405

LUMINESCENCE AND DEGRADATION OF NYLON POLYMERS III: EVIDENCE FOR TRIPLET–SINGLET RESONANCE ENERGY TRANSFER TO A COMMERCIAL DISPERSE DYE

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Summary

Evidence is presented for the occurrence of a triplet–singlet resonance energy transfer process between the α,β-unsaturated carbonyl impurities in nylon-6,6 polymer and a photoactive disperse dye. A value of 4.6 nm was obtained for the critical transfer distance between donor and acceptor, and this is within the range predicted by resonance transfer theory. The results are discussed in relation to the low lightfastness and phototendering activity of the dye on nylon fibre.

Introduction

The thermal and photochemical behaviour of luminescent chromophoric species in the polymer were dealt with in the earlier papers of this series (I, II) [1]. These chromophoric species are impurities introduced adventitiously during manufacture [2] together with dyes or pigments that are added to colour or delustre the polymer [3, 4]. Here we provide direct evidence for a triplet–singlet resonance energy transfer process between the photoactive α,β-unsaturated carbonyl impurities in the polymer and a strongly photosensitizing dye, Disperse Yellow 13 (3-methoxybenzanthrone (MBA)) [5]. This observation is of great value in the interpretation of the lightfastness and phototendering activity of the wide range of dyes and pigments used commercially with nylon-6,6, particularly when the polymer is spun into filament form for use as a textile fibre [6].

The observation of triplet–singlet resonance energy transfer in a polymer matrix is also of direct interest to the photochemist. As will be shown it allows an experimental value for the critical transfer distance R_0 to be calculated which can be compared with theoretical estimates based on the mechanisms of energy transfer originally developed by Förster [7].

Experimental

Materials

Nylon-6,6 film (200 μm thickness) containing no commercial additives was supplied by I.C.I. (Plastics Division) Ltd. Samples of Disperse Yellow 13 (MBA) were obtained from the Fine Chemicals Service of I.C.I. Ltd. and were thoroughly purified by chromatography on an alumina column using chloroform as eluant followed by crystallization from ethanol (m.p., 174 - 175 °C) [8].

The dye was applied to the nylon-6,6 film under the normal conditions for disperse dyeing [9] (aqueous dyebath at 110 °C for 1 h). A control film was similarly treated. The dye concentration was calculated from absorption measurements at 450 nm using a value for log ϵ = 4.0 for the dye in N,N-dimethylformamide. The extinction coefficient of the dye at its longest wavelength absorption maximum is little affected by solvent polarity [8].

Luminescence measurements

Fluorescence and phosphorescence spectra and phosphorescence lifetimes were obtained as described earlier [1] using a double grating (1200 lines mm^{-1}) corrected Hitachi Perkin–Elmer MPF-4 spectrofluorimeter.

Results and discussion

Figure 1 demonstrates the effect of the addition of MBA on the native phosphorescence emission (λ_{max} = 410 nm) of the polymer. As the intensity of polymer phosphorescence decreases with increasing MBA concentration, so also the fluorescence emission (λ_{max} = 520 nm) of MBA increases. Indeed at concentrations of dye above about 8 × 10^{-3} M only the dye fluorescence is observed from the polymer, and a typical spectrum under these conditions is also shown in the figure.

The interesting feature of the dye fluorescence obtained in these experiments, however, is that the mean lifetime of the emission is of the order of 1.2 s. Thus, it is very much greater than that of normal fluorescence but is remarkably close to that of the lifetime of the native phosphorescence of the polymer [10, 11]. Figure 2 compares the kinetics of decay of the native phosphorescence emission from the polymer with the sensitized long lived fluorescence emission from the dye. It is seen that both exhibit first order kinetics. In part I we showed that the native phosphorescence emission of the polymer is from α,β-unsaturated carbonyl impurity groups with an excitation λ_{max} at about 295 nm. Only when an excitation in this spectral region was used was the fluorescence emission from the dye long lived. Excitation of the dyed polymer film in the region of the longest wavelength absorption band of the dye (about 450 nm) gave normal emission lifetimes (about 5 ns).
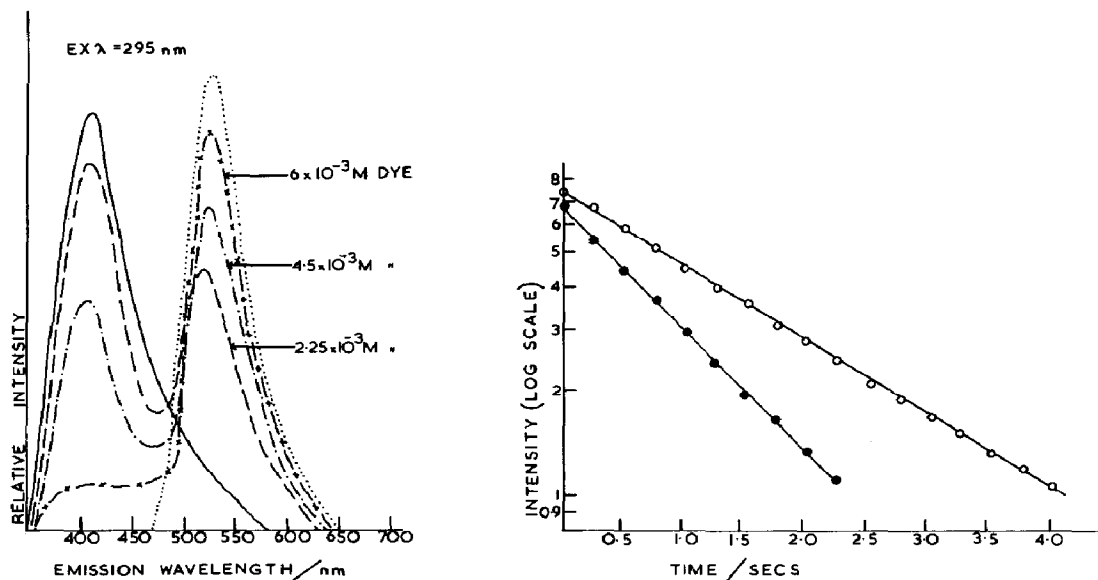
Fig. 1. Increase in the ratio of the 295 nm sensitized long lived fluorescence of MBA to the phosphorescence of nylon at 77 K with increasing MBA concentrations of 2.25 × 10^{-3} M (– – –) (S × 30), 4.5 × 10^{-3} M (–·–) (S × 100), 6 × 10^{-3} M (– × –) (S × 100) and 8 × 10^{-3} M (. . .) (S × 100), where S is the sample signal intensity. The solid curve is the normal phosphorescence emission from nylon-6,6 film containing no MBA (Ex λ_{max} = 295 nm) and the dotted curve is the normal room temperature fluorescence from MBA in nylon-6,6 film (Ex λ_{max} = 450 nm).

