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The Sensitized Fading of Triphenylmethane Dyes in Polymer Films. Part 1

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ABSTRACT

The photochemistry of four acid triphenylmethane dyes, viz. Acid Blue 1, Acid Green 9, Acid Blue 15 and Acid Violet 17, was studied in model systems of dyed poly(vinyl alcohol), methylcellulose and gelatin films, in order to elucidate the complex photochemical reactions occurring in a dyed-wool/water/air system upon exposure to ultraviolet radiation.

A variety of chemicals that model protein-bound amino acids, and sodium azide and cadmium sulphate octahydrate were added to each dyed-polymer system in order to determine the importance of specific photochemical reactions anticipated for a dyed-wool substrate.

A comparison between the dye spectra in various solutions and in the polymer substrates revealed that triaminotriphenylmethane dyes, in particular, show a propensity to aggregate. This was particularly evident in poly(vinyl alcohol) and gelatin substrates; in methylcellulose the monomeric forms of all dyes predominated.

Dye fading appears to be governed by (a) the ability of the substrate, or residual solvent within the substrate, to donate electrons or hydrogen atoms to the dye and (b) the degree of dye aggregation, which may be partially determined by (c) the chemical and physical structure of the substrate.

Two dissociative pathways were proposed for the fading of dimeric dye molecules in protein substrates. For monomeric dye molecules, it was found that fading was photosensitized by components of the protein structure, in particular the guanidino group of arginine and the carboxylate groups of glutamic and aspartic acids. In contrast, neither lysine, histidine nor excited singlet-state oxygen appears to sensitize the fading of triphenylmethane dyes in protein substrates.

1 INTRODUCTION

Triphenylmethane dyes form a very important class of commercial dye renowned for their outstanding intensity of colour and their brilliant shades of red, blue and green. Unfortunately, the textile application of these dyes has been limited by their low lightfastness on many substrates, particularly on natural fibres such as silk, cotton and wool. However, with the advent of acrylic fibres based on poly(acrylonitrile), it was found that moderate lightfastness could be attained.[1,2]

To date, most research concerned with understanding this difference in photochemical behaviour has been confined to understanding the photochemical reactions of basic triphenylmethane dyes, with little attention being paid to the acid dye subclass. Furthermore, even though wool is a well-known photoactive substrate,[3] very little research has been devoted to specifically examining the possibility that photoactive groups present in wool might play an important role in the photodegradation of triphenylmethane dyes in a dyed-wool system.[4–12]

With the need for bright, fast colours on wool to compete with those available for acrylic fibres, it is desirable to achieve a clear understanding of the photochemical reactions promoting the fading of triphenylmethane dyes on wool.

Since both triphenylmethane dyes and wool are photochemically active, quite complex photochemical reactions may be anticipated for the dyed-wool system. Accordingly, the studies presented here in Part 1 of this work have been performed on model systems of polymer films containing acid triphenylmethane dyes. The systems selected were based on methylcellulose (MC), poly(vinyl alcohol) (PVA) and gelatin films. By adding a variety of chemicals to each system, the importance of protein-bound amino acids and other species in the photochemistry of the dyes on wool could be gauged. In addition, solution studies have been employed to elucidate the effect of dye–dye and dye–polymer interactions and their bearing on dye photochemistry in solid substrates.

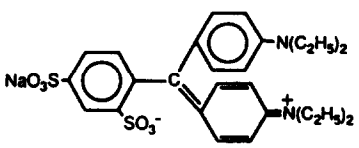
2 MATERIALS AND METHODS

Four water-soluble triphenylmethane dyes were selected for study. These were Acid Blue 1 (C.I. 42045; Lissamine Turquoise VN 150, ICI), Acid Green 9 (C.I. 42100; Sandolan Brilliant Green E-6B 300%, Sandoz), Acid Blue 15 (C.I. 42645; Coomassie Blue FF, ICI), and Acid Violet 17 (C.I. 42650; Coomassie Violet R 200, ICI); the structures of the dyes are given in Fig. 1. Dyes were incorporated into the films to achieve a concentra-

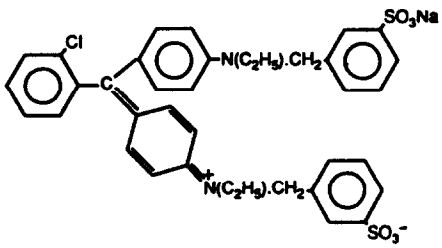
tion of (2·7 ± 7%) × 10^{-6} mole/g polymer. All four dyes photodegrade on tone, in the polymer substrates chosen, with no new absorption peaks being observed in the visible region or dark reactions over a 24-h period.

Purification of the dyes was achieved by performing two extractions of the commercial dye powder in tetrachloroethylene. This was followed by removal of salt from the dye powder by dissolving the dye in ethanol, filtering the solution and subsequently evaporating the solvent. The total procedure was repeated until a constant extinction coefficient was obtained.

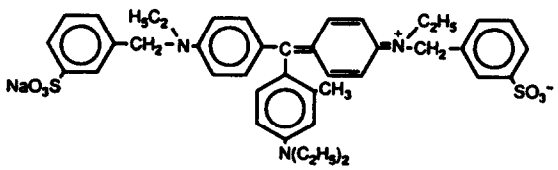
Acid Blue 1 C. I. 42045



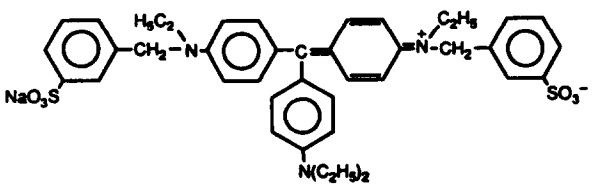
Acid Green 9 C. I. 42100



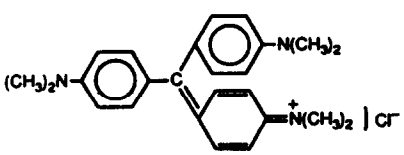
Acid Blue 15 C. I. 42645



Acid Violet 17 C. I. 42650



Basic Violet 3 C. I. 42555



Basic Green 4 C. I. 42000

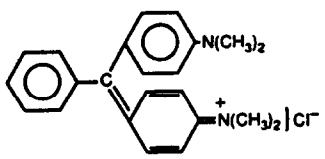


Fig. 1. Relevant triphenylmethane dye structures.

Methylcellulose (Fluka) was specified as having a methoxy content of 27·5–32·0% and a viscosity of 350–550 mPa s for a 2% concentration at 20°C. Methylcellulose films containing Acid Blue 1, Acid Blue 15 and Acid Violet 17 were prepared by casting 50 g of an aqueous 2% (w/w) methylcellulose solution containing dye and additives onto a glass plate with dimensions 15·2 × 15·2 cm^2. This resulted in films of thickness 30 ± 2 μm being produced. Due to a lower extinction coefficient than the other dyes in MC (Table 1) and greater dye migration to the perimeter of the film during drying, methylcellulose films containing Acid Green 9 were made thicker (37 ± 2 μm). This was achieved by casting 65 g of an aqueous 2% (w/w) methylcellulose solution containing dye and additives per glass plate.

PVA (Polyscience Inc.) was specified as 99% hydrolyzed, with a molecular weight of 133 000 and a viscosity of 28–32 mPa s for a 4% aqueous solution at 20°C. PVA films containing dye and additives were cast from 25 g of an aqueous 4% (w/w) PVA solution onto a glass plate in the manner described for MC films. PVA films were typically 33 ± 2 μm thick.

Gelatin (Ajax Chemicals) films were cast from 50 g of an aqueous 2% (w/w) gelatin solution containing dye and the required amount of additives onto a perspex plate cut to the same dimensions as the glass plates. This produced films of thickness 32 ± 2 μm.

All films were protected from dust during the drying process, which occurred over a period of several days in an air-conditioned laboratory (T = 20°C; RH = 50%). The MC and PVA films obtained were trans-

TABLE 1

The Molar Extinction Coefficients and Corresponding Wavelengths at which Dye Fading was Monitored

Dye	*Molar extinction coefficient × 10^{-7} (cm^2/mole)*									
	MC		*PVA*				*Gelatin*			
	α-band ε	λ^a *(nm)*	*α-band* ε	λ^a *(nm)*	*β-band* ε	λ^a *(nm)*	*α-band* ε	λ^a *(nm)*	*β-band* ε	λ^a *(nm)*
AB 1	9·2±0·1	636·4	9·9±0·1	644·8	—	—	8·8±0·2	646·8	—	—
AG 9	4·2±0·1	646·2	11·4±0·3	645·1	—	—	16·0±1·0	648·5	—	—
AB 15	9·8±0·4	606·3	5·5±0·2	606·3	6·9±0·2	567·8	5·9±0·3	606·3	6·4±0·2	583·5
AV 17	13·0±1·0	598·5	6·4±0·3	598·5	7·4±0·1	555·8	7·5±0·1	598·5	7·7±0·1	561·1

[a] λ denotes the wavelengths at which dye fading was monitored in each polymer.

AB 1, AG 9, AB 15 and AV 17 represent Acid Blue 1, Acid Green 9, Acid Blue 15 and Acid Violet 17, respectively.

parent to radiation of wavelengths greater than 250 nm. Gelatin films are transparent above 360 nm (Fig. 2). Only the central area (approximately 13·5 × 13·5 cm^2) of the prepared films was used for dye photodegradation studies, since both dye distribution and film thickness were found to be uniform in this region.

The pH of all additive solutions (except those used for gelatin film preparation) was adjusted to 7, using sodium hydroxide and sulphuric acid, prior to their addition to the polymer solutions used for film casting. This ensured that the pH of a dry polymer film with additives or dye was between 5·5 and 7, in which range the optical density of the dye was found to be pH-independent. In addition, this ensured that the pH of the dry films had the approximate pH of wool, i.e. pH 6. MC, PVA and gelatin films without dye or additives had pH values estimated to be 6,

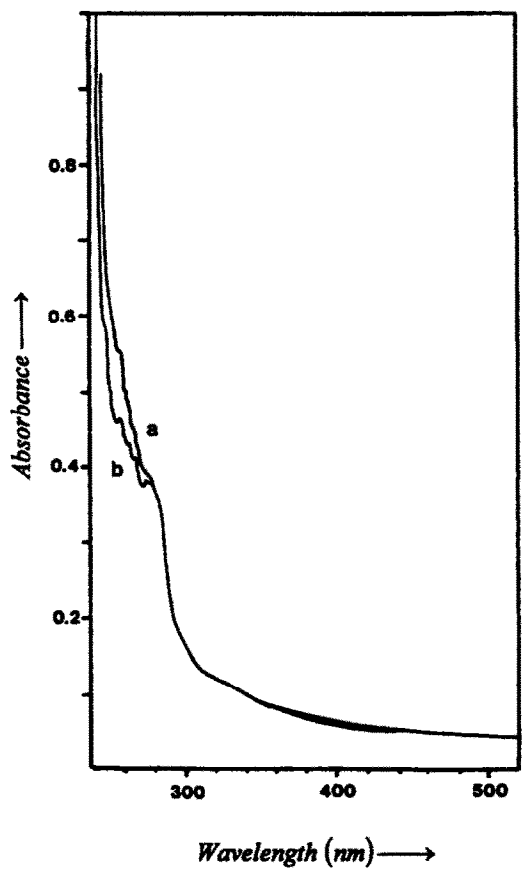


Fig. 2. Absorbance spectra of a 32 ± 2 μm thick gelatin film before and after 80 min exposure to the Oliphant radiation source. a: Absorbance after irradiation; b: absorbance before irradiation. The reference was air.

