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The photocrosslinking of styrylpyridinium salts via a [2+2]-cycloaddition reaction

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Abstract

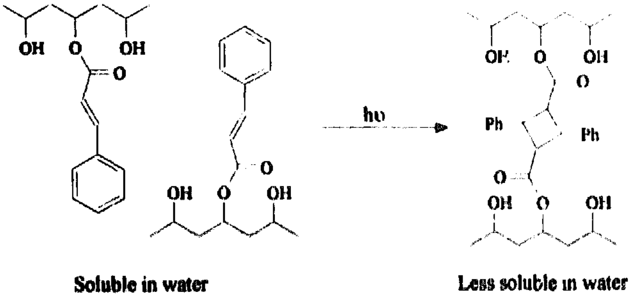
It has been shown that two *N*-methylstyrylpyridinium salts weakly associate in aqueous solution. When styrylpyridinium groups are attached to poly(vinyl alcohol) as pendant groups, the association is much more marked and its efficiency is greater for the 4-styrylpyridinium salt than for the 2-styrylpyridinium salt. From fluorescence measurements, it is concluded that the cycloaddition reactions occur via the associated pendant groups.

Keywords: Photocrosslinking; Styrylpyridinium salts; [2+2]-Cycloaddition reaction

1. Introduction

Photostimulated [2+2]-cycloaddition reactions have found extensive use in synthesis [1] and imaging. Perhaps the most well-known example of the latter is the reaction of cinnamoylated poly(vinyl alcohol) (PVA) [2] (Scheme 1). The derivatized polymer, when crosslinked via the [2+2]-cycloaddition process, becomes less soluble in water than the non-irradiated areas, thereby opening up a way to obtain a water developable image. It has been found that these systems can be successfully sensitized towards visible light by the use of triplet sensitizers such as ketocoumarins [3]. The cycloaddition reaction has to compete with cis–trans isomerization which also occurs from the triplet state, i.e. there is competition between a unimolecular and bimolecular process. Given the high viscosity of the derivatized PVA, there is little chance for a bimolecular reaction to occur via the diffusing together of the reaction partners and, consequently, the efficiency of the cycloaddition process is highly dependent on the degree of pre-organization.

The association of cinnamoyl groups may well occur in these systems since they are relatively hydrophobic compared with the PVA backbone. Improvement in the degree of association has been achieved by the mixing of PVA derivatized with a cinnamate containing electron-donor groups with a PVA derivatized with a cinnamate containing electron-withdrawing groups [4].



Scheme 1.

Styrylpyridinium groups undergo [2+2]-cycloaddition reactions [5], and these have also been used to make photosensitive polymers [6–8] with some being based on PVA [7–9]. To this collection of photoactive materials, styrylthiazolium salts have recently been added [10].

The cycloaddition reactions of certain styrylpyridinium compounds have been shown to occur via the excited singlet state [5] and are favoured by aggregation. Under such circumstances, these compounds exhibit excimer emission. For this emission to be observed and for cycloaddition to occur, it is imperative that the styrylpyridinium compound has an appropriate counterion, e.g. 4-chloro- or 4-bromobenzenesulphonate. With bromide or tetrafluoroborate as counterions, neither cycloaddition nor excimer emission is observed [5].

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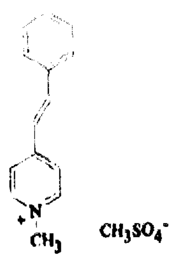
No clear explanation has been given for this counterion dependence and it would be valuable to know to what extent the counterions affect the aggregation and quenching of the excited singlet state (electron transfer and/or heavy atom effect).