Fig. 2. First order plots of the phosphorescence emission (λ_{max} = 410 nm) from nylon-6,6 film (O) and the sensitized long lived fluorescence emission (λ_{max} = 520 nm) from MBA-dyed nylon-6,6 film (8 × 10^{-3} M) (●). Ex λ = 295 nm.

It is evident that the long lived dye fluorescence is due to an energy transfer process from the α,β-unsaturated carbonyl impurities (donor) to the MBA (acceptor). Further, the long mean lifetime and kinetics of the fluorescence of the acceptor indicate the donor to be in its triplet state. Thus a mechanism of triplet–singlet resonance energy transfer is indicated and, although this process is forbidden by spin-conservation rules, Förster [7] has suggested that such a process may be partially "allowed" provided that the lifetime of the donor is sufficiently long. This appears to be the case here.

Further evidence for a triplet–singlet resonance energy transfer process is obtained from the value of the critical transfer distance R_0 which is normally within the range 3 - 10 nm [12] and is given by the expression [13]

$$R_0 = 7.35/([C]_{1/2})^{1/3}$$

where $[C]_{1/2}$ is the critical acceptor concentration. This is the concentration of acceptor required to reduce the emission lifetime of the donor to one-half
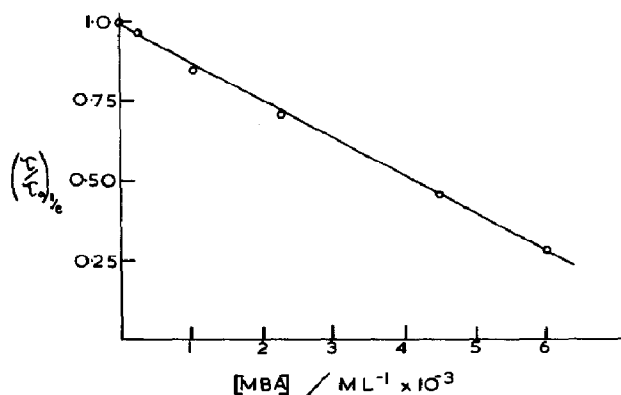
Fig. 3. Quenching of nylon-6,6 phosphorescence at 410 nm by MBA, where τ_0 and τ are the mean exponential phosphorescence emission lifetimes (λ_{max} = 410 nm) for the nylon-6,6 film control and MBA-dyed polymer films respectively.

of its initial value in the absence of acceptor. Figure 3 shows a plot of the ratio of the phosphorescence emission lifetimes of the donor (polymer) in the absence (τ_0) and presence (τ) of acceptor (MBA) *versus* the concentration of MBA. The plot is linear over the concentration range examined and gives a value for the critical acceptor concentration of 4×10^{-3} M. From the above expression a value of 4.6 nm is obtained for the critical transfer distance R_0. This value falls within the limits expected.

Finally, in a recent study [14] of the photophysical properties of MBA we concluded that the poor lightfastness and strong phototendering action of this dye could be due to its high charge transfer content in the first excited singlet state. Now we have found that there is a further process that can lead to and thus enhance the same technological effects. In addition to the radiation which is directly absorbed by the dye, the dye is also capable of being photoexcited into its first excited singlet state indirectly by the triplet—singlet resonance transfer process shown here. This will only occur, of course, with radiation absorbed by the α,β-unsaturated carbonyl impurities in the spectral range 290 - 330 nm [1]. In many cases, however, this can be the most damaging region for polymer photodegradation [6].

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