7, and 6, respectively. Solution pH measurements were taken on an Orion Research digital ionalyzer 501, whereas the pH of the dry films was estimated by incorporating universal indicator solution (BDH Chemicals) into the polymer film solutions used for film casting.

The film thicknesses were measured on a Minicom E-MD-M30H high-speed electronic micrometer (Tokyo-Seitmitsu Co. Ltd).

All films were stored away from light until required. Neither MC nor PVA showed any degradation when exposed to ultraviolet light for times well in excess of those used during the photodegradation studies. Whilst gelatin showed a small amount of photodegradation, this was small enough for it to be ignored for purposes of calculating the quantum yields of dye photodegradation (Fig. 2).

The film additives methylguanidine sulphate (Eastman Kodak Organic Chemical, USA), sodium acetate (BDH Chemical, Australia), ethylammonium hydrochloride (Hopkins and Williams, England), imidazole (crystalline grade III, Sigma Chemical, USA), sodium azide (Fluka), and cadmium sulphate octahydrate (Merck Pro Analyst), were used without further purification. None of these additives absorb radiation of wavelengths greater than 270 nm. All were present at concentrations of ($3{\cdot}3 \times 10^{-5} \pm 7\%$) mole/g polymer unless otherwise indicated.

An Oliphant irradiation chamber (model PCR-128 W with internal temperature 40 ± 2°C), containing sixteen ultraviolet lamps (Oliphant FL8E and Clemco 9008) which emit 90% of their irradiation in the 280–360 nm region (with peak output at 310 nm[13]) was used to irradiate the samples. Five samples (including a control containing dye only) clipped to a slowly rotating holder centrally located in the chamber were exposed to the radiation. At 4–5 subsequent times, the group of samples was removed from the irradiation chamber. The maximum visible absorbance of each film was then measured at four different locations on the film (see Table 1 for the wavelengths at which they were measured). The natural log of the average of these four absorbance values was plotted against the time of exposure to the light source. This provided sufficient points to plot a dye fading curve (ln *A versus t*) for each film. The absorbance spectrum of each film, using a blank film (free of dye) as reference, was recorded between 200 and 800 nm on a Cary 210 spectrophotometer (with a modified sample holder[13] before and after completion of the experiment.

Dye fading was assessed in terms of the quantum yield of dye fading, Q. It relates the rate of dye molecules degrading, R_0 (molecules/(min cm^2) of film) to the rate of light absorbed by the dye, I_{abs} (quanta/ (min cm^2) of film):

$$Q = R_0/I_{abs} \tag{1}$$

Since it was previously noted in these laboratories[11] that it is difficult to measure reproducible values of R_0 for triphenylmethane dyes fading in MC and PVA substrates, dye fading was also assessed in terms of the relative quantum yield of dye fading:

$$Q_{rel} = Q_s/Q_c \tag{2}$$

where Q_s and Q_c are the respective quantum yields of dye degradation for films containing dye plus additives and the control film which contains dye alone. The main advantage of using Q_{rel} to assess dye fading is that if there is a change in the irradiation conditions between experiments, then Q_s and Q_c will change in a similar manner. The error associated with Q_{rel} is thus smaller than that observed for the absolute quantum yields Q_s and Q_c. It was found that Q_{rel} could be determined to an accuracy of ±8% in the case of linear fading curves and ±10% in the case of non-linear fading curves, when triplicate runs of each Q_{rel} were examined.

Comparisons for each dye were made only between films with the same dye absorbance (±10%), to ensure that the observed changes in the relative quantum yield of dye fading represented changes caused by the additives and not variations in dye concentration:[14]

To calculate the quantum yield, it is necessary to determine both I_{abs} and R_0. I_{abs} was calculated via the equation

$$I_{abs} = \sum_{\lambda_1}^{\lambda_2} E_\lambda(1 - 10^{-A_\lambda})\, d\lambda \tag{3}$$

where E_λ and $1 - 10^{-A_\lambda}$ are the spectral output of the lamps and the fraction of quanta absorbed (I_λ), respectively, both as a function of wavelength. E_λ and I_λ were examined at 4 nm intervals in the region of overlap between the emission curve of the lamps and the absorption curve of the film, $\lambda_1 \rightarrow \lambda_2$. A_λ is the absorbance of the film measured at wavelength λ. E_λ was determined from the relative spectral output of the Oliphant FLBE lamps which had been corrected for the transmission characteristics of the S/N 165 grating monochromator (Farrand Optical Co. Inc.) used to measure the curve.[13] The output intensity of the lamps in terms of number of quanta/(s cm^{-2}) was determined by the potassium ferrioxalate actinometer technique of Hatchard and Parker.[15]

R_0 is also known as the initial rate of dye fading and it is given by

$$R_0 = \frac{N_a A_0 k_0}{\varepsilon} \qquad \text{at } t = 0 \tag{4}$$

for dyes undergoing first-order fading. Here, N_a is Avogadro's number, ε is the molar extinction coefficient (in cm^2/mole) for the dye in the film, corresponding to the wavelength at which the initial absorbance A_0 is measured and k_0 is a first-order rate constant determined from the

gradient of the dye fading curve. As a matter of convenience, however, the value of A_0 used in eqn (4) was actually A_0', the absorbance value obtained by extrapolation of the fading curve back to $t = 0$ (Fig. 3). This choice does not invalidate comparisons between fading in different films because the quantum yield of dye fading may be shown, both theoretically (via series expansion techniques) and experimentally, to be insensitive (within the accuracy of these experiments) to the value of A_0 used in eqn (4).

The molar extinction coefficient (ε in cm^2/mole) for each dye in each polymer substrate (Table 1) was determined for each wavelength used to monitor fading via eqn (5).

$$A = \varepsilon \frac{m}{A_f} \tag{5}$$

In this modified version of the Beer–Lambert law, A is the film absorbance, m is the number of mole of absorbing compound and A_f is the area of the film (in cm^2); m was determined from calibration curves that relate the absorbance measured for samples of film dissolved in water to standard solutions prepared from the same ratio of volume of water to weight of polymer as in the dissolved film solution.

In accordance with suggestions made by Ershov and Krichevskii[16,17] and others,[18] the initial rates of fading were determined, whenever possible, by examination of photodegradation to 10% dye loss. This ensures that the initial rate of dye fading is not affected by a concentration gradient within the film, nor a buildup of photoproducts.

3 RESULTS AND DISCUSSION

3.1 Shape of the fading curves

An examination of the fading curves (plots of $\log_e A$ *versus* t) obtained in this work revealed that they are not always linear. In some instances the fading curves showed either (a) an initial rapid fade or initial negative fade (a rise in absorbance with exposure to radiation), each followed by first-order decomposition (see Fig. 3) or (b) curvature throughout the period of examination (see Fig. 4). The fading curves, however, may be broadly classified into two types, namely (a) those that were linear ($r^2 \geq 0{\cdot}99$) at some stage of fading and (b) those that exhibited curvature ($r^2 < 0{\cdot}99$) throughout. The corresponding fading curves will be referred to as linear (e.g. Figs 3 and 5) and non-linear (e.g. Fig. 4), respectively. When dye fading was examined in gelatin, all four dyes exhibited non-linear fading curves, whereas when MC was the substrate all dyes exhibited linear fading curves. In PVA, linear fading curves were observed only

when fading was monitored at the α-band. The initial rapid fade or negative fade sometimes observed in the linear fading curves (close to $t = 0$) can, on the basis of the work by Giles and co-workers[19(a),20,21] be correlated to changes in the physical state of aggregation of the dye. Since such changes occurred rapidly here, the onset of first-order decomposition always occurred before the dye had degraded by 10%. Thus, R_0 was derived using k_0 (in eqn (4)) determined from the linear portion of the fading curve.

The non-linear fading curves were not well approximated by second-order or other simple kinetic relationships over the entire time range, nor did they appear to be the result of a buildup of photoproducts. However,

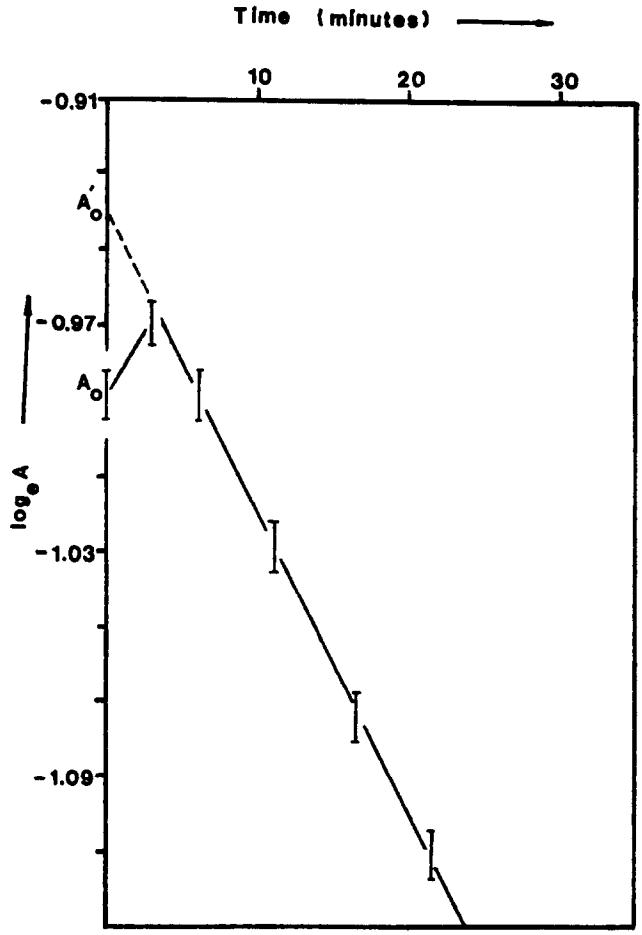


Fig. 3. Fading curve for Acid Green 9 in methylcellulose (MC). [Dye] = (2·7 ± 0·2) × 10^{-6} mole/g MC. Dye fading was monitored at 646·2 nm. A_0 is the initial film absorbance measured on the Cary spectrophotometer. A_0' is the film absorbance extrapolated back to $t = 0$. The reference film was MC.

