Thermochimica Acta, 85 (1985) 395—398
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE CONSEQUENCES OF BEGINNING SLOW THERMAL DECOMPOSITION ON THE MOLECULAR WEIGHT OF NITRATED CELLULOSE

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ABSTRACT

On slow heating the average molecular weight of nitrated cellulose decreases markedly before the decay of nitrate concentration is conceived. A polymeric degradation model correlates both reactions.

INTRODUCTION

The thermal decomposition of nitrated cellulose (NC) is generally accepted to proceed by homolytic cleavage of the $O\text{-}NO_2$ ester bond. Thereby NO_2 and intermediates with oxygen radicals sites are formed. Kinetic data obtained from slow thermal decomposition studies on weight loss, heat release, NO_2 evolution and change in functional group concentration support this model (ref.1-5).

The emphasis of these studies was on the degradation of the nitrate groups with no relation to the fate of the polymeric chain. Such information, however, is essential to fully understand the mechanism. In fact, detailed analysis of decomposed NC residues showed that subsequent reactions of the highly reactive intermediates lead to chain cleavage and the degree of polymerisation is substantially lowered (ref. 6).

Moreover, if chain scission is a major consequence of the nitrate group loss, monitoring the changes of the polymerisation degree would be a very sensitive approach, especially at high molecular weights.

With this approach this study focusses on beginning NC decomposition. Kinetic parameters will be presented derived by a fit of the data to a polymeric degradation model.

MODEL OF MOLECULAR WEIGHT DEGRADATION

The model is based on the following assumptions:

1. A number i_0 of polymeric chains will be considered each of which consists of n chain segments of mass m.
2. A first order reaction with constant k(T) decomposes the chain segment.

0040-6031/85/$03.30

3. The decomposition of one segment leads to chain scission.

The number of chains i(t) increases with time t by the number of decomposed segments (N_0 - N). These are obtained by the first order reaction of the total amount of segments N which initially is $N_0 = i_0 n$:

$$\frac{dN}{dt} = - k N ; \qquad N = N_0 \exp(-kt) \tag{1}$$

$$N_0 - N = N_0 (1 - \exp(-kt)); \quad i(t) = i_0 + N_0 - N \tag{2}$$

The initial molecular weight M_0 and the average molecular weight M(t) at any time can be expressed by:

$$M_0 = N_0 m / i_0 \tag{3}$$

$$M(t) = N m / i(t) \tag{4}$$

The combination of equs. (1) to (4) results in an expression for the molecular weight depending on the rate constant k:

$$\frac{M(t)}{M_0} = \frac{\exp(-kt)}{1 + n (1 - \exp(-kt))} \tag{5}$$

From equ. (5) it is obvious that $M(t)/M_0$ decreases substantially already at an early stage of decomposition if the degree of polymerization n is high. The measurement of the molecular weight, therefore, is a very sensitive method to study polymer decomposition. Consequently, $kt \ll 1$, and equ. (5) reduces to:

$$M(t)/M_0 = 1 / (1 + n k t) \tag{6}$$

The decay of molecular weigth behaves like a reaction of second order with a reaction constant n k.

The non-isothermal case is derived by the substitution of kt by $\int k(T)dT/B$, with B representing the linear heating rate.

METHODS

NC (1.4% H_2O, 13.3% N) was decomposed by slow heating in a commercial thermal analyzer (DuPont 990). The heating rate was 0.5 $Kmin^{-1}$ and the sample weight was 5 mg. Under these conditions no self-heating occurred (ref. 3,5).

The decomposition progress was recorded by quenching the reaction at a series of fixed temperatures. The residue was recovered, dissolved in THF and

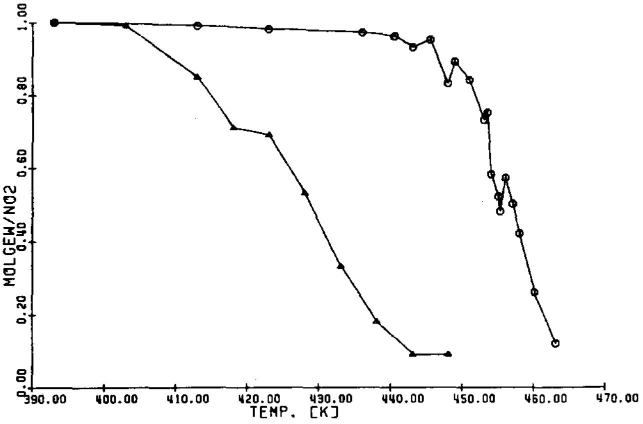

Fig. 1: Experimental curves of the absorptance of the 1280 cm^{-1} band of the nitrate groups (○) and the (normalized) average molecular weight (△).

analyzed by IR (Perking Elmer 580B, CDS data station) and GPC (Hewlett-Packard 1084 B chromatograph, LDC 1107 refractometer, Water Ultrastyragel columns, calibration relative to polystyrene standards). The temperature interval investigated was 270 - 460 K , limited by the solubility of the residue in THF. In this range the IR absorbance of the nitrate groups obeyed Beer´s law. Due to the quenching procedure the experimental error is about 5%.

RESULTS AND DISCUSSION

The results are presented in Figs. 1 and 2.

Fig.1 compares the absorptance of the nitrate group and the average molecular weight as a function of temperature. The significant result is that on heating a marked decrease in molecular weight occurs before any change in the nitrate absorbance is noticable. This is important with respect to the polymeric degradation model.

The decay of the nitrate concentration is autocatalytic. The kinetic parameters of this process were discussed previously (ref. 5). Since the decomposition of the nitrate group is small up to 450 K, the rate can be approximated by a first order reaction.

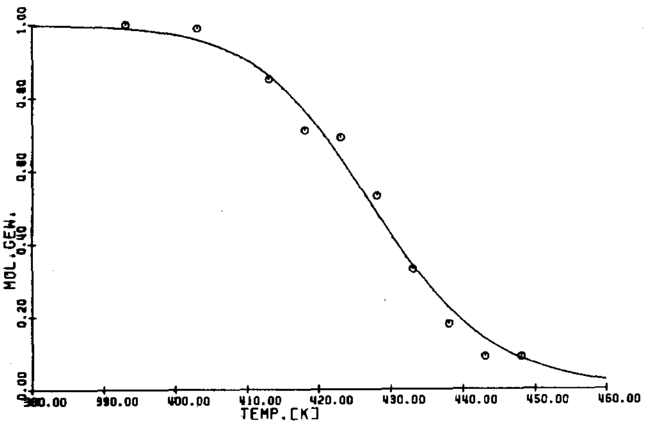

Fig. 2: Fit of equ. (6) in its non-isothermal form to the experimental average molecular weight. $k(T) = Z \exp(-E/RT)$; $\log Z = 16.6$; $E = 42.6$ kcal/mole (from ref. 5). Fit parameter n was found to be 110.

Fig. 2 shows the fit of the polymeric degradation model to the molecular weight data. The good fit states that equ. (6) satisfactorily describes the decay of molecular weight. The profiles of the theoretical and experimental curves are synchronous. The shape is symmetrical which is typical for 2. order. Important is, that at 450 K (onset of the nitrate group decay) the model predicts a decrease in the polymerisation degree by a factor of about 100 which is in accordance with the experimental results.

The findings suggest that the decomposition of one segment (nitrated ß-glucose anhydride unit) leads to the scission of the chain. As a consequence, the split-off of the nitrate group is the rate determining step.

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