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Kinetics of the Thermo-Oxidative Degradation of Nylon 66 by Oxyluminescence Methods

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ABSTRACT

The chemiluminescence from stabilized nylon 66 fibers during oxidation above T_g has been studied to determine the activation energies of the initiation, propagation and termination reactions. When oxygen is admitted to a nylon 66 sample heated in an inert atmosphere, a pulse of chemiluminescence is observed corresponding to a nonstationary alkyl peroxy radical concentration in the polymer. The analysis of the decay to the steady state can provide kinetic data for peroxy radical reactions in the induction period of the oxidation and the effect of stabilizers on these reactions.

INTRODUCTION

The weak chemiluminescence emitted from organic materials during oxidation, known as oxyluminescence, has been studied in detail to yield kinetic parameters for autoxidation in solution [1-3]. The oxyluminescent reaction is generally regarded as the bimolecular termination of primary or secondary alkyl peroxy radicals which disproportionate by the Russell mechanism to produce a ketone, alcohol, and oxygen as shown in reaction (5) of the reaction scheme.

Initiation:

$$\text{ROOR'} \xrightarrow[\text{heat}]{\text{catalyst}} \text{RO}\cdot + \text{R'O}\cdot$$

$$\text{RO}\cdot + \text{RH} \longrightarrow \text{R}\cdot + \text{ROH} \tag{1}$$

Propagation:

$$\text{R}\cdot + \text{O}_2 \xrightarrow{k_2} \text{RO}_2\cdot \tag{2}$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_3} \text{ROOH} + \text{R}\cdot \tag{3}$$

Termination:

$$\text{R}\cdot + \text{R}\cdot \xrightarrow{k_4} \text{R–R} \tag{4}$$

$$\text{RO}_2\cdot + \text{RO}_2\cdot \xrightarrow{k_5} \text{ROH} + \text{O}_2 + \text{R}_2''\text{C=O}^* \tag{5}$$

Inhibition:

$$\text{RO}_2\cdot + \text{InH} \xrightarrow{k_6} \text{ROOH} + \text{In}\cdot \tag{6}$$

where

$\text{R}\cdot = \sim\sim\text{CH}_2\text{CONH}\dot{\text{C}}\text{HCH}_2\sim\sim$ and R' may be hydrogen.

Reaction (5) is exothermic ($\Delta H \approx$ 500 kJ/mole), and emission occurs from either the first excited singlet or triplet state of this ketone, or a complex with singlet oxygen [4], with an efficiency of about 10^{-4}. The efficiency of excitation is less than 10^{-5}, so the overall oxyluminescence quantum yield ϕ is typically 10^{-9}. The intensity of emission I is given by Eq. (7)

$$I = \phi k_5 [\text{RO}_2\cdot]^2 \tag{7}$$

and reflects the rate of the peroxy radical termination reaction throughout the oxidation.

Oxyluminescence has been reported during the autoxidation of polyolefins [5, 6], polyamides, polyesters [6], and polydienes [7] and has been used to measure: (1) the activation energy for the initiation of oxidation from the temperature dependence of I, and (2) the comparative stabilization efficiency of added antioxidants [6, 8, 9]. Since the inhibitor reduces the steady-state peroxy radical concentration by reaction (6), the oxyluminescence intensity is similarly reduced.

The investigations of stabilized polymers have been concerned with the kinetics of polymer oxidation at high temperature and large extents of oxidation. It has been observed that for many polymers the critical mechanical properties of fibers and films are severely degraded before the limiting rate of oxidation is attained [10, 11]. Kinetic information at low extents of oxidation is therefore required to enable the ultimate useful lifetime of these materials to be predicted. Recently oxyluminescence has been applied to this problem in the investigation of the unbranched, initiated oxidation of polystyrene below T_g [12] and in the prediction of the service life of elastomers and polyurethanes [7].

This paper reports a study of the oxyluminescence of nylon 66 fibers to determine the kinetic parameters for the autoxidation, particularly during the early stages of oxidation at temperatures from 50°C to 150°C.

EXPERIMENTAL

The photon counting oxyluminescence apparatus has been described elsewhere [13]. The material studied was a commercial nylon 66 taffeta, fiber diameter 20 μm containing a hindered phenol antioxidant, characterized elsewhere [13]. Most of this antioxidant could be removed by prolonged extraction with methanol.