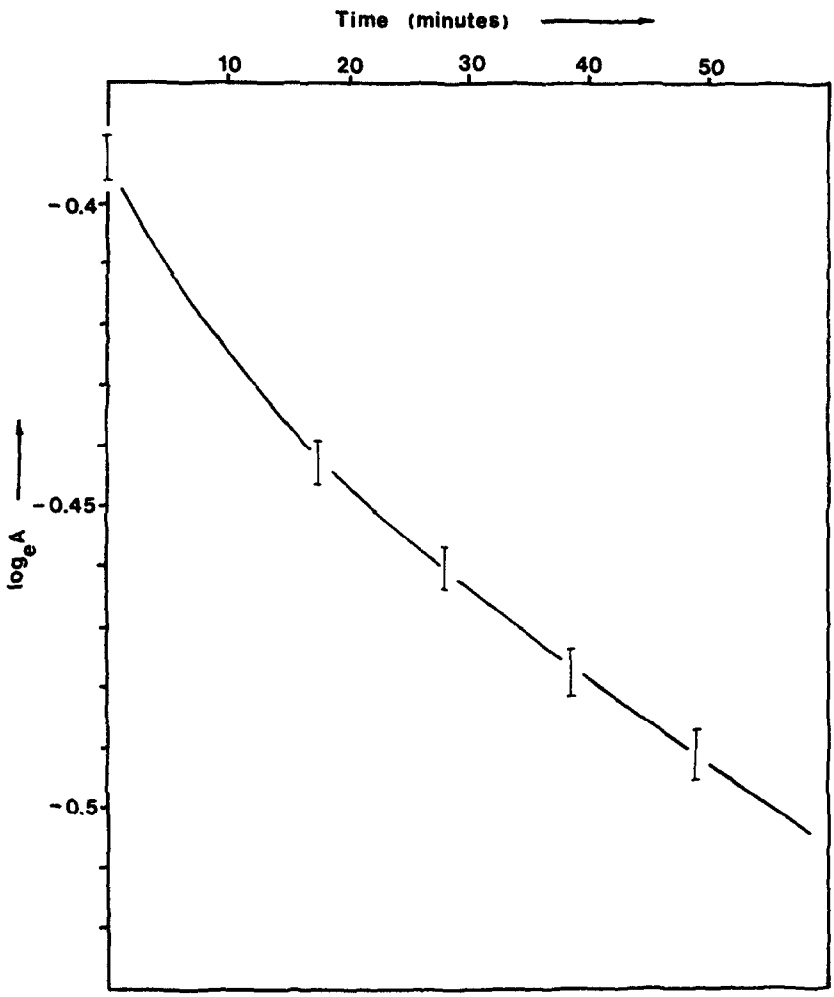


Fig. 4. Fading curve of Acid Blue 15 in poly(vinyl alcohol). [Dye] = (2·7 ± 0·2) × 10^{-6} mole/g PVA. Dye fading was monitored at 567·8 nm. The reference film was PVA.

a plot of $\log_e A$ *versus* t is reasonably linear, with correlations for a linear fit (r^2) typically ≥0·98 over the time interval 20–50 min, indicating that in this period 'pseudo' first-order fading may be considered to be the predominant photodegradation mechanism. Furthermore, in most cases (the exceptions are indicated in the text by the symbol *b*) dye fading over this time interval corresponds to no more than 10% dye loss. Thus, in the case of the non-linear fading curves, k_0 and R_0 were calculated for fading at the 35 min mark (from eqn (4)) by determining the line of best fit for fading data corresponding to 20, 30, 40 and 50 min exposure to radiation.

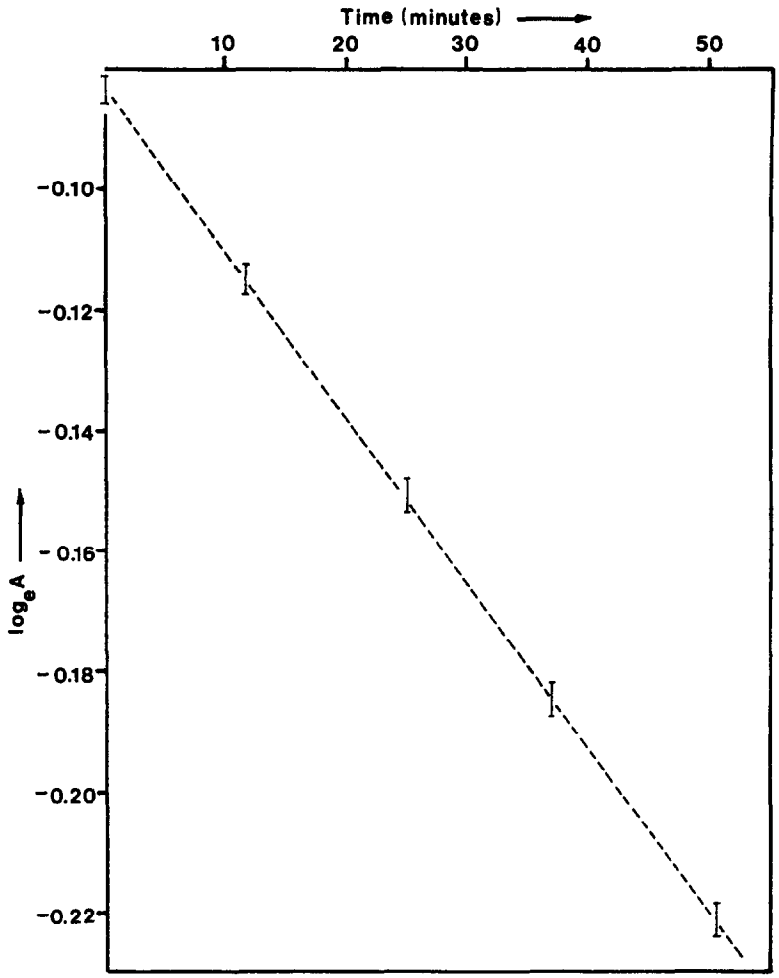
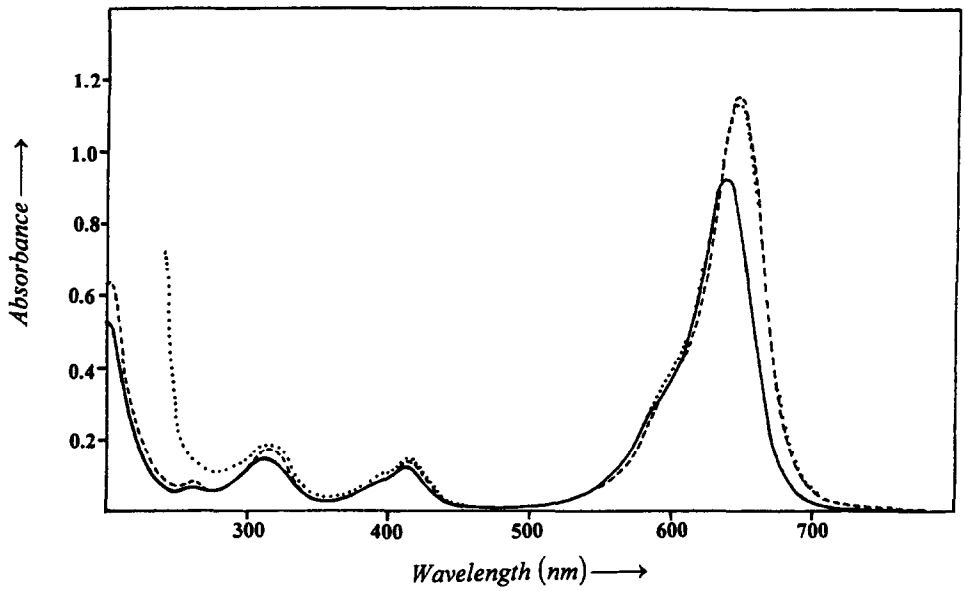


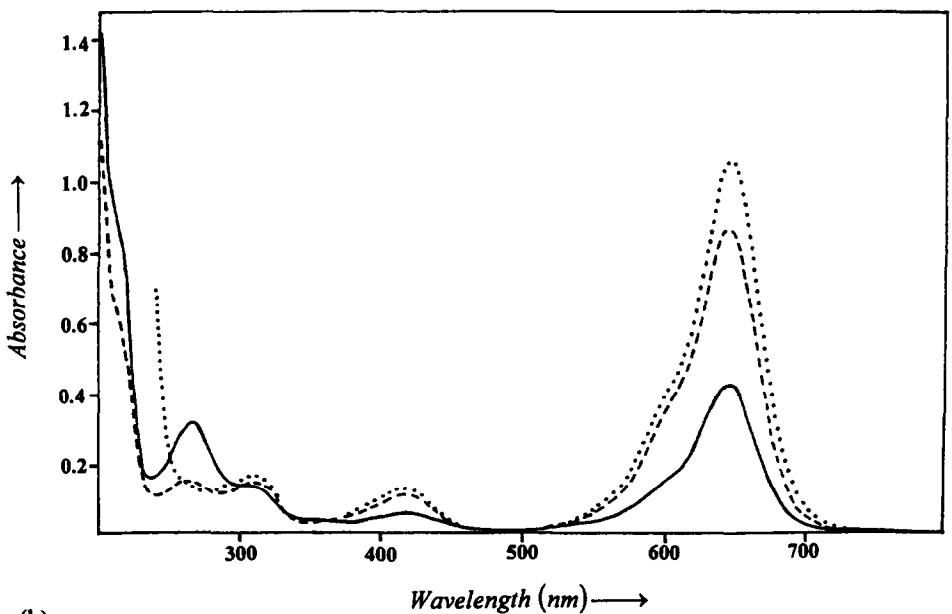
Fig. 5. Fading curve for Acid Blue 1 in methylcellulose (MC). [Dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mole/g MC. Dye fading was monitored at 636·4 nm. The reference film was MC.

3.2 Dye spectra and the physical state of the dyes in the polymers

A comparison of the dye spectra in MC, PVA and gelatin reveals that the shape of the main absorbance band is sensitive to the substrate (Figs 6 and 7). The effect is particularly evident for the dyes Acid Blue 15 and Acid Violet 17, where it is seen that the short wavelength shoulder of the main absorbance band predominates in PVA and gelatin but not in MC. Such spectral behaviour had been previously documented in the literature and has recently been reviewed in Ref. 12. The literature shows that the 'splitting' of the main absorption band has been the subject of much

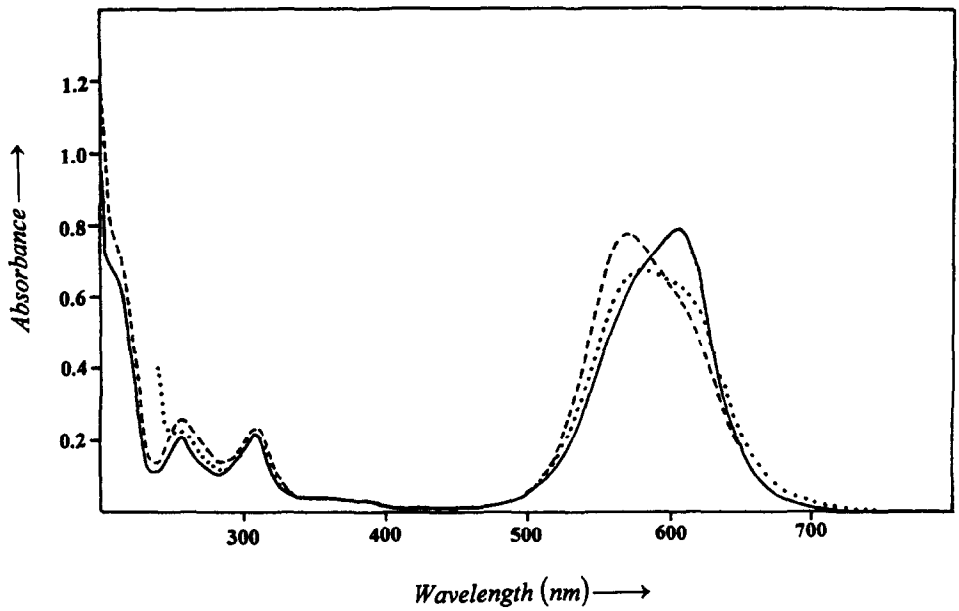


(a)

