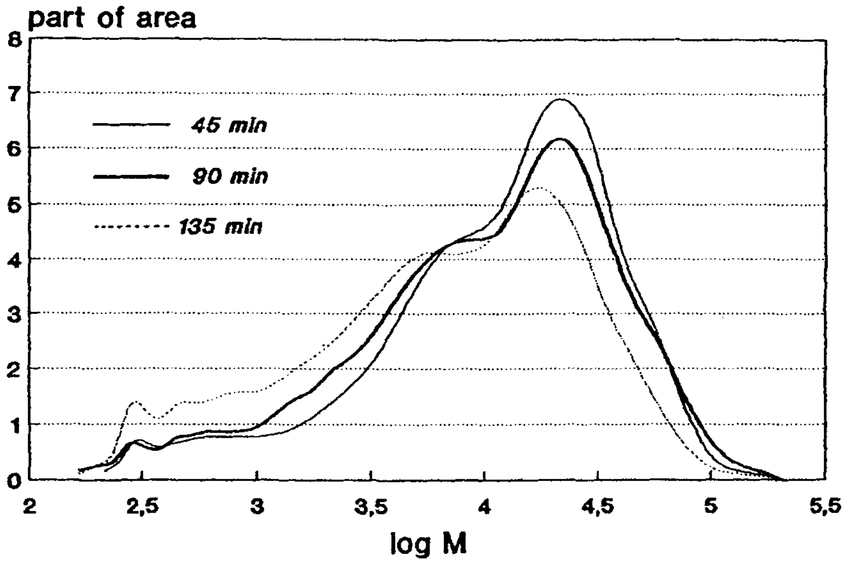

Fig. 2 Distribution of molecular masses in MWL after different periods of irradiation

TABLE 2

Distribution of molecular Masses in MWL after different Periods of Irradiation

| **Duration of exposure** | **45 min** | **90 min** | **35 min** |
|---|---|---|---|
| high molecular mass part, % | 4.8 | 6.3 | 1.6 |
| low molecular mass part 1, % | 35 | 37 | 45 |
| low molecular mass part 2, % | 8 | 12 | 16 |
| $M_n$ | 2,700 | 2,200 | 1,400 |
| $M_w$ | 19,900 | 19,100 | 13,700 |

*High and low molecular part*: the portion of area (Fig. 1) before the first and behind the second inflection point, respectively
*Low molecular part two*: part of area (Fig. 2), which belongs to substances with elution times greater than in experiment one

degradation by light. The average molecular mass decreases with prolonged time of exposure. Furthermore, substances with low molecular mass are formed. Some of them elute out from the GPC column later than components of lowest molecular mass in the original lignin; this portion is called low molecular mass fraction two. The elution profiles vary, indicating that the new components are able to undergo further reactions.

On the other hand, the high molecular mass fraction shows irregular variation in elution profiles. This finding shows that in the beginning of irradiation, reactions take place which lead to the formation of high molecular mass substances. After a long period of time fragmentation reactions dominate; the high molecular mass portion decreases clearly in quantity.

In order to obtain more information about the initial processes, the time of exposure was shortened. Because of the better film producing properties, acetylated lignin was used in this case. Figure 3 and Table 3 show the results of the experiments. The portion of high molecular mass substances and $M_W$ increase after short-term exposure, which is a result of secondary reactions between lignin and active degradation products. This phenomenon is more pronounced than in the previous experiment. Moreover, there is a difference in the variations of molecular masses. The values of $M_n$ show that the cleavage of bonds in the acetylated substances proceed, to a lesser extent, slower than in the original lignin. This behaviour should be discussed in terms of the light-stabilizing effect caused by acetylation of lignin which, however, has to be verified by further experiments.

