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EMISSION THERMOPHOTOMETRY.
V. PREMELTING LIGHT EMISSION OF SOME NYLON POLYMERS

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ABSTRACT

The premelting light emission (LE) of a series of nylon polymers was determined using the technique of emission thermophotometry (ETP). Light emission can begin at temperatures as low as 80 ° C, in a flowing oxygen atmosphere. The effect of heating rate and sample size on the LE process was determined. Isothermal LE measurements were also recorded at various temperatures.

INTRODUCTION

Using the thermal analysis technique of emission thermophotometry (EPT) [1], Wendlandt recorded the ETP curves of various nylon polymers [2,3]. In this technique, the light emission (LE) of a polymer heated at 10–20 ° C $\min^{-1}$ in an oxygen atmosphere, is recorded as a function of sample temperature. The ETP curve can be used to characterize the polymer because each ETP curve is unique and can therefore serve as a "fingerprint" of the substance. The ETP curves contained peak maxima whose magnitudes and temperatures provided a unique characterization of the substance, similar to that of DSC and/or DTA.

Previous ETP investigations were concerned with the characterization of nylon polymers to temperatures above their melting points. Thus, the LE of the premelting, melting, oxidative degradation and decomposition reactions were recorded simultaneously in the same curve. In this investigation, only the premelting LE behavior is determined. This approach requires a somewhat higher photometric sensitivity measuring device, but it was revealed that the LE process can begin at temperatures as low as 80 ° C.

EXPERIMENTAL

Apparatus

The ETP apparatus has been described previously [1]. A new higher sensitivity photometer, model M460 Schoeffel photometer, has replaced the

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older less-sensitive unit. The analog output signal from the photometer was digitized and stored in a microcomputer data station and replotted as a function of time or temperature at various photometric sensitivities.

Procedure

The nylon polymer samples, with masses ranging from 5 to 45 mg, were heated from room temperature to a maximum of 200–220 °C at a furnace heating rate of 20 °C min^{-1} in a flowing oxygen atmosphere (about 40 ml min^{-1}). Each sample, which consisted of a spherically shaped solid of 4–5 mm in diameter, was contained in a 7-mm diameter disposable Al container. It was found that no corrections were necessary for background thermal radiation.

Samples

The nylon polymer samples were obtained from Scientific Polymer Products, Inc. (Webster, NY). They were used without further modification or purification.

RESULTS AND DISCUSSION

In previous investigations, the ETP curve consisted of a series of peak maxima with the initial and final LE values approaching zero. The ETP curves reported here show only a part of the LE process: that due to the premelting behavior of the polymer. Light emission was found to begin at temperatures (T_i) as low as 80 °C for nylon 6/10; values for the other polymers are tabulated in Table 1. Some of the ETP curves contained shoulder peaks whose peak maximum temperature values, T_{max}, are also given in Table 1.

The effect of heating rate on the LE of nylon 6 is shown in Fig. 1. Two heating rates were examined: 10 ° and 20 °C min^{-1}. The curve shapes were similar except at higher temperatures (ca. 180 °C). Increasing the sample size by a factor of three (from 15 to 45 mg) for nylon 6 (Fig. 1) revealed the formation of a slight shoulder perturbation in the ETP curve. The same effect could also be observed by increasing the photometric sensitivity by computer manipulation of the stored data.

The change in LE with time at a fixed temperature (isothermal ETP curves) is shown for nylon 12 in Fig. 2. Three temperatures were studied: 133, 155 and 170 °C. As expected, the rate of LE increased with an increase in temperature.

The computer manipulation of the ETP curve of nylon 6/T is shown in Fig. 3. Expanding the LE axis by a factor of three (3 ×) increased the

TABLE 1

ETP initial (T_i) and peak maximum (T_{max}) temperatures for nylon samples [a]

Polymer	T_i (°C)	T_{max} (°C)
Nylon 11	115	198
Nylon 12	113	192
Nylon 6/T	97	166
Nylon 6/12	90	
Nylon 6/9	84	
Nylon 6/10	80	155
Nylon 6/6	100	
Nylon 6	85	

[a] Heating rate of 20 °C min^{-1} and fixed photometric sensitivity of 100 mA.