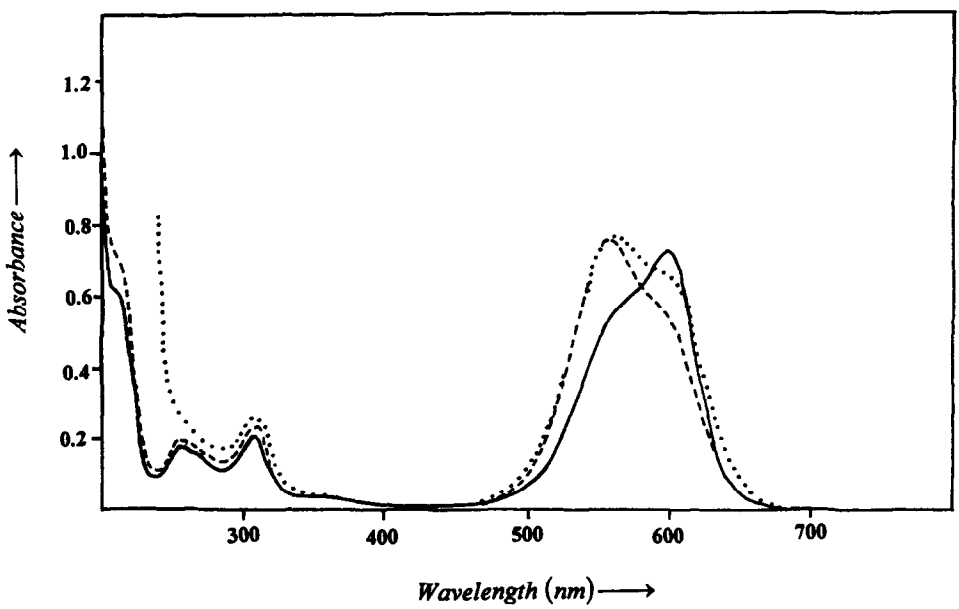


(b)

Fig. 6. Absorbance spectra of Acid Blue 1 and Acid Green 9 in MC, PVA and gelatin, prior to irradiation. (a) Acid Blue 1 in MC (——), PVA (– – –) and gelatin (· · · ·); (b) Acid Green 9 in MC (——), PVC (– – –) and gelatin (· · · ·). [Dye] = (2·7 ± 0·2) × 10^{-6} mole/g polymer. Reference films were MC, PVA and gelatin.



(a)



(b)

Fig. 7. Absorbance spectra of Acid Blue 15 and Acid Violet 17 in MC, PVA and gelatin, prior to irradiation. (a) Acid Blue 15 in MC (——), PVA (– – –) and gelatin (· · · ·); (b) Acid Violet 17 in MC (——), PVC (– – –) and gelatin (· · · ·). [Dye] = (2·7 ± 0·2) × 10^{-6} mole/g polymer. Reference films were MC, PVA and gelatin.

debate, and that it is more pronounced for triaminotriphenylmethane dyes than diaminotriphenylmethane dyes.[12,22-42] The current consensus is that the observed deformation of the main absorbance band with changing environmental conditions (with temperature and pressure constant) can be attributed to dye aggregation.[12] The absorbance peak corresponding to a dye dimer is commonly referred to as the β-band[19(b)] and it is observed for a number of dyes including the triphenylmethane dye Basic Violet 3.[19(b)] By contrast, the absorbance peak corresponding to the dye monomer is commonly referred to as the α-band.[12,19(b)]

Similar spectral changes to those induced by increasing the dye concentration can be observed when a dye binds to a polyelectrolyte. In this context the phenomenon is often known as metachromasy, and has recently been reviewed.[12]

Since dye–dye interactions and dye–substrate interactions may alter the fading characteristics of a dye, the spectral changes observed when varying the polymer substrate were studied. The absorbance spectra of Acid Blue 15 and Acid Violet 17 in water were examined for dye concentrations of $26{\cdot}4 \times 10^{-6}$ M, $6{\cdot}6 \times 10^{-6}$ M and $1{\cdot}65 \times 10^{-6}$ M. The spectra are presented in Fig. 8 and clearly indicate that the intensity of the short-wavelength band increases, relative to the intensity of the long-wavelength band, with increasing dye concentration. This observation and the proximity of the two absorption bands allows the short-wavelength band to be tentatively assigned as the β-band and the long-wavelength band to be tentatively assigned as the α-band, corresponding to the dimeric and monomeric forms of the dye, respectively (see also Refs 19(b) and 43). In accordance with this assignment, both dyes exhibit non-linear Beer–Lambert plots (Fig. 9). Furthermore, the similarity of the dye spectra obtained at high concentrations ($26{\cdot}4 \times 10^{-6}$ M and $6{\cdot}6 \times 10^{-6}$ M) to those obtained in PVA films suggests that Acid Blue 15 and Acid Violet 17 may be more aggregated in PVA than in MC (compare Figs 7 and 8). In support of this suggestion, the Beer–Lambert plots for Acid Blue 15 in PVA and MC were found to be non-linear and linear, respectively, when the dye absorbance was measured at the wavelength of maximum absorbance of the α-band in each of these substrates. No such dramatic spectral changes were observed when Acid Blue 1 and Acid Green 9 were monitored in MC, PVA and H_2O. Since it has been proposed that dyes which contain amino groups aggregate via hydrogen bonding,[43] and the above dyes only have two *para* amino groups in their structure (Fig. 1) it is possible that they do not aggregate significantly at the concentrations examined ($26{\cdot}4 \times 10^{-6}$ M, $6{\cdot}6 \times 10^{-6}$ M and $1{\cdot}65 \times 10^{-6}$ M).

The Beer–Lambert plot for the long-wavelength peak of Acid Green 9 in water, however, shows a slight curvature at high dye concentrations,

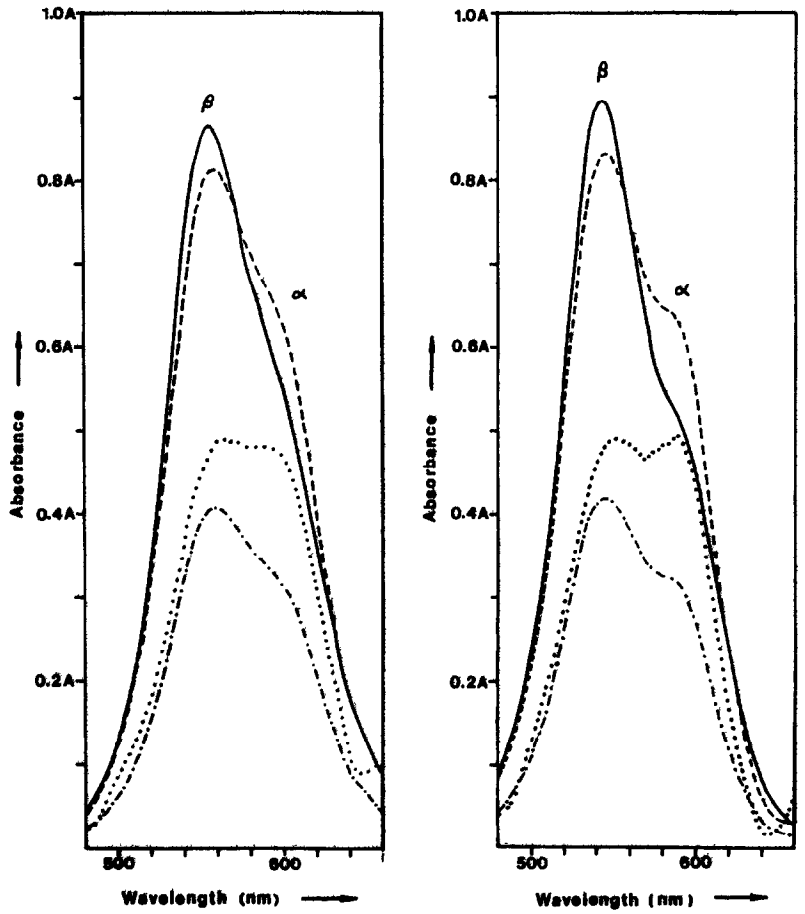


Fig. 8. Absorbance spectra of aqueous solutions of Acid Blue 15 and Acid Violet 17. (a) Acid Blue 15 in water; (b) Acid Violet 17 in water.

Spectrum	*Dye concentration* $\times 10^6$ *M*	*Optical pathlength (cm)*	*Value of multiplier A on the absorbance axis*
———	26·4 ± 0·9	0·5	1
– – – –	6·6 ± 0·2	1	0·5
· · · · · ·	1·65 ± 0·06	1	0·2
–·–·–	6·6 ± 0·2	1	1

The reference solvent was water; α and β refer to the α- and β-bands, respectively.

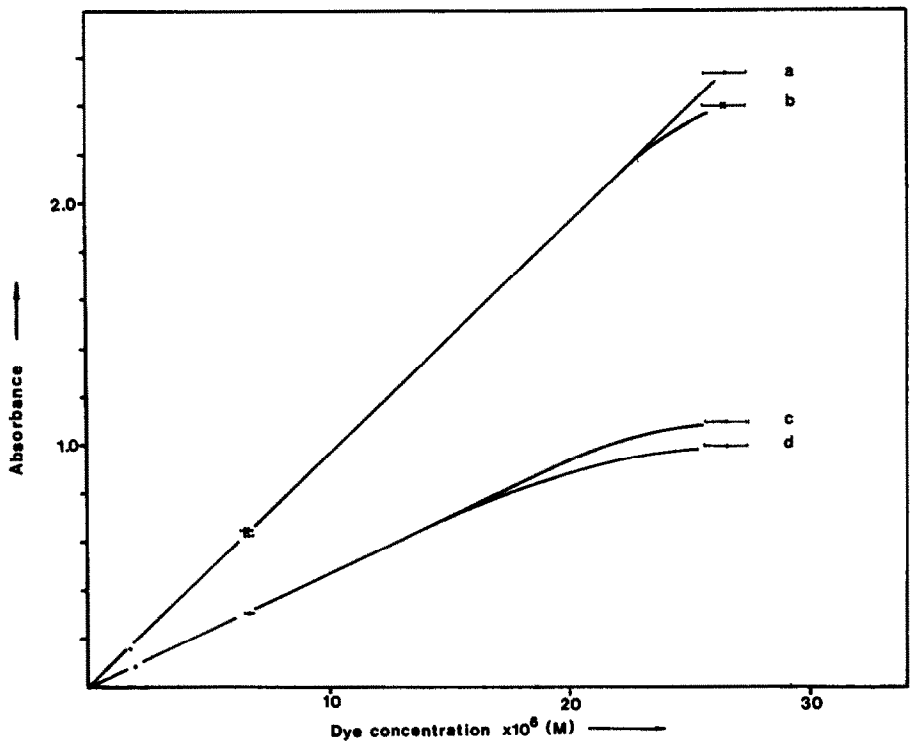


Fig. 9. Beer–Lambert plots for aqueous solutions of triphenylmethane dyes.

Spectrum	*Dye*	*Wavelength at which the absorbance was measured (nm)*
a	Acid Blue 1	638
b	Acid Green 9	632
c	Acid Blue 15	600
d	Acid Violet 17	592

The optical pathlength was 1 cm. The error associated with the absorbance was ±0·01. The reference solvent was water.

which implies that dye aggregation occurs to a small extent (Fig. 9). Examination of the spectra with changing dye concentration reveals that the short-wavelength band is intensified, since the α/β ratio decreases with increasing dye concentration (Table 2).

