EMISSION THERMOPHOTOMETRY. III. SOME NYLON POLYMERS *

W.W. WENDLANDT

Department of Chemistry, University of Houston, Houston, TX 77004 (U.S.A.)

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ABSTRACT

The emission thermophotometry (ETP) curves of selected nylon polymers are presented. The ETP curves, which are recordings of the polymer light emission versus temperature, are used as characterization tools for the compounds. Each curve is unique and specific for a given polymer. The light emission is probably due to an $n \rightarrow \pi^*$ transition from an electronically excited ketone formed by the decomposition of a peroxy radical during the polymer oxidation process.

INTRODUCTION

The thermal analysis technique of emission thermophotometry [1] consists of the non-isothermal recording of the light emission of a substance as a function of temperature. The substance may be an organic compound, polymer, coordination compound, naturally occurring substance, inorganic compound, and so on. The resulting emission thermophotometry (ETP) curve can be used as a means of characterization of the substance since each ETP curve appears to be unique. The curves contain peak maxima whose magnitude and location with respect to the temperature axis provide a unique characterization of the substance similar to the thermal analysis techniques of DTA, DSC, DTG, EGA, and so on. As with the latter techniques, the curve peaks are dependent on heating rate, sample particle size, composition of the furnace atmosphere, instrumentation variables, and so on [2].

This report presents new ETP curves of some selected nylon polymers recorded on a recently described improved apparatus.

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* For Part II, see Thermochim. Acta, 99 (1986) 61.

TABLE 1

Composition of selected nylon polymers

Designation	Composition
Nylon 6	Polycaprolactam
Nylon 6/6	Polyhexamethylene adipamide
Nylon 6/T	Polyhexamethylene terephthalamide
Nylon 6/9	Polyhexamethylene nonanediamide
Nylon 6/10	Polyhexamethylene sebacamide
Nylon 11	Polyundecanoamide
Nylon 12	Polylauryllactam

EXPERIMENTAL

Apparatus

The ETP apparatus employed has previously been described [1]. The microcomputer data logging, display and printing system provided improved recording and printing of the ETP curves. Variable scaling was permitted on both the light emission and temperature axes, as well as other features.

Procedure

The nylon polymer samples, with masses ranging from 5 to 10 mg, were heated from room temperature to about 400°C at a heating rate of 20°C min^{-1} in a flowing oxygen furnace atmosphere (40 ml min^{-1}). Each polymer sample, which consisted of a spherical mass of 4–5 mm in diameter, was pyrolyzed in a 7 mm diameter disposable aluminum container. No correction was needed for background emission of the ETP curve, as was necessary in a previous investigation [3].

Samples

The nylon polymer samples were obtained from Scientific Polymer Products, Inc. (Webster, NY). They were all used without further modification or purification. The chemical composition of the polymer is given in Table 1.

RESULTS AND DISCUSSION

As found in a previous oxyluminescence (OL) investigation [3], the ETP curves consisted of one peak (except for nylon 6/10), with peak maximas in the temperature range 200–350°C. These curves are illustrated in Fig. 1.
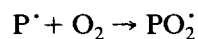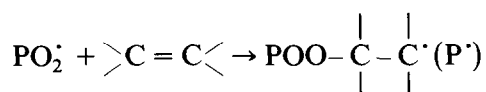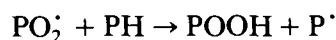
The origin of the light emission process has been reviewed by Wendlandt [4], Reich and Stivala [5], and others [6]. Although a mechanism is not known for the nylon polymers, for many hydrocarbon polymers the oxidation steps involved in molecular oxygen are [6] as follows.
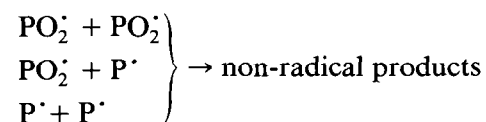
Initiation

$$PH \overset{O_2}{\to} PO_2^{\cdot}$$

$$POOH \to PO_2^{\cdot}$$
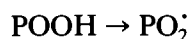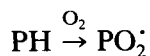
where PH = polymer; H = active hydrogen; $PO_2^{\cdot}$ = peroxy radical (free radical).

Propagation

$$PO_2^{\cdot} + PH \to POOH + P^{\cdot}$$

$$PO_2^{\cdot} + {>}C = C{<} \to POO - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}}{}^{\cdot}(P^{\cdot})$$

$$P^{\cdot} + O_2 \to PO_2^{\cdot}$$

where $P^{\cdot}$ = polymer radical.

Termination

$$\left. \begin{array}{l} PO_2^{\cdot} + PO_2^{\cdot} \\ PO_2^{\cdot} + P^{\cdot} \\ P^{\cdot} + P^{\cdot} \end{array} \right\} \to \text{non-radical products}$$

The light emission from the polymer is thought to originate during the termination step [5], or:

$$PO_2^{\cdot} \to \text{products*} + O_2$$
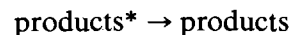
products* → products

The products* may be an electronically excited ketone in which a transition of the type $n \to \pi$ can give rise to phosphorescence. It has been found that the maximum luminosity of the emitted light was related to the ability of the polymer to absorb oxygen and that is should be able to estimate the light emission from oxygen uptake [7].