We have previously reported our preliminary findings concerning the mechanism of the cycloaddition reactions of 4-styrylpyridinium methosulphate salts attached to a PVA backbone via an acetyl group; we concluded that an excimer lies along the reaction pathway [9]. Given that the reaction occurs via an excited singlet state, it becomes axiomatic that the styrylpyridinium groups are pre-organized in the PVA matrix. We now address the question as to whether there is any evidence for the pre-organization. Furthermore, does the effectiveness of pr-organization account for the claimed [7,8] greater reactivity of PVA derivatized with 4-styrylpyridinium methosulphate compared with the corresponding 2-styrylpyridinium compound? To answer these questions, we studied the model compounds **1** and **2** in addition to the 4- and 2-styrylpyridinium compounds **3** and **4** respectively.



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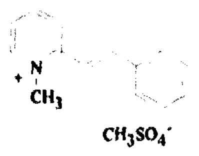

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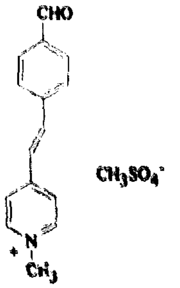

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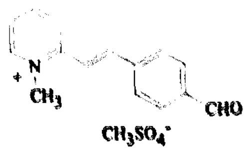

(4)

2. Experimental details

2.1. Equipment

UV–visible spectra were recorded on a Philips PU spectrophotometer. Diffuse reflectance spectra were recorded using an integrating sphere accessory with a Perkin-Elmer Lambda 5 spectrophotometer. IR spectra were recorded as nujol mulls or potassium bromide discs using either a Perkin-Elmer 983G spectrophotometer or a Bio-Rad FTS-60 FTIR spectrometer. ^{1}H NMR spectra were recorded on a Jeol PM x 60 si 60 NMR spectrometer using tetramethylsilane as internal standard in conjunction with deuterated solvents (deuterochloroform, deuteroacetone and deuterium oxide). Fluorescence spectra were recorded as aqueous solutions or as thin films coated on paper using a drawbar and a Perkin-Elmer MPF-4 spectrofluorometer, and are uncorrected. Where applicable, spectrophotometric grade solvents were used and solvent blanks were recorded in each case to ensure that they did not emit significantly over the wavelength ranges being monitored. Solutions were made up in 1 cm path length quartz, rectangular fluorometer cells to an optical density (OD) of 0.1 at the excitation wavelength. Polymer samples in film form were studied by placing them at 45° to the incident radiation, so as to minimize the effects of stray light on the emission spectra. Mass spectra were run on a Kratos MS 30 electron impact mass spectrometer linked to a Kratos DS 50 data system. Elemental analyses were carried out on a Carlo Erba model 1106 elemental analyser. Melting points (uncorrected) were recorded on a Griffin & George UK apparatus.

UV curing of thin films was carried out on a Colordry unit (Colordry Ltd., Chessington, Surrey) which housed a medium pressure mercury lamp (80 W in^{-1}) mounted over a conveyor belt system which was run at 12 m min^{-1}. Photosensitive films were cured as thin films on screens (120 HDW mesh, 2+2) using a Platemaker exposure unit which housed a 5 K lamp. All samples, unless stated otherwise, were irradiated for 200 light units. Stepwedge values were obtained with a square root of two Stouffer Stepwedge (DuPont-Howson). Viscosities were determined using an RVTD Brookfield viscometer.

2.2. Chemicals

The following chemicals were used as received from Aldrich Chemical Co. Ltd.: 2- and 4-picoline, terephthaldehyde and dimethyl sulphate.

2.2.1. Preparation of 1-methyl-2-[2-(phenyl)ethenyl]-pyridinium methosulphate (2)

2-[2-(Phenyl)ethenyl]pyridine (1 g, 0.006 M) was dissolved in methanol. Dimethyl sulphate (1 g, 0.008 M) was added slowly and the reaction mixture was allowed to stand overnight. On cooling, a yellow precipitate was formed. The precipitate was filtered and oven dried (yield, 90%). Melting point, 125 °C. IR (KBr disc): 3050, 2965, 1640, 1600, 1575, 1520, 1500, 1480, 1075 and 840 cm^{-1}. NMR (DMSO) (ppm): 9.24–7.49 (11H, m), 3.51 (3H, s) and 2.16 (3H, s). $C_{15}H_{17}NSO_4$: theory: C, 58.62%; H, 5.57%; N, 4.56%; found: C, 58.02%; H, 5.27%; N, 4.60%.

