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EMISSION THERMOPHOTOMETRY. II. THE SPECTRAL DISTRIBUTION OF EMITTED LIGHT FROM POLY(ETHYLENE OXIDE)*

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ABSTRACT

The spectral distribution of the light emission of poly(ethylene oxide) was determined at 300 ± 5°C by use of a modified ETP apparatus. In this apparatus a small grating type monochromator, which was mechanically scanned from 400 to 700 nm, was attached to the sample and furnace enclosure. It was found that the broad peak maximum was centered at about 500 nm, in agreement with previous studies using wavelength filters.

INTRODUCTION

The thermal analysis technique of emission thermophotometry (ETP), which was recently described by Wendlandt [1], measures the light emitted by various substances as they are heated in an air or oxygen atmosphere. Generally, the light is emitted by organic compounds, polymeric materials, coordination compounds containing oxidizing and reducing ligands, inorganic compounds, and others. The intensity of the light emission is very low and requires a sensitive photomultiplier tube (PMT) and photometer to detect it, although some investigators have reported that the emitted light can be seen by the human eye if viewed in a darkened room.

The spectral distribution of the emitted light for certain polymers has been measured in a crude manner by the use of wavelength filters. Ashby [2] found that the PMT anode current was attenuated by about 50% by interposing a filter that absorbed light of wavelengths shorter than 420 nm between the polymer and the PMT. No current could be detected if a filter was interposed that absorbed all wavelengths shorter than 515 nm. It was concluded that in oxyluminescence, the light emission by polymers in air or oxygen, 50% of the light emission had wavelengths between 420 and 515 nm and 50% between 300 and 420 nm. Barker et al. [3] also employed filters to

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determine the spectral distribution of light emission by certain polymers and found that the spectrum consisted of a broad peak from 400 to 610 nm with a maximum at 540 nm, and a shoulder peak at 475 nm. Using wavelength filters, de Kock and Hol [4] obtained the light emission spectrum of dicumyl peroxide in polypropylene. The spectrum extended from 360 to about 500 nm with a peak maximum at 420 nm. It was very similar to the phosphorescence spectrum of acetophenone dissolved in poly(methylmethacrylate).

In order to measure the light emission wavelength distribution of poly(ethylene oxide), a strong emitter, the emitted light was passed through a grating monochromator which could be scanned mechanically over the wavelength range of 400–700 nm. Due to the low-level light intensities involved and the wide monochromator slit widths employed, the spectrum obtained was only approximate.

EXPERIMENTAL

Monochromator system

An overall view of the monochromator and ETP system is shown in Fig. 1, while the monochromator attachment details are shown in Fig. 2.

A small grating monochromator, 40×65 mm (Kratos, Model GM100, Westwood, NJ) was attached to the light-tight enclosure for the DSC cell of the ETP system. This is the same ETP system that has previously been described by Wendlandt [1]. A 1P28 PMT connected to a photometer (Schoeffel, Model M460, Westwood, NJ) was used to detect the emitted light, which was recorded on the Y-axis of an X–Y recorder (Houston Instruments, Model 100, Austin, TX). Scanning of the monochromator was controlled by a small reversible AC motor, the direction of which was selected by a switch box. A retransmitting potentiometer, connected to the wavelength shaft of the monochromator, gave a voltage output that was proportional to the wavelength. This voltage was recorded on the X-axis of

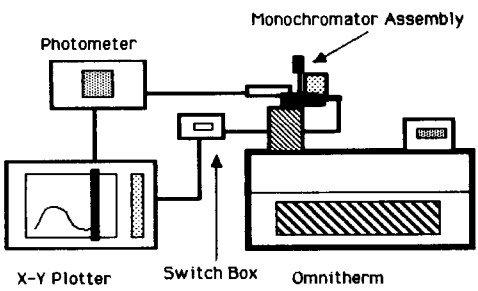

Fig. 1. Schematic diagram of the ETP system.