Although the mechanism of light emission from the nylon polymers is not known at this time, it probably involves some of the steps previously
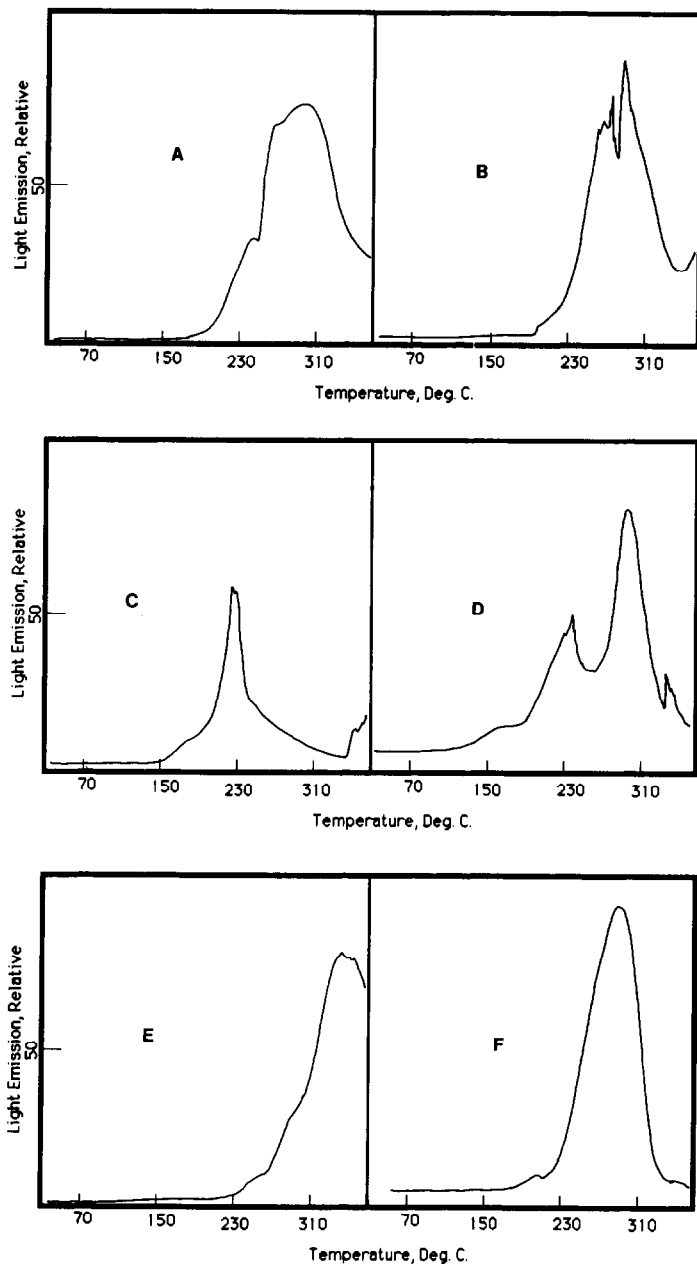
Fig. 1. ETP curves of: (A) nylon 6; (B) nylon 6/6; (C) nylon 6/9; (D) nylon 6/10; (E) nylon 6/T; (F) nylon 11.

outlined for pure hydrocarbon polymers like polyethylene and polypropylene. The qualitative features of the ETP curves, which may be useful as a characterization tool for the polymers, are described here.
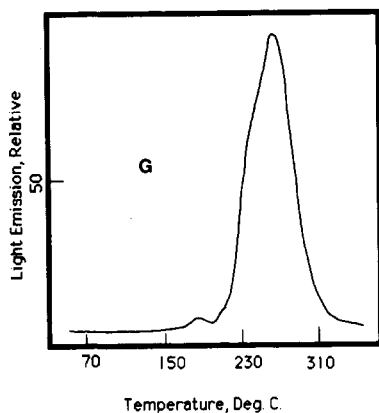
Fig. 1. (G) Nylon 12.

Each ETP curve is uniquely different, in reference to peak shape and peak maxima temperature. Nylon 6, 6/6 and 6/10 all had shoulder peaks on the low temperature side of the main curve peak. The curve peak maximum for nylon 6/9 is at about the same temperature, 220–230°C, as the shoulder peak for nylon 6/10. The nylon 11 and 12 ETP curves were of the same general shape except that the peak maximum for the former is 240°C versus about 270°C for the latter. The highest temperature curve peak maximum, 350°C, was found for nylon 6/T although there could have been one observed for nylon 6/9 had the temperature axis been extended past 400°C. Except for nylon 11 and 12, it is not possible to correlate the ETP curve with structural parameters of the polymers because the curves are so dissimilar.

CONCLUSIONS

The ETP curves may be used for the characterization of the seven nylon polymers investigated here. Each curve is unique for the polymer and could be employed for their qualitative identification. The origin of the light emission process is not known at this time but may be similar to that described for polyethylene or polypropylene.

ACKNOWLEDGMENT

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