RESULTS AND DISCUSSION

Oxyluminescence Curve and Autoxidation of Nylon 66

Figure 1 shows the change in emission intensity with time of oxidation for a sample of stabilized nylon 66 taffeta, heated to 125°C in a flow of nitrogen and the gas replaced by oxygen at zero time. There is an instantaneous increase in intensity, followed by a decay over several minutes to a steady count rate. The count rate is constant or increases at a low rate for about 2 hr before a sharp increase corresponding to the onset of autoacceleration. This time can be identified with the induction period τ of the oxidation and depends on the sample temperature, for this sample of nylon 66, according to the relation (8)

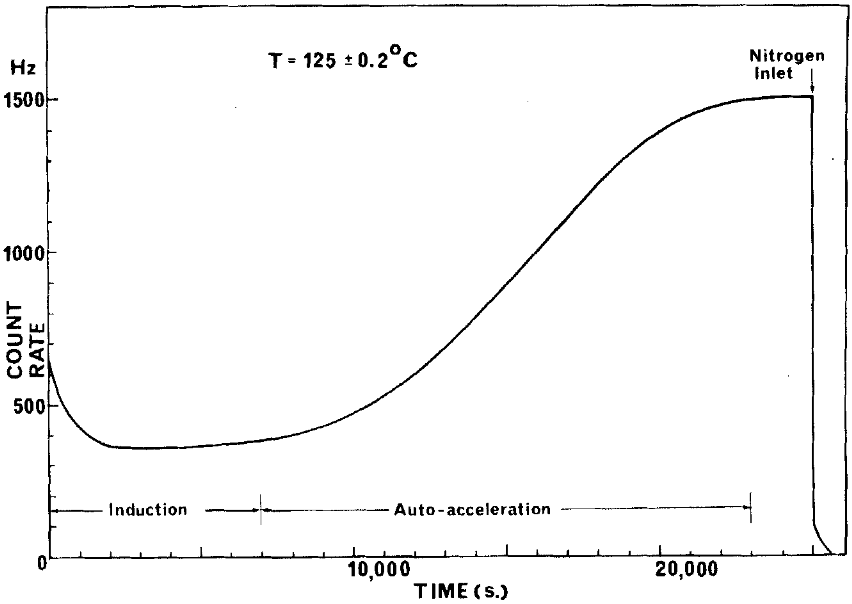


FIG. 1. Oxyluminescence curve (count rate vs. time of oxidation) from stabilized nylon 66 taffeta in oxygen at 125°C.

$$\log \tau = (8000/T) - 16.46 \tag{8}$$

where τ is in seconds and T lies in the range 383°K to 420°K. This induction period also depends on the oxygen concentration. For example in air at 414°K, τ is five times that in oxygen at the same temperature.

The activation energy E_1 for the initiation of oxidation [reaction (1)] is obtained directly from the temperature dependence of the steady luminescence intensity in this induction period. Since the rate of initiation r_i equals the rate of termination, Eq. (7) becomes

$$I = \phi r_i \tag{9}$$

The Arrhenius plot is linear over the temperature range 50°C to 150°C, which encompasses T_g of the drawn fiber (107°C at 0% RH). The value of E_1 appears in Table 1.

At the end of the induction period, the emission intensity increases sigmoidally as autoacceleration begins. The hydroperoxide formed in the propagation reaction (3) is responsible for chain branching,

TABLE 1. Activation Energies for Oxidation Reactions (1), (3), and (5)

Material	E_1 (kJ/mole)	E_3 (kJ/mole)	E_5 (kJ/mole)
Nylon 66[a]	67	73	~50
Model amide	99[b]	58[c]	~ 8[c]
Polypropylene	135[d]	50[e]	48[e]

[a] By oxyluminescence.

[b] Taken as the activation energy for decomposition of 1-propionamidopropyl hydroperoxide from 77 to 131°C [14].

[c] Taken from data of Sager [14] for the autoxidation of N-n-propylpropionamide.

[d] Data of Zolotova and Denisov [21].

[e] Data of Chien and Wang [15].

and there is a rapid increase in the oxidation rate until the limiting rate is attained. This is shown as a constant emission intensity, and from Fig. 1 this occurs after about 6.5 hr. This maximum emission intensity is maintained until there is a change in the oxidation rate of the substrate or there is a physical change such as yellowing or production of a quenching species that lowers the quantum yield. In Fig. 1 the experiment was terminated by admitting nitrogen soon after the steady rate was reached. The count rate immediately dropped back to the dark count rate of around 2 Hz.