1-Methyl-4-[2-(phenyl)ethenyl]pyridinium methosulphate (**1**), 1-methyl-4-[2-(4-formylphenyl)ethenyl]-pyridinium methouslphate (**3**) and 1-methyl-2-[2-(4-formylethenyl)phenyl]pyridinium methosulphate (**4**) were prepared according to literature procedures [8].

Compounds **3** and **4** were acetalized onto PVA using standard procedures [8].

3. Results

3.1. Model compounds 1 and 2

The absorption spectra of these compounds show a concentration dependence (Table 1). Solutions made up to an OD of 0.1 and 0.2 at 340 nm indicate that, at the higher concentration, the λ_{max} values exhibit a small bathochromic shift. The fluorescence spectra of these solutions, obtained by excitation at 340 nm, are shown in Figs. 1 and 2. For imaging purposes, the compounds of direct interest are the styrylpyridinium compounds **3** and **4** grafted onto a PVA backbone by acetalization. The fluorescence spectra of **1** and **2** were therefore recorded in a solution of PVA in order to determine whether PVA influences aggregation. The spectra are shown in Figs. 3 and 4.

Table 1
UV absorption maxima for aqueous solutions of **1** and **2** made up to OD values of 0.1 and 0.2 at 340 nm

OD	Compound **1** λ_{max} (nm)	Compound **2** λ_{max} (nm)
0.1	338	331
0.2	341	334

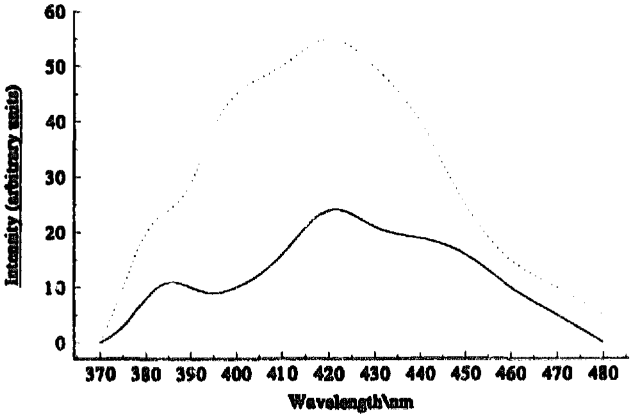

Fig. 1. Fluorescence spectra of solutions of **1** made up to OD values of 0.1 (——) and 0.2 (·····) at 340 nm.

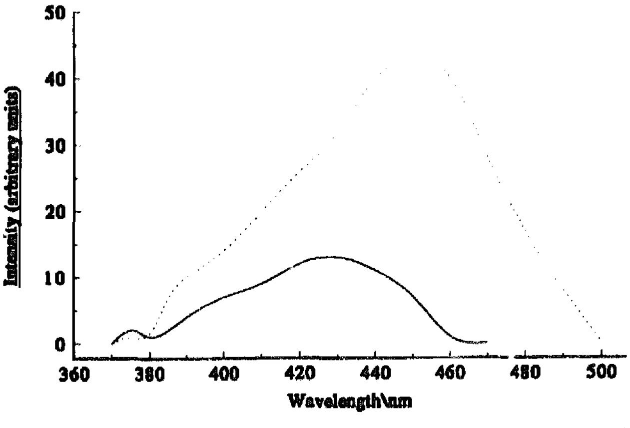

Fig. 2. Fluorescence spectra of solutions of **2** made up to OD values of 0.1 (——) and 0.2 (·····) at 340 nm.