Various organic solvents such as acetone and alcohols are known dissociating solvents,[44–46] and so ethanol, butanol, benzyl alcohol and acetone and ethyl acetate were tested for their ability to dissociate the dyes studied here. All solvents exhibited a dissociating effect. This can be seen for Acid Blue 15 by comparing the spectra obtained for

TABLE 2

The α/β Ratios for Triphenylmethane Dyes in Solution and Solid Polymer and the Wavelengths at which these Ratios were Measured

Dye and dye concentration $\times 10^6$	*Solid or solution*	*α-band (nm)*	*β-band*[a] *(nm)*	*α/β ratio*
Acid Blue 1				
2·7	MC	636·4	584	3·50 ± 0·1
2·7	PVA	644·8	590	3·8 ± 0·1
2·7	Gelatin	646·8	590	3·5 ± 0·1
26·4	Water	638	584	3·05 ± 0·08
6.6	Water	638	584	3·12 ± 0·08
1·65	Water	638	584	3·06 ± 0·06
26·4	5% ethanol	638	584	3·16 ± 0·08
6·6	5% ethanol	638	584	3·20 ± 0·09
1·65	5% ethanol	638	584	3·18 ± 0·07
Acid Green 9				
2·7	MC	646·2	592	3·5 ± 0·3
2·7	PVA	645·1	596	2·8 ± 0·1
2·7	Gelatin	648·5	592	3·4 ± 0·1
26·4	Water	632	582	2·94 ± 0·08
6·6	Water	632	582	3·20 ± 0·08
1·65	Water	632	582	3·50 ± 0·08
26·4	5% ethanol	632	582	3·12 ± 0·08
6·6	5% ethanol	632	582	3·48 ± 0·09
1·65	5% ethanol	632	582	3·68 ± 0·08
Acid Blue 15				
2·7	MC	606·3	567·8	1·34 ± 0·04
2·7	PVA	606·3	567·8	0·77 ± 0·02
2·7	Gelatin	606·3	583·5	0·94 ± 0·02
26·4	Water	600	556	0·63 ± 0·01
6·6	Water	600	556	0·77 ± 0·02
1·65	Water	600	556	0·98 ± 0·02
26·4	5% ethanol	600	556	0·65 ± 0·01
6·6	5% ethanol	600	556	0·85 ± 0·02
1·65	5% ethanol	600	556	1·06 ± 0·02
Acid Violet 17				
2·7	MC	598·5	555·8	1·38 ± 0·04
2·7	PVA	598·5	555·8	0·73 ± 0·02
2·7	Gelatin	598·5	561·1	0·86 ± 0·02
26·4	Water	592	542	0·56 ± 0·01
6·6	Water	592	542	0·74 ± 0·02
1·65	Water	592	542	1·02 ± 0·02
26·4	5% ethanol	592	542	0·61 ± 0·01
6·6	5% ethanol	592	542	0·83 ± 0·02
1·65	5% ethanol	592	542	1·09 ± 0·02

[a] The β-band will develop when the dye aggregates. The dye concentration units are mole/g polymer for the solid substrates and M for solutions. The errors for the polymer and solution concentrations are ± 7% and ± 3·5%, respectively.

$26{\cdot}4 \times 10^{-6}$ M, $6{\cdot}6 \times 10^{-6}$ M and $1{\cdot}65 \times 10^{-6}$ M aqueous dye solutions (Fig. 8) with those prepared using 5% (v/v) ethanol in water as solvent (Fig. 10). Similar results were obtained for Acid Violet 17. An examination of Figs 9 and 11 reveals that the curvature of the Beer–Lambert curve is reduced by the presence of ethanol and that the extinction coefficient is increased. The results in Table 2 also support these observations, since the α/β ratio is larger in the presence of dissociating solvent. The addition of ethanol to aqueous solutions containing Acid Blue 1 had no effect on the dye spectra, and appeared to have no effect on the spectra of Acid Green 9 (Fig. 12). The Beer–Lambert plots (Figs 9 and 11) and the α/β ratios (Table 2) confirm the result for Acid Blue 1. For Acid Green 9 the curvature of the Beer–Lambert plot is reduced and both the α/β ratio and the extinction coefficient are increased by the presence of ethanol.

Changes in spectral distribution become more obvious, for aggregating dyes, as the amount of dissociating solvent is increased. In fact, it is possible to mix suitable combinations of solvents to produce spectra where either the short-wavelength peak or the long-wavelength peak predominates, thereby producing spectra similar to those obtained in PVA, gelatin and MC, respectively. This is shown, along with the intermediate situation, by the series of curves (for Acid Blue 15 and Acid Violet 17), presented in Fig. 13. Here the dye concentration $(6{\cdot}6 \pm 0{\cdot}2) \times 10^{-6}$ M is kept constant and the percentage of dissociating solvent (in this case acetone) in the aqueous dye solution is varied.

In order to determine whether the enhancement of the β-band of the dyes in PVA and gelatin could be attributed to dye binding to the substrate, the absorbance behaviour of a $26{\cdot}4 \times 10^{-6}$ M aqueous solution of Acid Blue 15 was examined in the presence of various amounts of gelatin and PVA polymers. The quantities employed were 0, 0·5, 1 and 2% (w/v) of polymer. The resulting absorbance spectra were analyzed by determining the α/β ratio for each absorbance curve. The results presented in Table 3 show that the α/β ratio remains unchanged by addition of PVA. In contrast, increasing amounts of gelatin increase the absorbance of the α-band more than the β-band, since the α/β ratio increases. Thus for the triphenylmethane dyes studied, it would appear that dye–dye rather than dye–polymer interactions are responsible for the β-band, and that some of the aggregated dye molecules dissociate upon addition of gelatin to the aqueous solution, presumably by preferentially bonding with the positively charged amino acid residues in the polymer.

There is some evidence that Acid Blue 1 and Acid Green 9 interact with the gelatin substrate, because the absorbance intensity of the visible absorbance peak of each dye is increased uniformly (as there is no

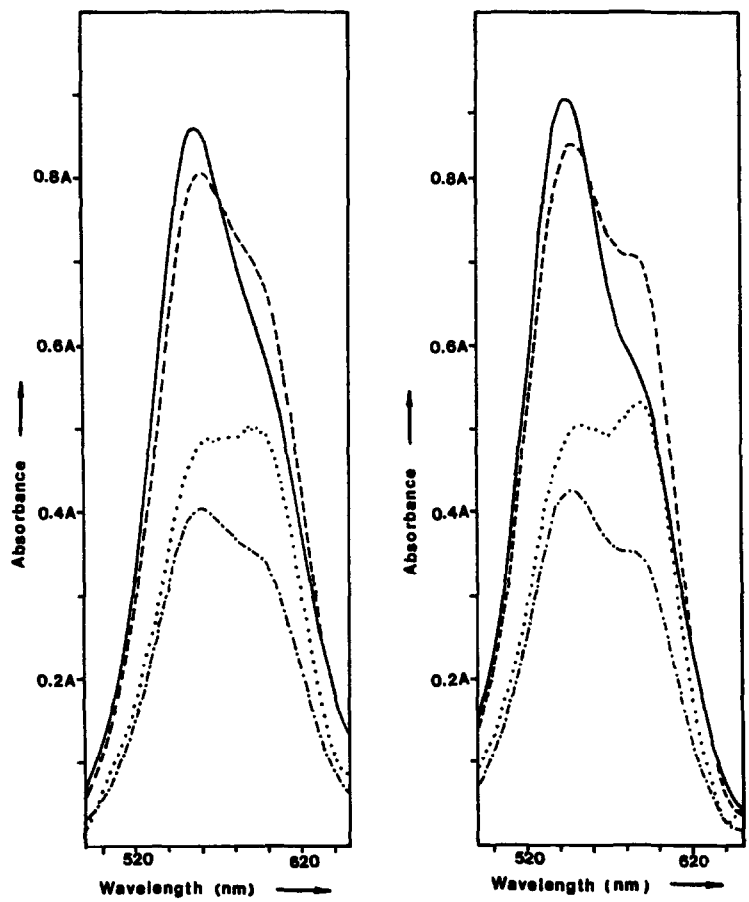


Fig. 10. Absorbance spectra of 5% (v/v) ethanolic solutions of Acid Blue 15 and Acid Violet 17. (a) Acid Blue 15 in aqueous ethanol; (b) Acid Violet 17 in aqueous ethanol.

Spectrum	*Dye concentration* $\times 10^6$ *M*	*Optical pathlength (cm)*	*Value of multiplier A on the absorbance axis*
———	26·4 ± 0·9	0·5	1
– – – –	6·6 ± 0·2	1	0·5
· · · · · ·	1·65 ± 0·06	1	0·2
– · – · –	6·6 ± 0·2	1	1

The reference solvent was 5% (v/v) ethanol in water.

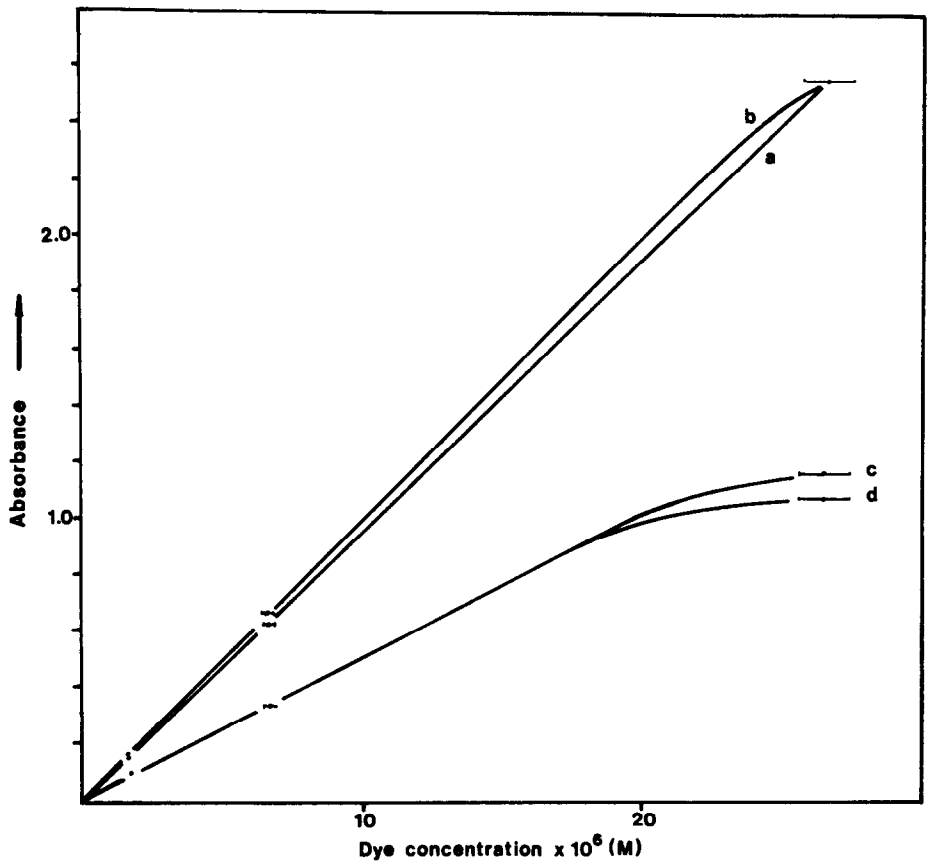


Fig. 11. Beer–Lambert plots for 5% (v/v) ethanolic solutions of triphenylmethane dyes.

Spectrum	*Dye*	*Wavelength at which the absorbance was measured (nm)*
a	Acid Blue 1	638
b	Acid Green 9	632
c	Acid Blue 15	600
d	Acid Violet 17	592

The optical pathlength was 1 cm. The error associated with the absorbance was ±0·01. The reference solvent was 5% (v/v) ethanol in water.

