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## SHORT COMMUNICATION

# A MECHANISTIC STUDY OF THE PHOTOCROSSLINKING OF POLY(VINYL ALCOHOL) FILMS MODIFIED WITH PENDANT STYRYL PYRIDINIUM GROUPS

by ELEANOR S. COCKBURN[a], R. STEPHEN DAVIDSON[a][c], (in part)
SUSAN A. WILKINSON[a] and JOHN HAMILTON[b]

(a) Department of Chemistry, City University, London EC1V 0HB, U.K.
(b) Sericol Group Ltd., Westwood Road, Broadstairs, Kent,CT10 2PA, U.K.
(c) author for correspondence

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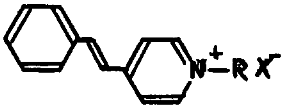
## ABSTRACT

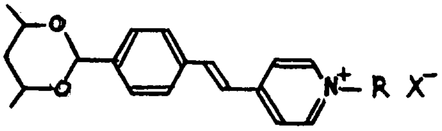
Films of poly(vinyl alcohol) carrying pendant styrylpyridinium groups exhibit fluorescence typical of the excimer of the pendant group. Irradiation of the films leads to elimination of the excimer emission band. Following the photoreaction by IR diffuse reflectance spectroscopy shows that there are unreactive chromophores which are presumably isolated styrylpyridinium groups or aggregates which cannot lead to photodimerisation. The photoreaction is so rapid that it was impossible to measure the fluorescence lifetimes of the chromophore using an argon ion laser as light source. The results show that in thin films there is considerable aggregation of the styrylpyridinium groups, accounting for the rapid photoreaction which presumably occurs via an excimeric intermediate.

## INTRODUCTION

Styrylpyridinium compounds such as A undergo photostimulated cyclisation to give cis-trans isomerism (1) as well as an azaphenanthren (2,3). Irradiation of these compounds in the solid state also leads to [2 + 2] cycloaddition products (3). It has also been reported that, in the solid state, compounds such as A exhibit excimeric emission (2) and this poses the question whether excimer formation plays a part in the cycloaddition. By suitable functionalisation, styrylpyridinium groups have been attached to poly(vinyl alcohol) (PVA) as in B.



A



B

The films are remarkably photosensitive, with irradiation increasing the extent of crosslinking (4). The question arises as to whether the latter process involves [2+2] cycloaddition or whether there is photostimulated nucleophilic attack by OH groups of the PVA upon the double bond. Evidence for the latter reaction comes from the finding that irradiation of compounds such as styrylpyridines and quaternary salts of dipyridylethylenes in alcoholic solvents leads to nucleophilic addition of the alcohol (5). Recently, from examination of the UV absorption spectra of PVA films carrying pendant styrylpyridinium compounds, it has been suggested (6) that, during the film forming, the pendant groups aggregate so facilitating the cycloaddition. We now present further evidence for this view and for the participation of excimeric species in the reactions.

## RESULTS AND DISCUSSION

The absorption spectrum (diffuse reflectance) of the modified PVA films shows a maximum at 343 nm (Fig. 1) very similar to that observed for the same material in aqueous solution (6).

Although this technique fails to give unequivocal evidence for aggregation in the ground state, examination of the fluorescence spectra of the films showed that there is a high degree of aggregation since the spectra are dominated by an emission band (max. 450 nm) which can be attributed to the styrylpyridinium salt excimer. These compounds exhibit excimer fluorescence both in solution and in the crystalline state (2). Further, irradiation of the films leads to reduction in the intensity of the excimer emission. In one case, the films were irradiated using a conventional UV cure apparatus (Fig. 2) and in the other they were irradiated inside the sample compartment of a fluorimeter using the excitation source (Fig. 3). Fig. 2 shows that, as the irradiation proceeds, there is an increasing contribution from an emission band at shorter wavelength (max. 400-410 nm). Control experiments showed that this fluorescence was due to the paper support rather than the modified PVA.

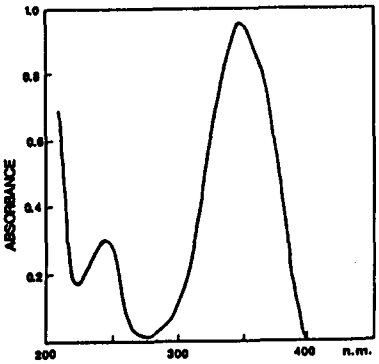


Figure 1.
Absorption spectrum of the modified PVA films.