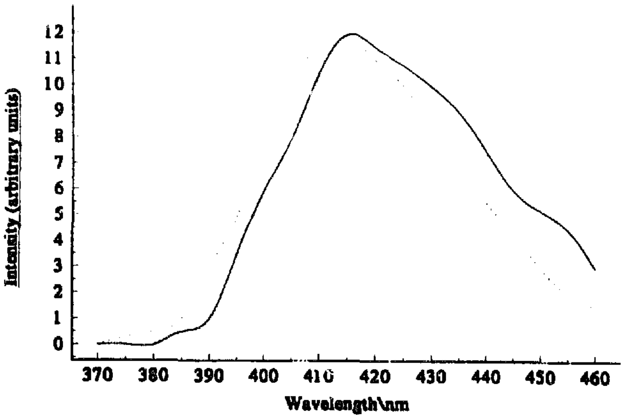

Fig. 3. Fluorescence spectra of solutions of **1** (0.5 g (·····) and 1.5 g (——)) in PVA (100 g).

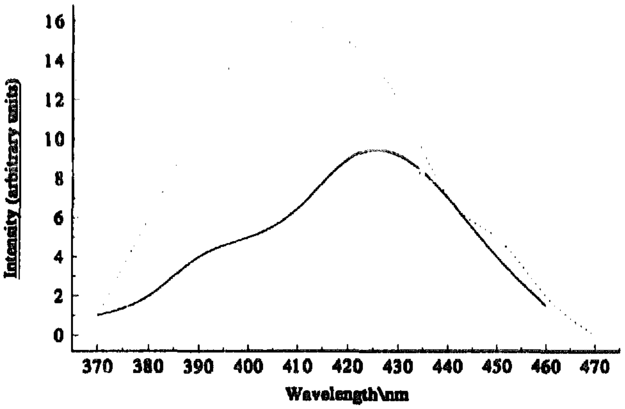

Fig. 4. Fluorescence spectra of solutions of **2** (0.5 g (·····) and 1.5 g (——)) in PVA (100 g).

3.2. Styrylpyridinium compounds 3 and 4

Compounds **3** and **4** when grafted onto PVA via acetalization, exhibit an increase in viscosity. The extent of this increase is dependent on the concentration and nature of the styrylpyridinium compound (Table 2). To check that the acetalization procedure was effective, the polymer was precipitated from aqueous solution by the addition of propan-2-ol. The precipitated polymer was dissolved in water and the concentration of the photosensitive group was determined by UV spectrometry. In all cases, the level of grafting exceeded 90%. UV–visible diffuse reflectance spectra were recorded for PVA films modified with **3** and **4**. On increasing the level of grafting, the absorption maximum shows a bathochromic shift (Table 3). Fluorescence spectra for aqueous solutions of PVA modified with **3** and **4** were also recorded (Figs. 5

Table 2
Viscosity of aqueous solutions of PVA modified by 3 and 4 at various concentrations

Concentration (mol.%)	Viscosity (cP)	
	PVA modified with 3	PVA modified with 4
0.5	12700	8560
1.00	32900	9800
1.25	>100000	11280
1.50	>100000	12240

Table 3
UV absorption maxima (diffuse reflectance) of PVA films modified with 3 and 4

Extent of modification (mol.%)	λ_{max} (nm)	
	PVA modified with 3	PVA modified with 4
0.5	360	349
1.00	365	352
1.25	368	358
1.50	374	360