An analysis of the autoacceleration has given the expression for the maximum rate of oxyluminescence increase [13] as

$$(dI^{1/2}/dt)_{max} = \phi^{1/2}(k_3[RH])^2/4k_5^{1/2} \tag{10}$$

The maximum oxyluminescence intensity in the limiting rate region is given [7] by

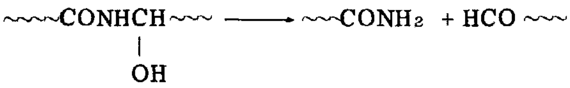
$$I_{max} = \phi(k_3[RH])^2/k_5 \tag{11}$$

By measuring the complete oxyluminescence curve over a range of temperatures, the activation energies for propagation (E_3) and termination (E_5) can be calculated from the above expressions. These are summarized in Table 1 and compared with the reported values for a model amide for nylon 66 [14] and polypropylene [15] over a similar temperature range.

The low activation energy for the initiation of the oxidation of nylon 66 is consistent with the induced decomposition of trace hydroperoxides—possibly by metallic impurities—rather than unimolecular homolysis. The activation energy for propagation in nylon 66 is greater than in polypropylene in which sequential hydroperoxide formation is favored. The value of 50 kJ/mole for the activation energy of termination is similar to that for polypropylene, and since the value for the liquid model amide is only 8 kJ/mole, the activation energy must reflect that for segmental diffusion in the polymer. The rate of bimolecular peroxy radical reaction is then the rate at which the two centers can diffuse together.

Oxidation of Nylon 66 in the Induction Period

At the completion of a prolonged oxyluminescence experiment it is found that the material is severely degraded; it has yellowed and has low residual tensile strength. Significant losses of mechanical properties occur during the early stages of oxidation. For example, at a temperature of 80°C in air, the induction period τ, extrapolated from Eq. (8), is 92 days. Mechanical measurements after this ageing period showed a strength loss of 19% and a decrease in the elongation to break of 30% [16]. Sagar [14] has shown that in the initiated oxidation of model amides at temperatures below 130°C the kinetic chains are quite short and quadratic termination dominates in product formation. In nylon 66 this reaction may lead to chain scission as the α-hydroxy amide formed in reaction (5) can immediately decompose:



$$\sim\sim\sim\text{CONH}\underset{\text{OH}}{\underset{|}{\text{CH}}}\sim\sim\sim \longrightarrow \sim\sim\sim\text{CONH}_2 + \text{HCO}\sim\sim\sim$$

This would be consistent with the observed decrease in $\overline{M}_v$ during the early stages of the oxidation of nylon 66 taffeta at 80°C in air [16].

Studies of the photo-oxidation of polypropylene fibers similarly reveal significant losses in mechanical properties during the so-called induction period [11]. It has been noted that the ultimate useful life of a stabilized polymer does not greatly exceed the induction period [10], so the kinetic data generated under conditions of high extents of oxidation may be of little value. Conventional oxygen uptake and product analysis studies of the autoxidation of polyolefins and polyamides have been performed in the steady state corresponding to the limiting oxidation rate because of an inherent lack of sensitivity in the techniques used [17]. The relations (10) and (11) similarly provide data in the later stages of oxidation, and the oxyluminescence from nylon

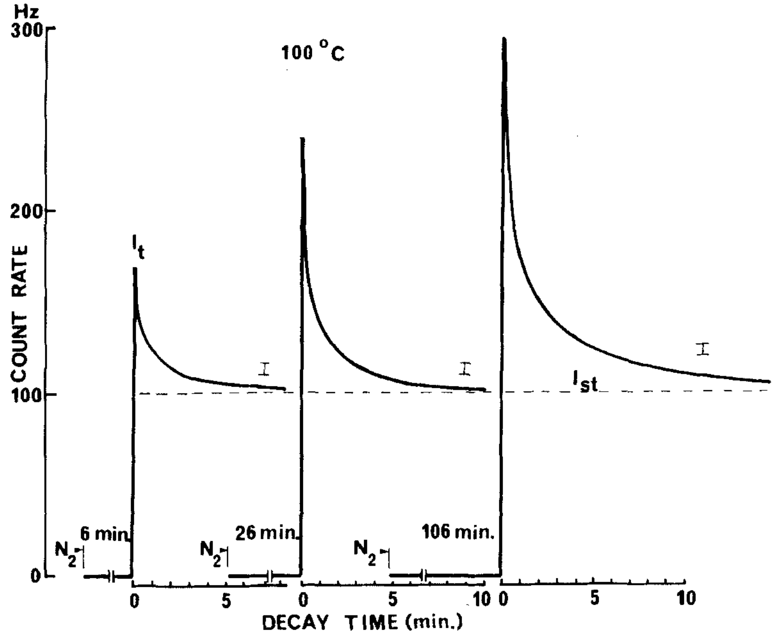


FIG. 2. Oxyluminescence pulse from nylon 66 in the induction period at 100°C after heating for the indicated time in nitrogen and then admitting oxygen. I_{st} is the steady count rate in oxygen.