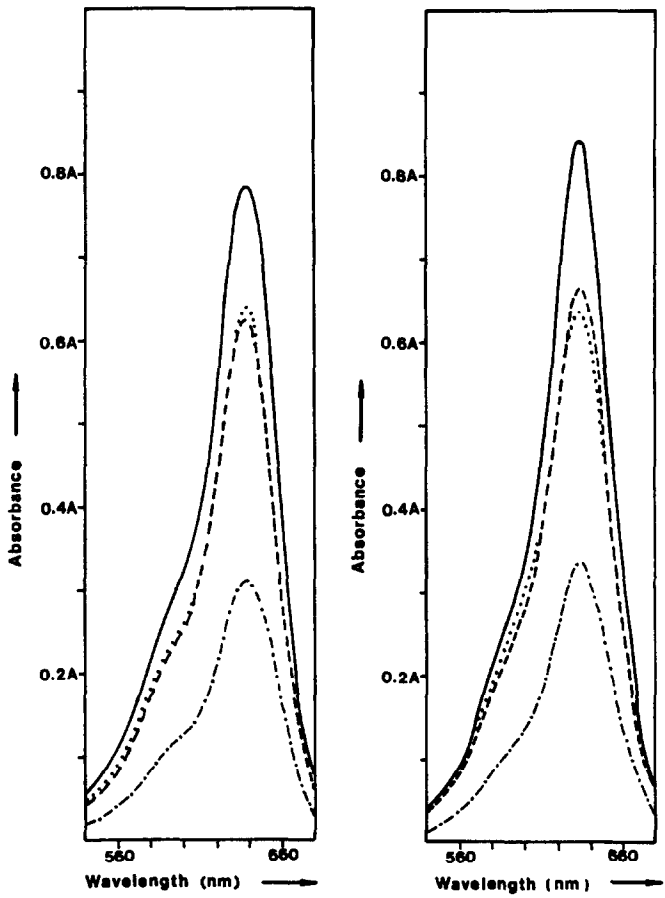


Fig. 12. Absorbance spectra of 5% (v/v) ethanolic solutions of Acid Blue 1 and Acid Green 9. (a) Acid Blue 1 in aqueous ethanol; (b) Acid Green 9 in aqueous ethanol.

Spectrum	*Dye concentration* $\times 10^6$ *M*	*Optical pathlength (cm)*	*Value of multiplier A on the absorbance axis*
———	1·65 ± 0·06	1	0·2
– – – –	6·6 ± 0·2	1	1
· · · · · ·	26·4 ± 0·9	0·5	2
– · – · –	1·65 ± 0·06	1	0·5

The reference solvent was 5% (v/v) ethanol in water.

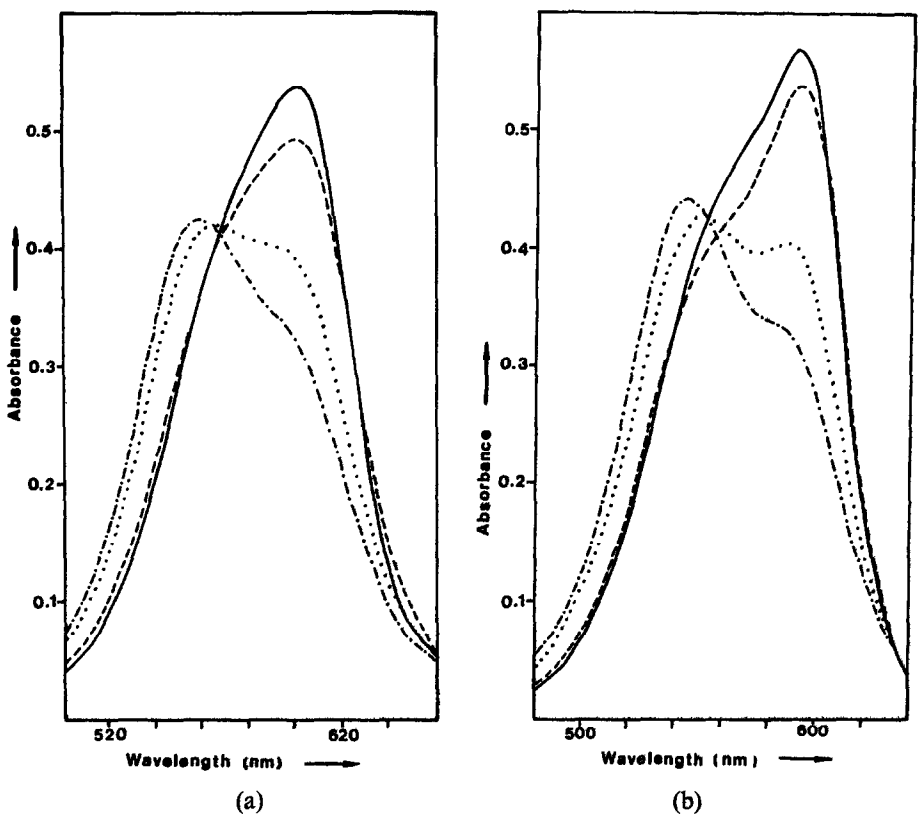


Fig. 13. Absorbance spectra of aqueous solutions of Acid Blue 15 and Acid Violet 17 in the presence of various amounts of acetone. (a) Acid Blue 15 in aqueous acetone; (b) Acid Violet 17 in aqueous acetone.

Spectrum	*% (v/v) of acetone in water*	*Reference solvent % (v/v) of acetone in water*
———	99	99
– – – –	29	29
. . . . .	5	5
– . – . –	0	0

The optical pathlength was 1 cm. [Dye] = (6.6 ± 0·2) × 10^{-6} M.

change in the α/β ratio, see Table 2) from that in MC (Fig. 6). Such an interaction may either facilitate absorption of light and/or retard dye migration to the edges of the film during the film drying process. The effect is more pronounced for Acid Green 9 than Acid Blue 1, and probably reflects the propensity of the sulphonate groups in the triphenylmethane dyes to complex to varying extents with the positively charged

TABLE 3

The α/β Ratios for a $(26{\cdot}4 \pm 0{\cdot}9) \times 10^{-6}$ M Aqueous Solution of Acid Blue 15 in the Presence of Various Amounts of PVA and Gelatin

Polymer	*Polymer concentration %(w/v) ± 1%*	*α-band (nm)*	*β-band (nm)*	*Absorbance at the α/β and ±0·01*	*α/β ratio ±0·01*
PVA	0·0	606·3	558	0·96	0·58
	0·5	606·3	558	0·99	0·59
	1·0	606·3	558	1·00	0·58
	2·0	606·3	558	1·02	0·61
Gelatin	0·0	606·3	560	0·97	0·58
	0·5	606·3	560	1·02	0·65
	1·0	606·3	560	1·11	0·68
	2·0	606·3	560	1·19	0·74

amino acid residues in gelatin. This is supported by the observation that of all the dyes studied, Acid Green 9 showed a similarly large increase in the main absorbance peak in MC when in the presence of ethylammonium hydrochloride, which models the positively charged amino acid residue of lysine (Fig. 14).

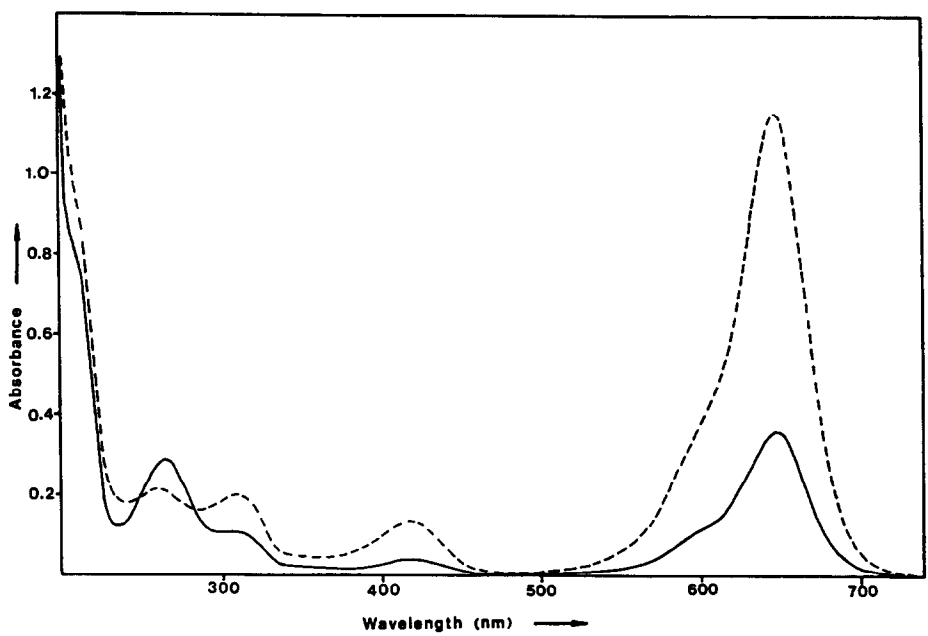


Fig. 14. Absorbance spectrum of Acid Green 9 in MC in the presence (– – –) and absence (——) of ethylammonium hydrochloride. The reference film was MC. [Dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mole/g MC. [Ethylammonium hydrochloride] = $(3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mole/g MC. Note that the films have not been exposed to radiation.

3.3 Dye fading in substrates that bind to the dye and/or promote dye aggregation

In a substrate where dye binding to the substrate or aggregation may occur, the term 'dye fading' in its most general sense refers to degradation of all forms of the dye present. Each form of the dye, be it unbound (dimer, DD_U, or monomer, D_U) or bound (dimer, DD_B or monomer, D_B), may contribute to the absorbance spectrum at the wavelength where fading is monitored. Thus, the rate of change of the absorbance A_T/dt will represent the rate of colourant loss, as perceived by the eye and be given by the general expression:

$$\frac{d(A_T)}{dt} = l\left[\varepsilon_{DU}\frac{dD_U}{dt} + \varepsilon_{DB_1}\frac{D_{B_1}}{dt} + \cdots + \varepsilon_{DB_n}\frac{dD_{B_n}}{dt} + \varepsilon_{DDU}\frac{dDD_U}{dt} + \varepsilon_{DDB_1}\frac{dDD_{B_1}}{dt} + \cdots + \varepsilon_{DDB_n}\frac{dDD_{B_n}}{dt}\right] \quad (6)$$

where A_T is the total absorbance, l is the film thickness, ε_{DU}, ε_{DDU}, ε_{DB_n} and ε_{DDB_n} (where $n \geq 1$) are the molar extinction coefficients for the unbound dye monomer and dimer and for the bound dye monomer and dimer, respectively. The subscripts n are used to denote that a given substrate may have more than one binding site for the dye (e.g. gelatin). Thus, it should be borne in mind that values of Q, Q_{rel}, R_0, k_0, A_0 and ε determined for such systems represent a sum for all species contributing to fading monitored at a specified wavelength. From expression (6) it is also apparent that if each form of the dye fades according to first-order decomposition, the rate of change of absorbance will be a sum of exponential decays. This illustrates why in PVA, where Acid Blue 15 and Acid Violet 17 aggregate, non-linear fading curves were observed. In gelatin, both dye–polymer interactions and dye–dye interactions may occur and contribute to non-linear fading curves. Furthermore, since there are many amino acid residues present, more than one type of interaction may occur between the dye and the protein. Thus, a dye molecule bound to one type of amino acid residue (say, arginine) may fade at a different rate to a dye molecule bound to another type of amino acid residue (say, lysine), and again expression (6) shows that non-linear fading is to be expected.