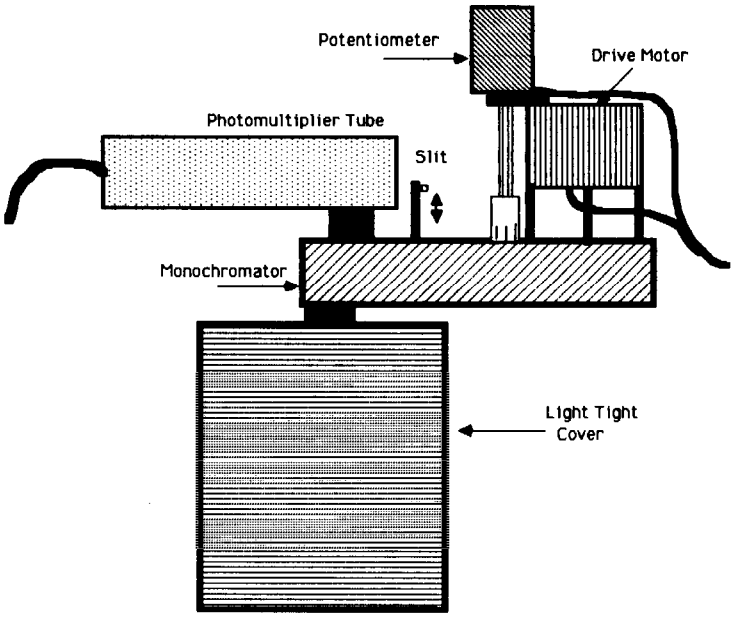

Fig. 2. Schematic diagram of attachment of monochromator to ETP system.

the $X-Y$ recorder. The sample was heated isothermally, at a temperature at which the light emission was at a maximum, by an Omnitherm thermal analysis controller.

In Fig. 2, the monochromator, drive motor, retransmitting potentiometer, and PMT are illustrated in greater detail. The slit width was interchangeable but due to the low-level light intensity, a slit width of 1.4 mm was necessary.

Procedure

The sample (30–50 mg) was weighed out into a platinum container and placed inside the furnace chamber of the ETP apparatus. The quartz light pipe was removed from the apparatus and replaced by the usual DSC cell silver metal cover containing a 1 cm diameter opening. A 50 mm diameter microscope slide cover glass was placed over the opening to aid in eliminating temperature gradients in the sample chamber and also to prevent the polymer decomposition products from condensing on the PMT surfaces attached to the sealed end of the enclosure. The furnace and sample were then heated to the desired temperature by the isothermal mode of the Omnitherm controller and the wavelength and photometer outputs recorded on the recorder. The scanning time was 1.0 min from 400 to 700 nm. Several scans could be made at any one temperature setting in either wavelength direction. During the light emission process, oxygen, at a flow rate of 40 ml min^{-1}, was passed through the furnace and sample chamber.

RESULTS AND DISCUSSION

The wavelength distribution curve for the light emission of poly(ethylene-oxide) is shown in Fig. 3.

The light emission spectrum at $300 \pm 5°C$ consists of a broad band from 400 to 700 nm with a peak maximum at about 500 nm. Since none of the previous investigations used poly(ethylene oxide), the peak maximum cannot be correlated with their data. However, the wavelength maximum is close to that reported by Barker et al. [3] for the light emission of polyethylene. It is somewhat greater than that found by the filter method of Ashby [2] for the same polymer. Thus, the emitted light from poly(ethylene oxide) is in the green region of the spectrum. It was not possible to detect the light emission from the polymer by the dark-adapted human eye.

ACKNOWLEDGEMENT

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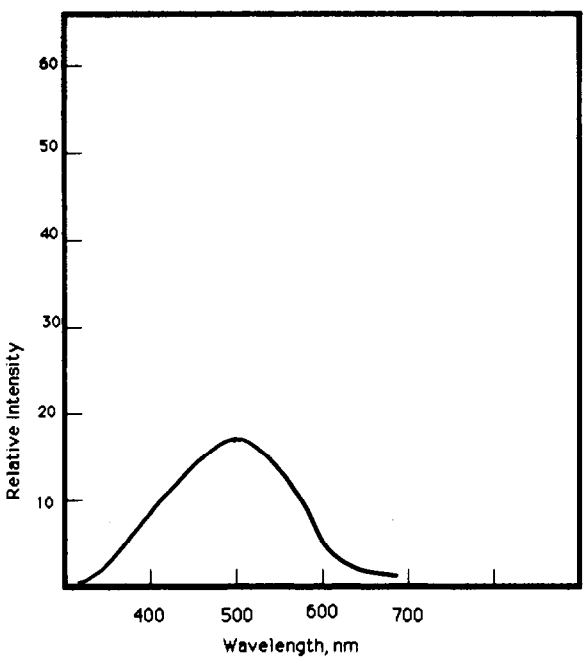

Fig. 3. Wavelength distribution curve for the light emission of poly(ethylene oxide) at $300 \pm 5°C$.

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