Letter to the Editor

The influence of levelling-off degree of polymerisation on the kinetics of cellulose degradation

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In a letter to the Editor published in a previous issue of Cellulose, Emsley et al. (1997) proposed an exponential decrease in rate constant \( k_1 \) to explain the downward curvature in the kinetic plots of cellulose degradation (Feller et al. 1986; Emsley and Stevens 1994; Heywood et al. 1999), that do not follow either the zero order
\[
\frac{1}{DP_t} - \frac{1}{DP_0} = k_1 t
\]
or the first order relationship
\[
\ln\left(1 - \frac{1}{DP_t}\right) - \ln\left(1 - \frac{1}{DP_0}\right) = k_1 t
\]
at long reaction times (low values of the degree of polymerisation DP).

The proposed kinetic equation is:
\[
\frac{1}{DP_t} - \frac{1}{DP_0} = \left( \frac{k_{10}}{k_2} \right) \left( 1 - e^{-k_2 t} \right)
\]
where \( k_{10} \) and \( k_2 \) are related by
\[
k_1 = k_{10} e^{-k_2 t}
\]
being \( k_1 \) the rate at which the DP decreases (Eqs.1 and 2) and \( k_2 \) the rate at which \( k_1 \) changes.

Although the model proposed by Emsley et al. gives an excellent fit of the experimental data, its physical basis remains unclear (Vrhovac and Rašajski 1977; Soares et al. 2001). However, a simple interpretation can be given. The first-order kinetics of degradation can be written as
\[
\frac{dS}{dt} = k(n^* - S)
\]
where \( S \) is the number of scissions and \( n^* \) the initial number of bonds available for the degradation.

When \( n^* \gg S \), the pseudo zero-order approximate solution of Eq. 5 is
\[
S = n^* k t
\]
otherwise the exact solution reads
\[
S = n^* (1 - e^{-k_1 t})
\]
It is easy to verify that Eqs. 1 and 2 can be derived from Eqs. 6 and 7 respectively, if we consider the number of scissions per anhydroglucose unit \( S = 1/DP - 1/DP_0 \) and the initial amount of cellulose bonds per anhydroglucose unit \( n^* = 1 - 1/DP_0 \).

However, Eqs. 1 and 2 hold for the degradation in homogeneous medium, where all the cellulose bonds are available for the degradation (Daruwalla and Narsian 1966; Sharples 1971; Krassig 1985). In heterogeneous medium, the influence of the levelling-off degree of polymerisation (LODP) (Nelson and Tripp 1953; Yachi et al. 1983) should be taken into account.

To this end, it is worth noting that while amorphous bonds degrade rather easily with a random mechanism until LODP \( 100 \) (Zou et al. 1996), as shown by the rapid decrease of DP with limited weight loss (Marx-Figini 1986), the further hydrolytic degradation requires very drastic conditions (Kusama et al. 1976; Yachi et al. 1983) and follows a different pathway.

Some authors (Nelson and Tripp 1953; Chang et al. 1973; Manley 1976; Chang and Tsao 1981; Bouchard et al. 1992) found a “quantum mode” of crystallite degradation, where the LODP did not change appreciably while the weight loss increased up to 70%. These findings indicate that crystallities decrease in quantity (resulting in soluble fragments of low molecular weight) while both the average chain length and the molecular weight distribution remain unchanged in the residual polymer (Chang et al. 1973; Marx-Figini 1986).
It follows that in heterogeneous medium Eq. 7 should be written as

\[
\frac{1}{DP - 1/DP_0} = \left(\frac{1}{LODP - 1/DP_0}\right) \times \left(1 - e^{-kt}\right)
\]

(8)

thus obtaining the same formal result of Emsley et al. (Eq. 3), although with a different meaning of the pre-exponential factor, without introducing a change in rate constant as the reaction proceeds.

An application of Eq. 8 is shown in Figure 1, where the first order kinetics gives \( k = 1.14 \text{ h}^{-1} \) and LODP = 195. The values of both \( k \) and LODP have been calculated with the aid of a non-linear curve fitting software (Origin 60 of the OriginLab Co.).

Nevertheless, both local and global deviations from Equation 8 are rather common in the literature and most of them can be easily explained.

After the LODP has been reached, for instance, the kinetic plots generally deviate from the first order kinetics, and the extent of the deviation (enhanced by the hyperbolic relationship between \( S \) and \( DP \)) depends on the experimental conditions. If the low-molecular weight fraction resulting from crystallite degradation was removed (intentionally or not) before measuring the DP, a slight upward drift of the kinetic plot is observed, due to the chopping of the dangling ends of the chains (see the last point of Figure 1). Conversely, if the low-molecular weight fraction remained in the analysed samples, the accumulation of the residues of crystallite destruction changes the chain-length distribution giving rise to a broad bimodal pattern and enhancing the upward drift of the kinetic plot.

A global deviation may be due to the presence of weak links in cellulose (Rowland and Roberts 1972; Feller et al. 1986; Emsley and Stevens 1994). From a kinetic standpoint, the presence of two simultaneously occurring reactions leads to the equation

\[
S = n_w^0 (1 - e^{-k_w t}) + n_a^0 (1 - e^{-k_a t})
\]

(9)

where the subscripts \( w \) and \( a \) are referred to the weak and amorphous links respectively.

An application of Eq. 9 is shown in Figure 2, and the best fit suggests the presence of weak links degrading at higher rate constant than the amorphous bonds (\( k_w = 0.11 \text{ and } k_a = 0.02 \text{ h}^{-1} \) respectively).

The weak links hypothesis might explain the results of Emsley et al. (2000), where cotton linters aged in air and oil showed a non-random mechanism of degradation, and it is likely that the resulting higher value of viscometric DP in the intermediate stage of ageing led Soares et al. (2001) to discard Eq. 8 without extending the analysis of the degradation to the LODP region.

Another cause of global deviation from Eq. 8 has been widely overlooked in the literature. Although it is known that oxidised cellulose degrades through a \( \beta \)-alkoxy mechanism in alkaline medium (O’Meara and Richards 1958; Kolar 1997), many authors did not treat the aged cellulose samples with a reducing agent before the viscometric determination of the degree of polymerisation. The resulting degradation of oxidised units during the