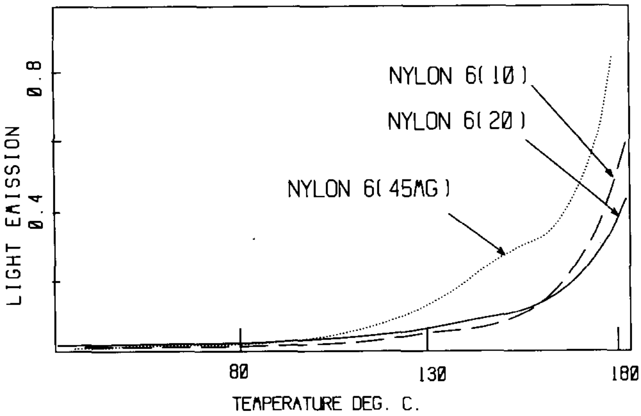


Fig. 1. The ETP curves of nylon polymers.

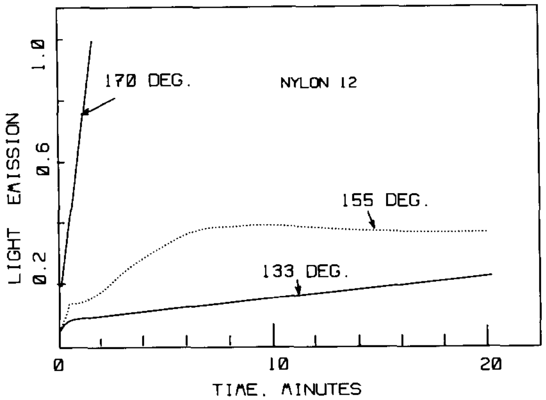


Fig. 2. The isothermal LE curves of nylon 12.

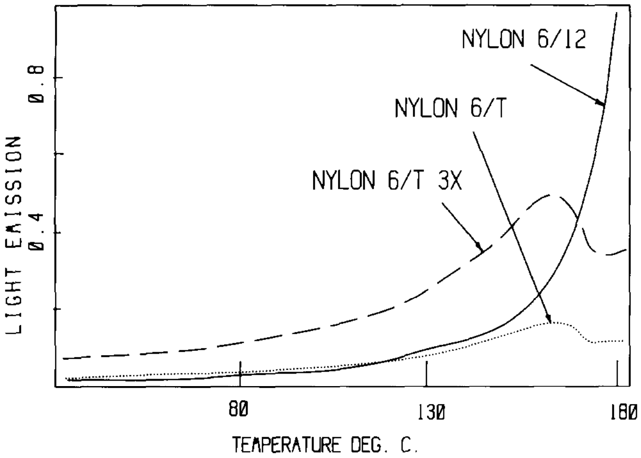


Fig. 3. The ETP curves of nylon polymers.

magnitude of the shoulder peak at a T_{max} of 166 °C. This is similar to the previous example of increasing the sample size by the same magnitude (nylon 6).

The ETP curves for the other polymers are illustrated in Figs. 4 and 5. The curves for nylon 11 and 12 (Fig. 5) were similar, with a T_{max} for the former at a higher temperature, 198 °C (versus 192 °C for the latter polymer). In Fig. 4, a broad shoulder peak at a T_{max} of 155 °C was observed for nylon 6/10.

Although the origin of the LE process is not known for the nylon polymer, it is no doubt similar to that of hydrocarbon polymers such as polyethylene [4–6]. In the case of the latter, the LE is thought to originate during the termination step [5] from a transition in an electronically excited