3.4 A comparison between dye fading in MC and PVA

The fading of the four triphenylmethane dyes in PVA was compared to the fading observed in MC (Table 4). For all aggregating dyes (including Acid Green 9) there is a reduction in the quantum yield for dye fading in

PVA, measured at the α-band, relative to dye fading in MC. For Acid Blue 1, an examination of Q_{rel} reveals that dye fading is slightly increased by changing the substrate from MC to PVA. There are at least four possible sources that could explain the observed trends for PVA and MC. These are related to (1) the effect of dye aggregation, (2) the role of oxygen in dye fading, (3) electron transfer and (4) hydrogen atom abstraction. Each of these is now discussed.

TABLE 4
Dye Fading in MC, PVA and Gelatin and in the Presence of Cd^{2+} and NaN_3

Film composition	*Substrate*	$Q \times 10^5 \pm 15\%$		Q_{rel}	
		α-band[a]	*β-band*[a]	*α-band*[a]	*β-band*[a]
Acid Blue 1	MC	6·3	—	1·0	—
Acid Blue 1	PVA	7·0	—	1·11 ± 8%	—
Acid Blue 1	Gelatin	14·6[b]	—	2·3 ± 10%[b]	—
Acid Blue 1 + NaN_3	MC	17·6	—	2·8 ± 8%	—
Acid Blue 1 + Cd^{2+}	MC	5·2	—	0·83 ± 8%	—
Acid Blue 1	PVA	7·0	—	1·0	—
Acid Blue 1 + Cd^{2+}	PVA	6·0	—	0·86 ± 8%	—
Acid Green 9	MC	20·0	—	1·0	—
Acid Green 9	PVA	14·2	—	0·71 ± 8%	—
Acid Green 9	Gelatin	20·0[b]	—	1·0 ± 10%[b]	—
Acid Green 9 + NaN_3	MC	Very large	—	Very large	—
Acid Green 9 + Cd^{2+}	MC	12·4	—	0·62 ± 8%	—
Acid Green 9	PVA	14·2	—	1·0	—
Acid Green 9 + Cd^{2+}	PVA	12·9	—	0·91 ± 8%	—
Acid Blue 15	MC	3·6	—	1·0	1·0
Acid Blue 15	PVA	2·65	6·1	0·73 ± 10%	1·7 ± 10%
Acid Blue 15	Gelatin	3·6	4·2	0·99 ± 10%	1·15 ± 10%
Acid Blue 15 + NaN_3	MC	28·8	—	8·0 ± 8%	—
Acid Blue 15 + Cd^{2+}	MC	1·95	—	0·54 ± 8%	—
Acid Blue 15	PVA	2·65	6·1	1·0	1·0
Acid Blue 15 + Cd^{2+}	PVA	2·4	4·8	0·90 ± 10%	0·79 ± 10%
Acid Blue 17	MC	4·3	—	1·0	—
Acid Blue 17	PVA	2·4	6·8[b]	0·55 ± 10%	1·6 ± 10%[b]
Acid Blue 17	Gelatin	3·5	4·7[b]	0·81 ± 10%	1·1 ± 10%[b]
Acid Blue 17 + NaN_3	MC	30·1	—	7·0 ± 8%	—
Acid Blue 17 + Cd^{2+}	MC	1·7	—	0·40 ± 8%	—
Acid Blue 17	PVA	2·4	6·8[b]	1·0	1·0
Acid Blue 17 + Cd^{2+}	PVA	2·15	7·8[b]	0·90 ± 10%	1·15 ± 10%[b]

[a] See Table 1 for the wavelengths at which fading was monitored.
[b] For fading at 35 min exposure to radiation (see text).
[Dye] = (2·7 ± 0·2) × 10^{-6} mole/g polymer, [Cd^{2+}] = [NaN_3] = (3·2 ± 0·2) × 10^{-5} mole/g polymer. Thus the mole ratio for dye : additives is 1 : 12.

3.4.1. The effect of dye aggregation

Firstly, for aggregating dyes the observed reduction in the quantum yield of dye fading in PVA compared to MC may be attributed to either (a) dye radical recombination (like that proposed by Nakamura and Hida[47] and/or (b) dissociation of the dimer. Either mechanism would partially replenish the dye monomer concentration as it is being depleted by photodegradation. This is supported by the observation that the quantum yield of dye fading at the β-band (in PVA) is larger than that measured at the α-band for both substrates.

3.4.2 The role of oxygen in dye fading

A second reason may be inherent in the differences in the gas permeability of the substrates. MC is permeable to oxygen but PVA is oxygen-impermeable.[48] Gelatin is also believed to be oxygen permeable, as it has been show to have a larger pore size than wool (an oxygen-permeable substrate).[49] Thus, the mechanism of dye fading in PVA would be expected to be independent of oxygen, and perhaps the converse is true when MC and gelatin are used as substrates.

Attention was focused upon the role of singlet oxygen by incorporating the excited singlet-state oxygen quencher sodium azide[50] in dyed MC films. The results of the fading experiment are presented in Table 4. They show that dye fading is markedly increased by the presence of sodium azide. For Acid Green 9 dye fading down to 90% dye remaining occurred too quickly to allow a value for Q_{rel} to be obtained. The observed increase in Q_{rel} in the presence of sodium azide is in direct contrast to the result expected if singlet oxygen was sensitizing the fading of all dyes (except Acid Blue 1). The azide ion N_3^- is, however, known to be a typical electron donor.[51] These results suggest that electron-transfer reactions are more important in triphenylmethane-dye photodegradation in a solid substrate than singlet oxygen attack.

3.4.3 Electron transfer

The third possibility, which may account for the reduced dye fading in PVA compared to MC, is an electron-transfer mechanism. Where electron transfer occurs, two possible reaction schemes can be envisaged: photoejection of an electron by the dye and electron abstraction by the dye.

These possibilities were tested by incorporating cadmium sulphate octahydrate, a known electron scavenger[51] into dyed MC and PVA films. The results of the fading experiments are presented in Table 4. It can be seen that the presence of cadmium sulphate octahydrate causes a reduction in dye fading in MC.

The observed decrease in Q_{rel} rules out the possibility that dye fading involves photoejection of an electron by the dye. Instead, the result indicates that electron abstraction is occurring:

$$D \xrightarrow{h\nu} {}^*D \quad \text{(excitation)} \tag{7}$$

$${}^*D + R \rightarrow D^{\cdot-} + R^{\cdot+} \quad \text{(electron abstraction)} \tag{8}$$

$$D^{\cdot-} \rightarrow \text{products} \quad \text{(reaction)} \tag{9}$$

where D represents a dye molecule, R the reductant and e^- an electron. In the presence of cadmium sulphate octahydrate the electron would be intercepted before it reached the dye, thereby lowering the probability of degradation.

3.4.4 Hydrogen atom abstraction

Finally, an examination of the structures of PVA and MC reveals that both polymers may be effective hydrogen atom donors as both contain secondary alcohol groups.[52] Furthermore, in MC (which contains ether groups) the C–H bond of the ether-bearing carbon atom may be broken in the presence of light and a hydrogen atom acceptor.[53] However, on this basis it is difficult to explain the increase in Q observed for Acid Blue 1 in PVA relative to the dye in MC. It may, however, be tentatively suggested that ground-state oxygen quenches the excited triplet-state dye molecule in MC, thereby possibly depleting a significant photodegradative pathway,[54] but the singlet oxygen formed does not oxidize the dye.

3.5 Dye fading in MC, PVA and gelatin

The quantum yields and relative quantum yields of photodegradation obtained for each dye in each polymer are reported in Table 4. It is evident that the quantum yield of fading of Acid Blue 15 in PVA monitored at the β-band is larger than that monitored at the α-band. For Acid Blue 15 in gelatin the difference is barely significant. In the case of Acid Violet 17, Q and Q_{rel} measured at the β-band are not quantitative values, since they correspond to dye degradation by more than 10%. Nevertheless, the tabulated values of Q and Q_{rel} show qualitatively that the β-band of Acid Violet 17 disappears faster than the α-band in both PVA and gelatin. Several workers[20,47,55] have observed similar fading behaviour for Basic Violet 3 in solid polymer films.

Gelatin was used as a substrate in order to provide a link between the fundamental studies carried out in MC and PVA and those that might be occurring in an irradiated dyed-wool system. Table 4 shows that for all dyes, Q_{rel} in gelatin is larger than Q_{rel} in PVA for the results associated

with the α-band. However, it is not clear whether this result is due to the absence of oxygen in PVA or the absence of amino acids in PVA which might enhance dye fading in gelatin. It is perhaps more informative to compare dye fading in MC with dye fading in gelatin.

In the cases of Acid Blue 1 and Acid Green 9 in gelatin, dye fading occurred so rapidly that accurate determinations of Q and Q_{rel} were not possible. In fact, 10% dye loss occurred in approximately 10 min for Acid Blue 1 and in less than 4 min for Acid Green 9. Nevertheless, the observation of rapid fading provides sufficient evidence that the amino acids in gelatin sensitize the fading of these two dyes. This effect is clearly evident in Table 4 for Acid Blue 1.

In contrast to Acid Blue 1 and Acid Green 9, it would appear that for Acid Blue 15 and Acid Violet 17, there are other factors involved which may outweigh any sensitizing effect imparted by the amino acids present in gelatin. One such factor may be that the possible sensitization imparted by the amino acids in gelatin (as observed at the α-band) may be masked by the replenishment of the monomeric form of the dye as the aggregated particles break up.

In substrates such as PVA and gelatin, where the possibility of dye aggregation exists, the fading of the dimeric form of a dye must be considered. This is particularly pertinent to the fading of the triaminotriphenylmethane dyes Acid Blue 15 and Acid Violet 17.

Since the dimer–polymer residue interaction may be a sterically hindered process, particularly in gelatin, photodegradation of dimeric triphenylmethane dyes may be proposed to occur via the following two dissociative type pathways:

$$DD \xrightarrow{h\nu} {}^1[DD]^* \longrightarrow D^{\bullet}_{\bullet}{}^{+} + D^{\bullet}_{\bullet}{}^{-} \longrightarrow 2D \longrightarrow \text{reactions as for dye monomers in the presence of amino acid residues or other polymer residues}$$

$${}^3[DD]^* \quad \text{demethylation products} \qquad \text{reduction or oxidation products} \tag{10}$$

This mechanism is essentially based on that proposed by Nakamura and Hida,[47] but it also includes the possibility that the excited triplet-state dimer may be involved in the photodegradation of the dimeric form of the dye. The other photodegradative pathway is

$$DD \xrightarrow{h\nu} {}^1[DD]^* \longrightarrow 2D \longrightarrow \text{reactions as for dye monomers in the presence of amino acid residues or other polymer residues} \tag{11}$$

$${}^3[DD]^*$$

and this also includes the possibility that dye fading proceeds via the excited triplet-state dimer. Evidence to support the inclusion of triplet-state species in the above dissociative pathways is based on excited triplet-state quenching studies presented in Part 2 of this work.[56]

3.6 Dye fading in the presence of protein-bound amino acids

The amino acids arginine, histidine, lysine, glutamic acid and aspartic acid are present in wool in significant amounts[12,57,58] and so were chosen for study. For amino acids in the protein-bound state, both the non-terminal α-amino and α-carboxyl groups are involved in peptide bonds and are therefore not expected to be available to influence dye fading on the protein. Thus, protein-bound arginine, histidine and lysine were modelled by methylguanidine sulphate, imidazole and ethylammonium hydrochloride, respectively. Glutamic and aspartic acids were modelled by sodium acetate. All experiments were performed using the oxygen- and water-permeable polymer MC.