Based on Flory-Stockmayer theory[16-18], we have calculated the values

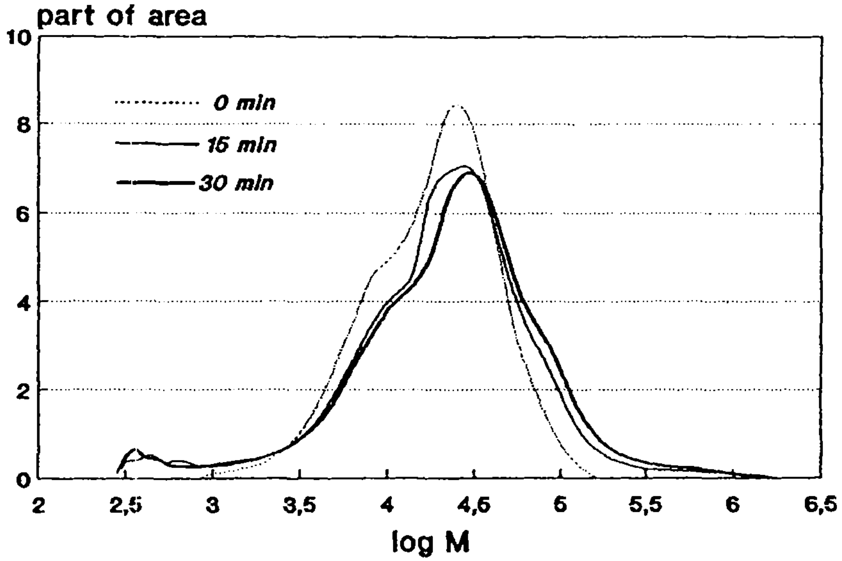

Fig. 3 Distribution of molecular masses in acetylated MWL after different periods of irradiation

TABLE 3

Distribution of molecular Masses in acetylated MWL after different Periods of Irradiation

| **Duration of exposure** | **15 min** | **30 min** | **45 min** |
|---|---|---|---|
| high molecular mass part, % | 8.2 | 11.1 | 10 |
| low molecular mass part 1, % | 26 | 27 | 28 |
| low molecular mass part 2, % | 4.1 | 4.1 | 3.2 |
| $M_n$ | 4.900 | 4,800 | 5,800 |
| $M_w$ | 31,200 | 38,400 | 33,600 |

Explanations: cf. Table 2

TABLE 4

Branching Characteristics of MWLs

| **Type of sample** | **p'** | **$\varrho$ '** | **$\alpha_f$** |
|---|---|---|---|
| MWL from TMP | 0.9846 | 0.002 | 0.013 |
| MWL from irradiated TMP | 0.9832 | 0.003 | 0.014 |
| MWL, irradiation time 45' | 0.914 | 0.037 | 0.282 |
| MWL, irradiation time 90' | 0.893 | 0.050 | 0.292 |
| MWL, irradiation time 135' | 0.825 | 0.090 | 0.298 |
| acet. MWL, irrad.time 15' | 0.954 | 0.018 | 0.273 |
| acet. MWL, irrad.time 30' | 0.952 | 0.020 | 0.287 |
| acet. MWL, irrad.time 45' | 0.961 | 0.014 | 0.265 |

of p', $\varrho$' and $\alpha_f$, modelling the branching characteristics of MWL (Tabl. 4).

In the case of irradiated samples, the branching coefficient $\alpha_f$ is comparable to other findings from delignification studies[18,19,20,21]. In contrast, the values for the original MWL are very low. This can be explicable in three ways:

1. The isolation method for MWL prefers unbranched parts of the polymer. If this is the case, then MWL is not a proper model for native lignin.
2. In the course of delignification, unbranched portions of lignin are cleaved more readily.

To verify one of these possibilities, further experiments are required.

## EXPERIMENTAL

### Milled Wood Lignin (MWL)

The MWL was prepared after the method of BJÖRKMAN[15], using TMP from pine as the raw material. Then milled and extracted TMP was stirred with 5 % cellulase from trichoderma viride (Fluka AG, Buchs) in 0.05 m acetate buffer at pH 4.8 with a solid/liquid ratio of 0.05 at 45° C for 48 h under $N_2$.

After usual extraction with dioxane/water 100:4 this procedure was repeated with Macerocyme R 10 from Rhizopus sp. (Serva GmbH, Heidelberg). The combined extract was purified as usual.

### Gel Permeation Chromatography (GPC)

GPC was conducted with a high pressure pump HPP 4001 and an UV filter detector LCD 2565 at 290 nm (Laboratorni pristoji, Praha). Three Eurogel columns (1000, 500, 50 Å, Knauer GmbH, Berlin) were used. Calibration was made with polystyrene standards from $M=2.75 \cdot 10^6$ to $5 \cdot 10^2$, then with vanillin and toluene. For analysis, lignin was acetylated with pyridine/acetic anhydride and methylated with ethereal diazomethane. The solvent was tetrahydrofuran.

### Preparation of Lignin Sample for Irradiation with Light

Lignin sample was dissolved in 90 % acetic acid or tetrahydrofuran. After evaporation of solvent, irradiation was effected by a Xenotest apparatus (Heraeus GmbH, Hanau) at 25°C and 50 % humidity.

## ACKNOWLEDGMENT

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