66 in the earliest stages of the induction period is being studied to determine if kinetic parameters from the unbranched oxidation can be measured.

A burst of oxyluminescence is observed when a sample of nylon 66 is heated in nitrogen and oxygen is then admitted. This is seen after the initial heat-up in Fig. 1 and can be repeated at any time in the induction period. This is shown in Fig. 2 for various times of heating at 100°C and it is evident that the magnitude of the pulse depends on the time of heating in nitrogen. In all cases the emission decays to the steady intensity characteristic of the induction period at that temperature. A preliminary analysis of these data has been made within the following framework which is similar to that reported for oxyluminescence decay during the initiated oxidation of hydrocarbons in solution [1].

(1) During heating in nitrogen, trace hydroperoxides in the sample are decomposed at a rate r_i, as shown in reaction (1).

(2) In the absence of oxygen, these radicals may terminate by reaction (4). (Other termination reactions such as disproportionation

may equally well take place.) A steady-state alkyl radical concentration of $(r_i/k_4)^{1/2}$ will be attained when $d[R\cdot]/dt = 0$.

(3) When oxygen is then admitted to the sample, the alkyl radicals are scavenged at a rate given by reaction (2), and a new stationary state with an alkyl peroxy radical concentration of $(r_i/k_5)^{1/2}$ will be established.

If reaction (2) is rapid, the instantaneous concentration of alkyl peroxy radicals in the polymer on admitting oxygen will be $(r_i/k_4)^{1/2}$ and, if $k_4 < k_5$ this will be higher than the final stationary state concentration. A burst of emission is then observed followed by decay back to the stationary state. The intensity of emission at any time, t, is given in the simplest case, by the solution to:

$$-d[RO_2\cdot]/dt = k_5[RO_2\cdot]^2 - r_i \tag{12}$$

On expressing the peroxy radical concentrations in terms of emission intensities by using Eq. (7), this solution is:

$$\ln\left[\frac{I_t^{1/2} + I_{st}^{1/2}}{I_t^{1/2} - I_{st}^{1/2}}\right]\left[\frac{I_m^{1/2} + I_{st}^{1/2}}{I_m^{1/2} - I_{st}^{1/2}}\right] = 2\,(2\,r_i)^{1/2}k_5^{1/2}\,t \tag{13}$$

where I_m is the peak intensity before decay and I_{st} the steady intensity reached after decay. Figure 3 is a plot, according to Eq. (13) of the initial decay from stabilized and extracted material at 120°C. The stabilized nylon shows a much faster decay, and I_{st} is reached approximately twice as fast as in the extracted material.

In both samples there is an initial fast decay over the first 1-2 min. The temperature dependence of this component has been measured for extracted nylon and the resultant activation energy is, from Eq. (12), $\frac{1}{2}(E_1 + E_5) = 41$ kJ/mole. Since $E_1 = 67$ kJ/mole, then $E_5 = 15$ kJ/mole. This is much smaller than the value of E_5 of 50 kJ/mole determined by analyzing the oxyluminescence curve in the auto-acceleration and limiting rate regions, and suggests that the oxyluminescence in the induction period results from the termination of those alkyl peroxy radicals formed quite close together. This is important in the stabilization of the polymer, as Mayo has pointed out that hindered phenol antioxidants cannot compete with the geminate recombination of alkyl peroxy radicals [18]. The faster decay of the oxyluminescence from the stabilized nylon 66 compared with that from the extracted material (Fig. 3) argues against the oxyluminescence arising from a single initiation event. If the rate of the reaction of the hindered phenol antioxidant with the alkyl peroxy radicals is competitive with the