3.6.1 The protein-bound basic amino acids

The results of dye fading shown in Table 5 indicate that neither ethylammonium hydrochloride nor imidazole sensitize dye fading.

The extent of fading of Acid Blue 15 and Acid Violet 17 is reduced by the presence of ethylammonium hydrochloride. Since this additive is positively charged at pH 6 (pKa = 10·807 at T = 20°C),[59] it may be expected to compete with the dye for available electrons and thus reduce Q_{rel} if the major mechanism by which the dyes fade is electron abstraction. In support of this it was noted that the fading of these two dyes was greatly accelerated by the electron donor sodium azide (Table 4). Acid Blue 1 was least affected by sodium azide which is in agreement with the results presented in Table 5. The fading of Acid Green 9, however, was greatly accelerated by the presence of sodium azide (Table 4) and so the value of Q_{rel} obtained in the presence of ethylammonium hydrochloride needs further consideration.

When films containing Acid Green 9 were prepared with ethylammonium hydrochloride, a marked change was observed in the absorbance spectrum recorded before irradiation (Fig. 14). The effect was not observed for any other dyes in the presence of basic groups and is not believed to be due to increased dye migration to the centre of the films during the drying process. The spectrum suggests that ethylammonium hydrochloride is able to complex with Acid Green 9. This would eliminate the scavenging effect of ethylammonium hydrochloride and the dye would be expected to fade at a rate similar to that in the absence of the additive.

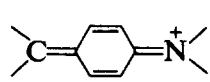
TABLE 5
Dye Fading in MC in the Presence of Compounds that Model Protein-Bound Amino Acids

Film composition	$Q \times 10^5 \pm 15\%$ *α-band*[a]	$Q_{rel} \pm 8\%$ *α-band*[a]
Acid Blue 1	6·3	1·0
Acid Blue 1 + ethylammonium hydrochloride	6·2	0·98
Acid Blue 1 + imidazole	5·6	0·89
Acid Blue 1 + methylguanidine sulphate[b]	8·2	1·3
Acid Blue 1 + sodium acetate	6·5	1·03
Acid Green 9	20·0	1·0
Acid Green 9 + ethylammonium hydrochloride	20·6	1·03
Acid Green 9 + imidazole	18·6	0·92
Acid Green 9 + methylguanidine sulphate[b]	24·0	1·2
Acid Green 9 + sodium acetate	26·0	1·3
Acid Blue 15	3·6	1·0
Acid Blue 15 + ethylammonium hydrochloride	2·75	0·76
Acid Blue 15 + imidazole	3·0	0·84
Acid Blue 15 + methylguanidine sulphate[b]	4·0	1·12
Acid Blue 15 + sodium acetate	5·8	1·6
Acid Violet 17	4·3	1·0
Acid Violet 17 + ethylammonium hydrochloride	3·5	0·81
Acid Violet 17 + imidazole	3·9	0·90
Acid Violet 17 + methylguanidine sulphate[b]	5·15	1·2
Acid Violet 17 + sodium acetate	7·1	1·65

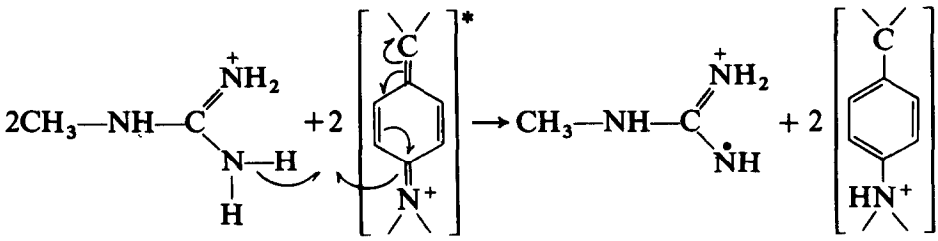
The model ratio for dye : additive is 1 : 12.
[Dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mole/g MC and [additive] = $(3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mole/g MC.
[a] See Table 1 for the wavelengths at which fading was monitored.
[b] [Methylguanidine sulphate] = 1/2[guanidino groups] (see text).

In contrast to ethylammonium hydrochloride and imidazole, methylguanidine sulphate was observed to sensitize photodegradation for all four dyes, although the result for Acid Blue 15 is barely significant (Table 5). It should be noted here that methylguanidine sulphate has the molecular formula $(CH_3NHC : NHNH_2)_2 . H_2SO_4$ and so all films containing this compound have twice the number of amino acid residue-type groups as those films containing ethylammonium hydrochloride and imidazole. However, variations in methylguanidine sulphate concentrations revealed that Q_{rel} is essentially constant for mole of dye to mole of methylguanidine sulphate ratios below 1 : 20 (see Table 2 of Part 2 of this work[56]). Consequently, all tables presented in the text have been interpreted on this basis, assuming that the observed trends are not attributable to differences in the concentrations of model amino acid residues.

In view of the fact that it has been reported that dyes which contain the component



can, in the photoexcited state act as powerful oxidizing agents,[60,61] and that benzhydrol, a hydrogen-atom donor, has been reported to enhance the fading of Basic Violet 3 and Basic Green 4,[62] it would appear that one possible explanation for these results is that the triphenylmethane dyes are abstracting a hydrogen atom from methylguanidine sulphate:



(12)

This process seems plausible, not only because the products exhibit resonance stabilization but because neither the dye nor the model amino acid compound become more positively or negatively charged as a result of the reaction. It is evident from the results presented in Table 5 for the three basic groups tested here, that only protein-bound arginine will sensitize dye fading.

3.6.2 The protein-bound acidic amino acids

Sodium acetate, which models protein-bound aspartic and glutamic acids, is observed to accelerate dye photodegradation for all dyes except Acid Blue 1 where no effect was observed (Table 5). These trends are similar to those observed for dye fading in the presence of the electron donor, sodium azide (Table 4). Thus, it appears probable that the free carboxyl group sensitizes dye fading by donating an electron to the dye molecule. Electron donation would be facilitated by charge delocalization in the resulting acetate radical. Further evidence in support of this proposal is that Basic Violet 3 oxalate fades faster than Basic Violet 3 chloride and Basic Violet 3 tosylate ($CH_3C_6H_4SO_3^-$) because in the former compound electron donation by the counterion is more likely.[63]

4 SUMMARY

From this work it is evident that both the absorbance spectra and photochemical reactions of triphenylmethane dyes are very sensitive to their environment. In MC the α-band of the visible absorbance peak of the triaminotriphenylmethane dyes predominated. In PVA the β-band had the highest intensity, whereas in gelatin the α- and β-bands were more

similar in intensity. No evidence was found to suggest that the observed β-band could be associated with dye–polymer interactions. However, the close parallel between the dye spectra in polymeric media with the spectra of solutions in which the dyes existed in various states of aggregation suggested that the α- and β-bands were associated with the absorbance of monomeric and dimeric forms of the dye, respectively. It should be noted, however, that there is a certain amount of overlap of the absorbance spectra of the two species. More dimers seem to be formed in PVA than in gelatin, and in MC the monomeric form of the dye predominates.

In contrast to the triaminotriphenylmethane dyes, the diaminotriphenylmethane dyes studied barely showed any tendency to aggregate. Consequently, the α-band predominated in all solvents and polymer substrates examined.

Kinetic analysis revealed that the shape of the dye fading curves can be attributed to dye–dye and dye–polymer interactions. In general, non-linear fading curves are to be expected for systems in which (a) monomeric and aggregated dye coexist and/or where (b) there are a number of different ways in which the dye may interact with the substrate. The former situation was found to be applicable to triaminotriphenylmethane dye fading in PVA, and both cases were found to be applicable to dye fading in gelatin. Linear fading curves were observed for all dyes in MC. Furthermore, the observed non-linear fading curves could not be explained by the buildup of photoproducts nor by simple kinetic functions which relate the dye absorbance to the time of exposure to radiation.

Comparative fading studies made for each dye in MC, PVA and gelatin revealed that dye fading in both protein and non-protein substrates is governed by many competing processes. These include (a) the ability of the substrate/residual solvent system to donate electrons or hydrogen atoms to the dye and (b) the degree of dye aggregation, which may be partially determined by (c) the chemical and physical structure of the substrate. Although the importance of ground-state oxygen in the dye fading mechanism was not examined, the role of excited singlet-state oxygen was considered. It was concluded that dye fading in MC was more likely to occur via electron abstraction than by singlet oxygen attack. Consequently, dye fading seems less likely to occur by singlet oxygen attack in gelatin and wool, where the excited singlet-state oxygen would be more likely to attack the protein substrates.[3]

In a substrate where the possibility of dye aggregation arises, the fading of the dimeric form of a dye must be considered. This is particularly relevant to the fading of the triaminotriphenylmethane dyes in PVA and gelatin, and possibly in wool. Here it is proposed that in such substrates, dimeric triphenylmethane dyes may fade via the two dissociative

pathways (10) and (11). In each case, dye monomers are formed, which in turn, appear to fade via photochemical interactions with the substrate or residual solvent within the substrate. Studies performed on model systems for proteins, such as gelatin and wool, indicated that certain dye–amino acid interactions influence dye fading.

The effect of ethylammonium hydrochloride and imidazole on dye fading was examined in MC films. This work indicated that neither protein-bound lysine nor protein-bound histidine are likely to sensitize the fading of triphenylmethane dyes. Furthermore, these results suggested that protein-bound lysine will cause a slight decrease in the quantum yield of fading of Acid Blue 15 and Acid Violet 17 on wool.

In contrast, the results obtained using methylguanidine sulphate and sodium acetate indicated that protein-bound arginine and glutamic and aspartic acids should sensitize dye fading. In wool, some of the glutamic acid and aspartic acid residues exist in the acid amide form, and although this possibility was not examined in detail, it is tentatively suggested that protein-bound glutamine and asparagine can sensitize dye fading via electron and/or hydrogen atom transfer mechanisms.

It has been suggested that in the presence of protein-bound amino acids which are capable of sensitizing dye fading, the fading of triphenylmethane dyes, in the most general sense, apparently involves hydrogen atom transfer for arginine residues and electron transfer for glutamic acid and aspartic acid residues.

These studies highlight the complexity of dye fading on protein substrates and have indicated which amino acid residues are likely to promote or retard dye fading. Consequently, if carboxylate and guanidino groups are removed and lysine residues are increased, fading may be retarded in the wool fibre.

The work presented here has raised many questions. In this respect, it is interesting to note that while the role of cystine was not examined, gelatin does not contain this amino acid, silk contains a low proportion of cystine,[58] and it is present in a larger amount in wool. Future studies could thus be directed toward examining the role of this amino acid residue in dye fading. They could also be directed toward elucidating, more fully, the kinetic mechanisms applicable to dye fading in wool.

In substrates where dye aggregation is apparent, application of techniques such as principal component analysis and its variations[64–69] may allow the independent monitoring of the fading of free and bound dimer and monomeric species. In this regard, the work presented here represents an important and useful preliminary step in unravelling the complex fading mechanisms present on solid natural and synthetic polymers for this class of dye.

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