

## Short Communication

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### Quenching of chromophoric species in nylon-6,6 by halide ions

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In earlier papers we reported on the fluorescence emission from nylon-6,6 polymer and discussed the role of the species responsible in its photo-oxidation [1 - 3]. The emission was found to originate from impurity oxidation products present in the nylon-6,6 salt, but their concentration was enhanced during the polymerization process [3]. We now report that the fluorescence from the oxidized salt is quenched by halide ions in the order  $I > Br > Cl > F$ . The significance of these important results are outlined here in relation to the light stabilizing action of halide ions in the commercial polymer [4 - 6].

Mild oxidation of nylon-6,6 salt at 130 °C for 1 h results in the formation of fluorescent species with excitation and emission wavelength maxima at 360 and 440 nm respectively. Stern-Volmer plots showing the quenching effect of halide ions are given in Fig. 1. The plots for all the halide ions were linear over the concentration range examined (0 to 0.2 M). Using single photon counting techniques we obtained a value of  $4.7 \pm 0.15 \times 10^{-9}$  s for the radiative lifetime. This value indicates that the configuration of the donor excited state is  $\pi\pi^*$  in nature [7]. Experimentally we have also found that with aqueous solutions equilibrated with air the presence of oxygen has no effect on the fluorescence intensity. Thus, this observation is consistent with the short fluorescence lifetime measured by single photon counting.

It has long been known that the addition of alkali metal halides (either alone or included in stabilizing compositions), improves the light stability of the polymer [4 - 6]. Further, the heavier halides such as the iodide and bromide ions have been found to be more effective [4]. Our findings here show that the same ions are the more effective in quenching the fluorescent oxidation impurities. Further details of this work will be described later when we shall deal with the precise mechanisms involved in nylon-6,6 photostabilization.

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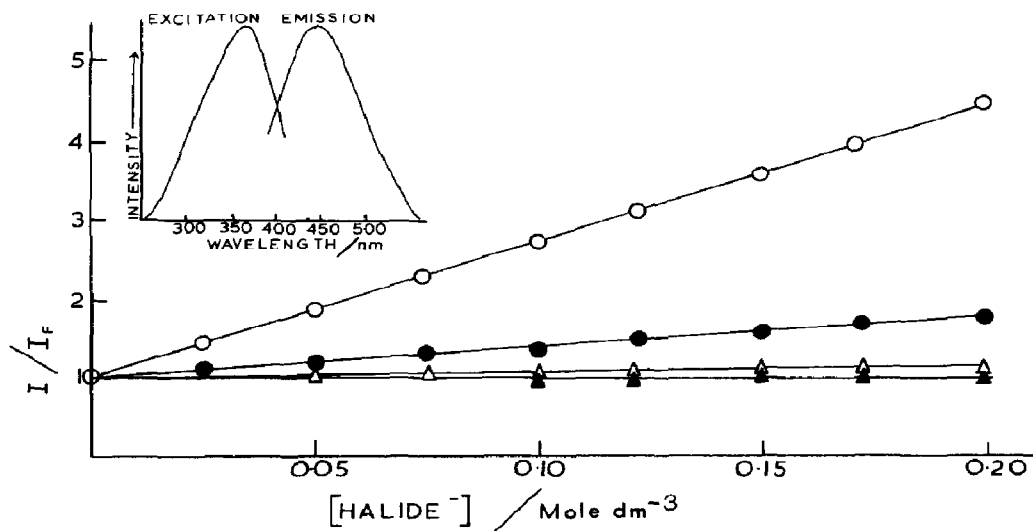


Fig. 1. Quenching of the fluorescence from thermally oxidized nylon-6,6 salt (20% w/v in water) by sodium halides;  $\circ$ , NaI;  $\bullet$ , NaBr;  $\triangle$ , NaCl;  $\blacktriangle$ , NaF. The plots were obtained using the Stern-Volmer relationship:  $I/I_F = 1 + \tau kq[Q]$ , where  $I$  = emission intensity without halide ions;  $I_F$  = emission intensity with halide ions;  $\tau$  = radiative lifetime of the fluorescence;  $kq$  = rate constant for bimolecular quenching;  $Q$  = halide concentration in  $\text{mol/dm}^3$ . Fluorescence measurements were obtained using a corrected Hitachi Perkin-Elmer MPF-4 spectrofluorimeter. The insert shows the fluorescence excitation and emission spectra of nylon-6,6 salt [3].

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