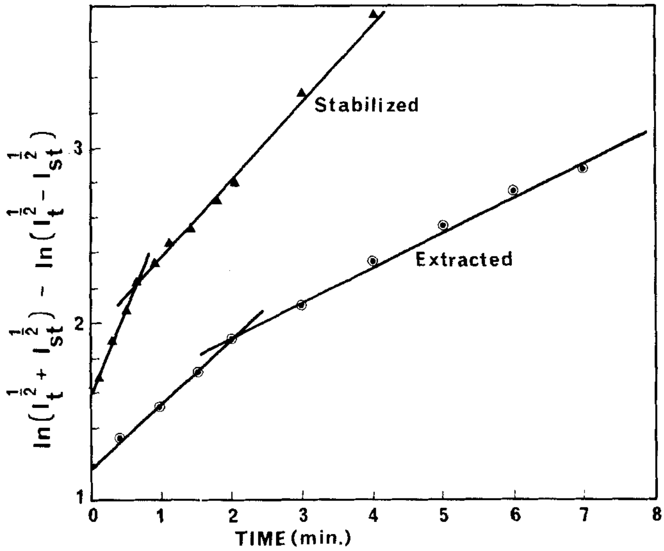


FIG. 3. Decay of the oxyluminescence pulse from nylon 66 taffeta at 120°C analyzed according to Eq. (13) for (▲) stabilized and (◉) extracted material.

bimolecular reaction, the decay curve from the stabilized polymer should then be described by:

$$-d\,[RO_2\cdot]/dt = k_5[RO_2\cdot]^2 + k_6[RO_2\cdot][InH] - r_i \tag{14}$$

This cannot be solved in a form such as Eq. (13). An approximate solution [19] has been tested to give, for $r_i \approx 0$, a value of the pseudo-unimolecular stabilizer rate constant $k_6[InH] \approx 150\ sec^{-1}$ at 120°C. Further refinement requires a numerical integration of Eq. (14).

Alkyl Radical Reactions during Oxidation in Air

It has been found that the steady-state oxyluminescence intensity from nylon 66 in air is about one-third that in oxygen. This ratio is found in the induction period, the limiting rate and also during non-stationary experiments. This suggests that the alkyl peroxy radical concentration may be dependent on the partial pressure of oxygen. This would be in marked contrast to the oxidation of most hydrocarbons

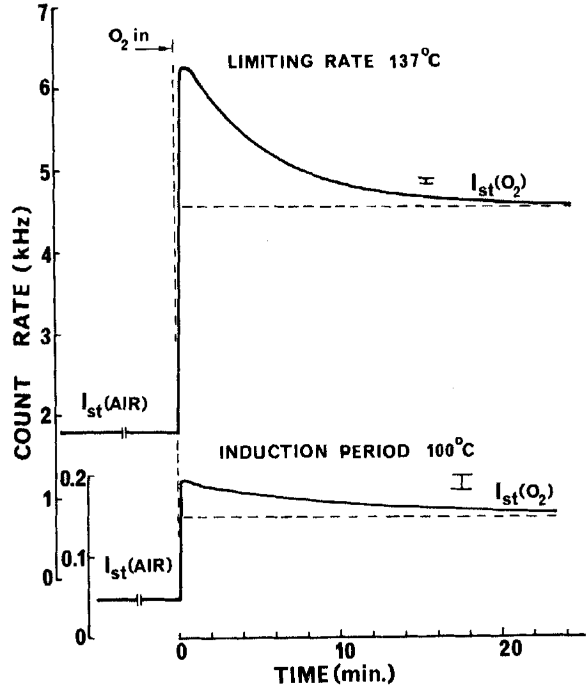


FIG. 4. Observed oxyluminescence pulse after admitting oxygen to a sample heated for 44 min in air at 137°C in the limiting oxidation rate region and 100°C in the induction period.

in solution where the oxidation rate is independent of the oxygen concentration above about 0.15 atmosphere. Direct evidence has been obtained for this from oxyluminescence in the limiting oxidation rate region at 137°C by rapidly admitting oxygen to a sample of nylon 66 during oxidation in air. A pulse is observed (Fig. 4) with a slow decay to the new steady state. The fast decay observed when the sample is preheated in nitrogen is absent. If the previous explanation of the nonstationary behavior of the oxyluminescence is correct, this pulse can arise only if there is a significant alkyl radical concentration in the polymer during oxidation in air. Some evidence has also been found for similar behavior in the induction period at 100°C, but here the pulse is very weak and precise analysis is difficult.

Reaction (2) can become rate-determining because of the low solubility of oxygen in the solid polymer. Alkyl radical reactions have been observed in the oxidation of polypropylene [20, 21] and in the photo-oxidation of thin films of nylon 6 [22]. An important consequence of this is that a more efficient stabilizer system for nylon 66 fibers would include an alkyl radical scavenger, as the hindered phenol class of antioxidants present in this nylon sample react only with alkyl peroxy radicals [23].

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