That styrylpyridinium groups remain after prolonged irradiation was shown by diffuse reflectance FT-IR spectroscopy (Fig. 4). This technique showed that the main cross-linking reaction occurs extremely rapidly and that the groups remaining are photochemically unreactive. This latter point suggests that little of the observed photoreactivity is due to nucleophilic attack by the OH groups of the PVA on the excited styrylpyridinium compound. The remaining styrylpyridinium groups are either isolated, thereby preventing dimerisation, or they are present as aggregates in which the groups are not correctly orientated for excimer formation and cyclodimerisation (7). The latter explanation seems more probable since emission from monomeric styrylpyridinium groups could not be detected. If present in

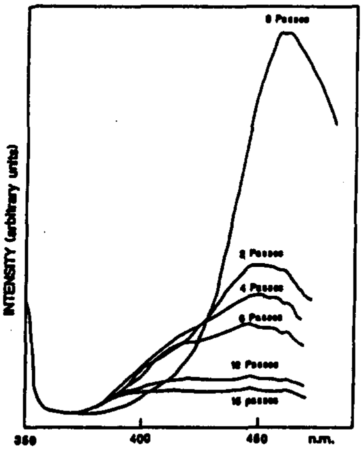


Figure 2.
Fluorescence spectra of films irradiated under UV curing conditions (12m/min).

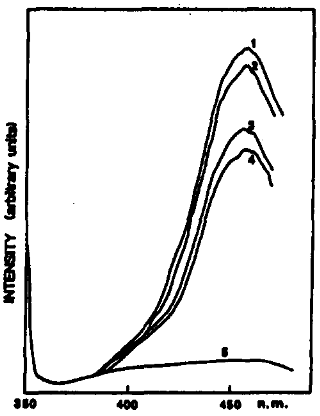


Figure 3.
Fluorescence spectra of films irradiated in the spectrafluorimeter (350 nm). (1)-(5) :- 60, 75, 135, 150 & 450 min. respec.

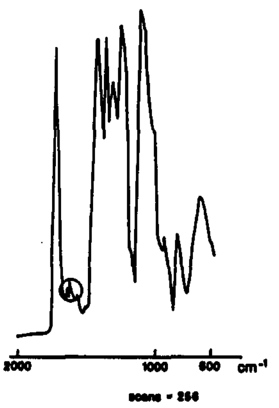


Figure 4.
Diffuse reflectance FT-IR spectrum of cured SBQ salt.

in aggregates, there is a high possibility of fluorescence quenching. The phenomenon of non-fluorescent excimers is well documented (7); in these cases, poor overlap of the aryl groups leads to efficient non-radiative decay.

Attempts were made to measure the fluorescence lifetime of the excimeric species using a fluorescence microscope. The illumination source was an argon ion laser (10 mW; 488 nm); fluorescence emission could be seen but photobleaching, i.e. photoreaction leading to the destruction of the styrylpyridinium group, was so fast that neither the fluorescence nor the fluorescence lifetime could be measured. For the latter purpose, the light beam from the laser was modulated using a Pockel cell which delivered pulses having a duration of 6 nanosec. Extensive photobleaching occurred during a single exposure. It has been noted that the crosslinking of such modified PVA's is extremely rapid and can be induced by an argon ion laser (6). In this reported case, it is even more remarkable considering that the styrylpyridinium group has such a low molar extinction coefficient at 488 nm.

## EXPERIMENTAL

Diffuse reflectance UV and FT-IR spectra were run on Perkin-Elmer Lambda 5 UV/Vis and Bio-Rad FTS-60 spectrometers respectively. Fluorescence spectra (uncorrected) were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter. UV curing of thin films was effected with a Colordry Unit which housed a medium pressure Hg lamp. Thin films of modified PVA were coated onto paper using a drawbar.

Commercially available PVA (80% hydrolysis, MW 71108, dp 1450 PVA) and terephthaldehyde, 4-picoline and dimethyl sulphate (Aldrich reagent grade) were used without further purification. 1-methyl-4-[2-(4-formylphenyl)ethenyl] pyridinium methosulphate (SBQ salt) was prepared as in the literature (4).

For modification of PVA with SBQ salt, the salt (0.9 g) was dissolved in water (100 ml) and added to PVA (97.5 g) in water (750 ml). When a homogeneous solution had been obtained, 90% phosphoric acid (2 ml) was added. The reaction mixture was kept at 60°C for 5 hours with occasional stirring; after cooling, it was neutralized to pH above 5 using ion exchange resin.

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