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Note

Continuous thermal analysis of bromide from bromine-bearing polymers

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Bromine-bearing polymers are often used as flame retarding agents. It is generally accepted that these agents liberate HBr when thermally decomposed. The HBr evolved during the decomposition retards the flame by acting as a free radical scavenger in the gas phase, interrupting the chain branching reactions taking place in the flame. It seems to us that continuous monitoring of HBr concentration evolved during the thermal decomposition of such agents might be of great importance when investigating the mechanism of flame retardation.

In the present work poly-tribromoethyl-acrylate (p-TBEA) was chosen for thermal decomposition to demonstrate continuous HBr monitoring. The polymer was obtained by the γ-irradiation of TBEA monomer in an evacuated ampoule for 20 h receiving a total dose of 6.0 Mrad.

A sample of p-TBEA was decomposed in the TG pyrolysis chamber of the 951 thermogravimetric analyzer connected to a DuPont 990 thermal analyzer. The gases evolved during decomposition were bubbled into a buffered aqueous solution (pH 6.9 phosphate) by flushing nitrogen through the TGA pyrolysis chamber. Any gaseous HBr formed during the thermal decomposition was dissolved in the buffered aqueous solution and continuously monitored by a specific bromide electrode. The Orion model 94-35 A electrode and a reference double-junction electrode, model 90-02-00, were connected to an Orion digital pH meter, model 701. The voltage signal obtained from the bromide electrode was differentiated by means of a RC circuit as shown in Fig. 1. The derivative and the original signals were displayed on a double-pen 3047

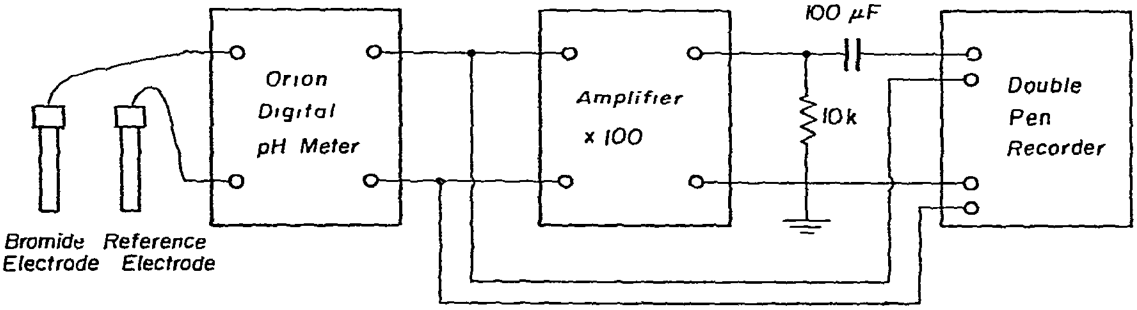

Fig. 1. Bromide detection system.