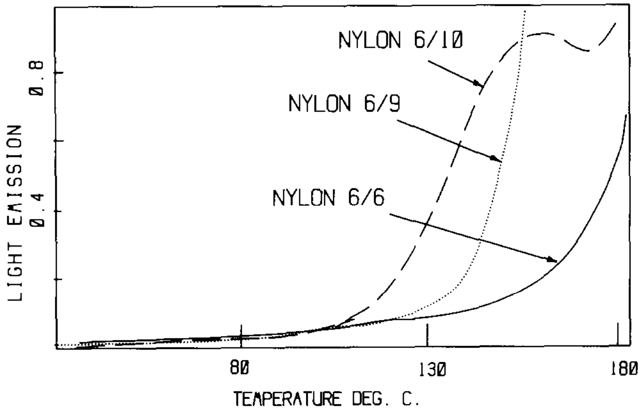
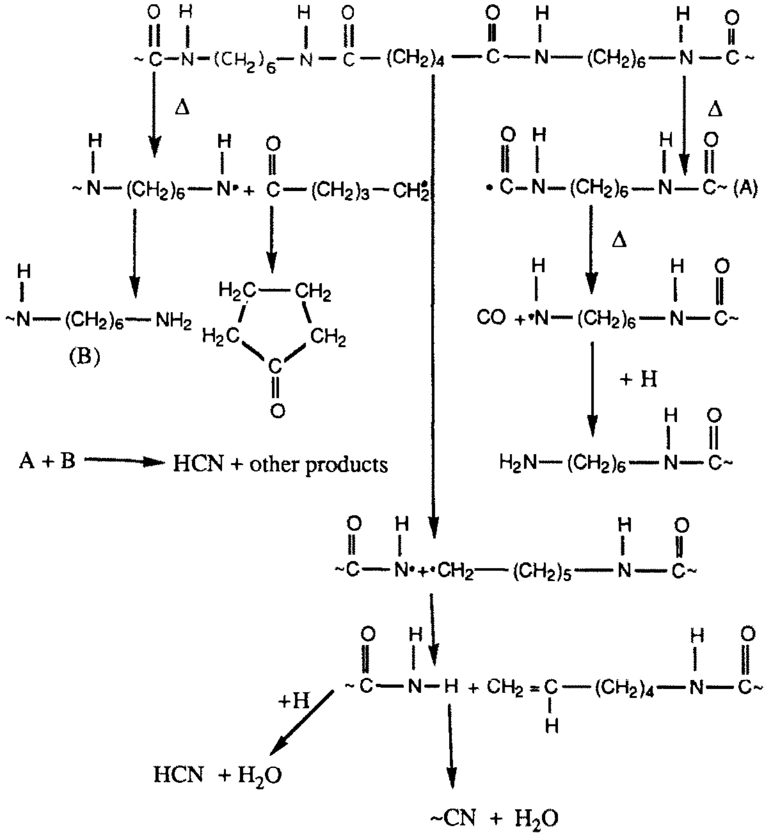


Fig. 4. The ETP curves of nylon polymers.

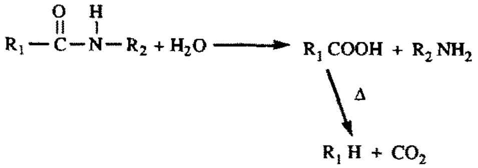
ketone of the type n* → π. This phosphorescence intensity was also found to be related to the ability of the polymer to absorb oxygen.

The thermal degradation of nylon polymers has been studied by a large number of investigators, due perhaps to the early development of these polymers and also to their industrial importance. It is beyond the scope of this brief report to describe this degradation in detail here although Jellinek and Dunkle [7] have summarized the important aspect of the kinetics and mechanisms of some of these restrictions. The degradation mechanism for nylon 6/6 at low temperatures is tentatively described as (the random chain scissors is assumed to be rate determining)

initiation



hydrolysis



$$R_1-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R_2 + H_2O \longrightarrow R_1COOH + R_2NH_2$$

$$R_1COOH \xrightarrow{\Delta} R_1H + CO_2$$

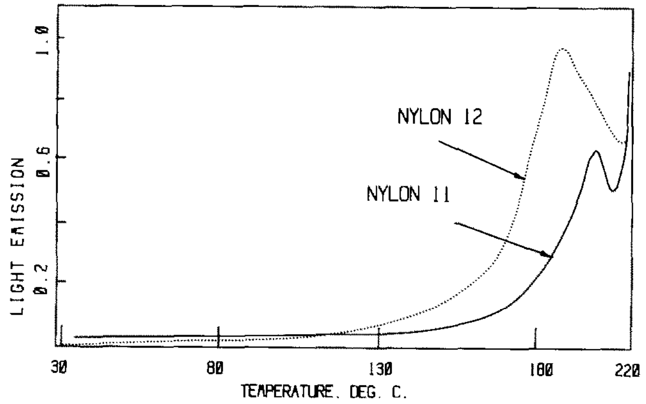


Fig. 5. The ETP curves of nylon polymers.

It is surprising that there is only one activation energy (about 180 kJ mol^{-1}). It is expected that on further purification, an activation energy of 120–250 kJ mol^{-1} would be obtained. The latter values would be sufficient for random chain scission of the peptide bond and of the next strongest bond.

Light emission could occur from an electronically excited ketone somewhere in the degradation scheme. However, no mechanism for this has been proposed.

ACKNOWLEDGMENT

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