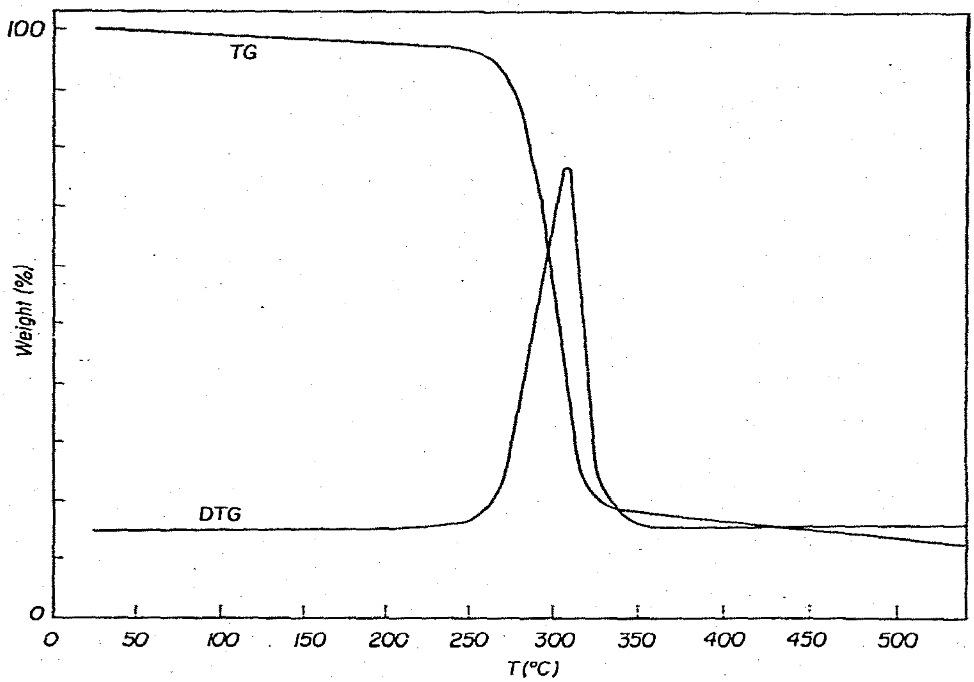

Fig. 2. TG and DTG of a 3.75 mg sample of p-TBEA under nitrogen atmosphere.

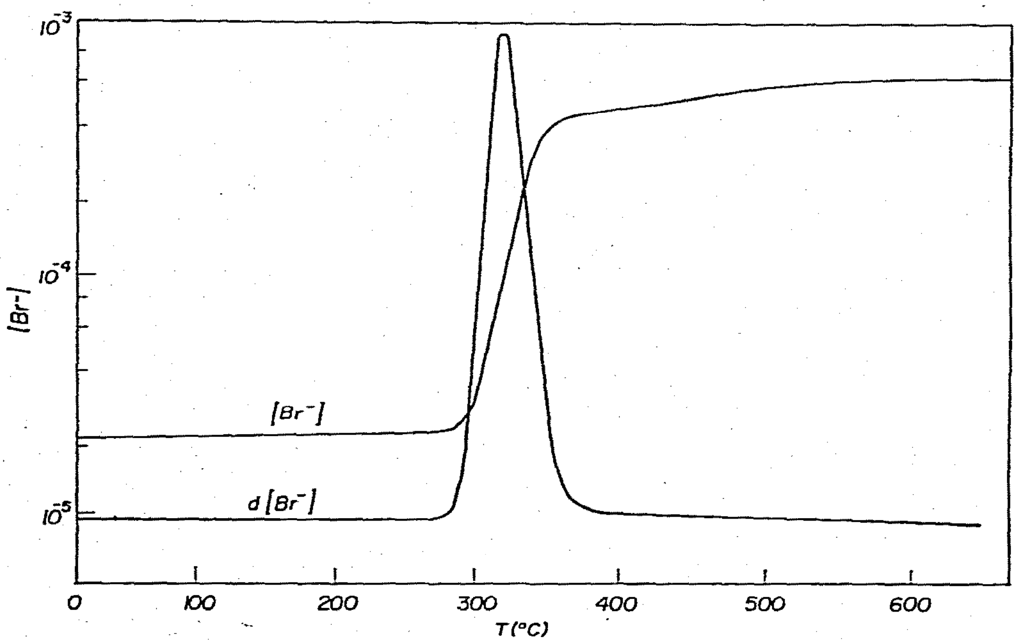

Fig. 3. Br⁻ concentration accumulated during the thermal decomposition of the sample whose curve is given in Fig. 2, and the derivative of the Br⁻ concentration curve, dBr⁻.

Yokogawa recorder. In this way the TG curve ,the increase in bromide concentration and the derivative signals were obtained simultaneously in a single run. Figure 2 represents the TG curve obtained with a 3.75 mg p-TBEA sample.

The [Br^-] signal appears ~10 sec after the weight loss signal in the TG curve. The delay time depends on the volume of the tubing connecting the pyrolysis chamber to the bromide electrode, and on the flow rate of the flushing gas. This delay time was taken into account when determining the temperature scale in Fig. 3.

About 40% of the total Br present in the polymer is evolved as HBr in the thermal decomposition of p-TBEA as calculated from Fig. 3. Such a high yield of HBr makes this polymer a good candidate for use as a flame retardant in other flammable polymers. Some properties of TBEA-grafted polyester were published recently[1]. A detailed paper on the flame retardation of fabrics grafted with TBEA and other monomers is in preparation[2].

REFERENCES

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