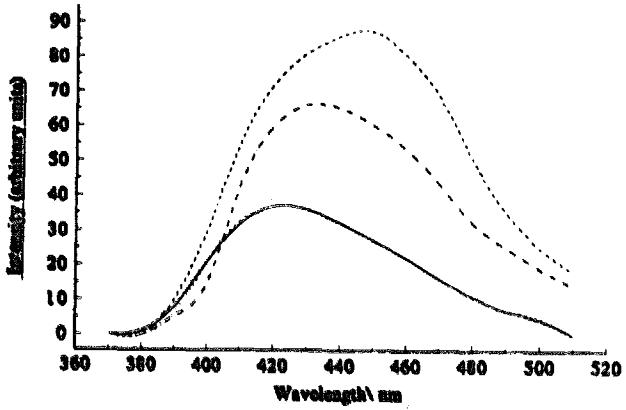

Fig. 5. Fluorescence emission spectra for aqueous solutions of PVA modified with 3. – – –, 10% H_2O dilution; –·–, 25% H_2O dilution; ·····, 50% H_2O dilution; ——, 75% H_2O dilution.

and 6). On dilution, the emission maxima show a hypsochromic shift with an associated drop in intensity, which is more marked for PVA modified with 3. PVA films modified with 4 are less fluorescent than those modified with 3 (Fig. 7). The fluorescence excitation spectra for films modified with 3 and 4 show maxima at 405 and 400 nm respectively. The positions of the maxima are independent of the level of grafting over the range 0.5–1.5 mol.%.

3.3. Irradiation of modified PVA films

The effectiveness of styrylpyridinium compounds in modified PVA in producing water insolubilization (via crosslinks) on irradiation was determined. Films were exposed to light through a stepwedge and developed with water. The results are shown in Table 4. As presented earlier [9], films modified with 3 exhibit excimer emission at 450 nm, and irradiation of the films leads to the gradual disappearance of this band. IR spectra of the irradiated films confirm that olefinic residues have been consumed. A more detailed study of the photoreactions was made by exposing the films to a light source through a glass filter and recording the decrease in fluorescence of the films caused by irradiation. The results shown in Table 5 confirm that 3 is a more effective crosslinker

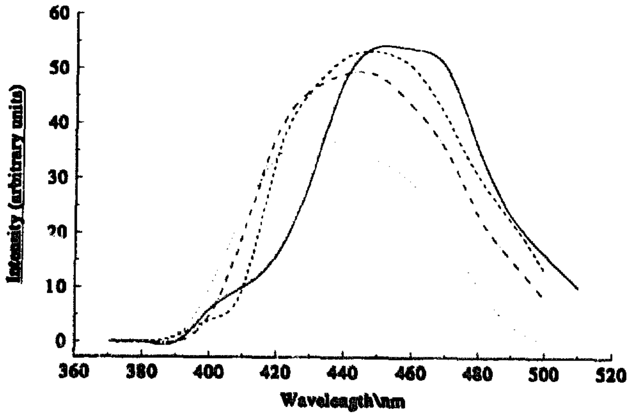

Fig. 6. Fluorescence emission spectra for aqueous solutions of PVA modified with 4. ——, 10% H_2O dilution; – – –, 25% H_2O dilution; –·–, 50% H_2O dilution; ·····, 75% H_2O dilution.

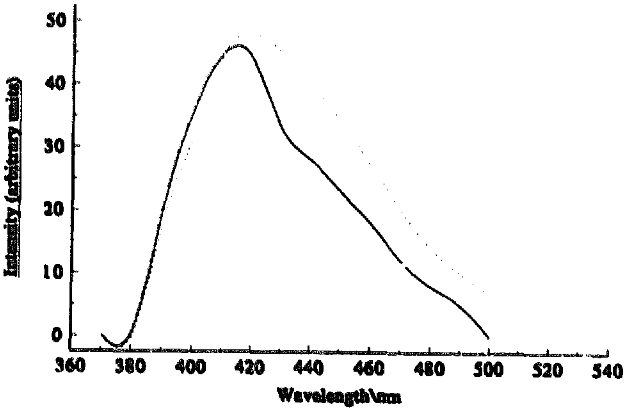

Fig. 7. Fluorescence emission spectra of PVA films modified with 3 (·····) and 4 (——) at 0.5 mol.%.

Table 4
Stepwedge values [a] of PVA modified with 3 and 4

Concentration (mol.%)	PVA modified with 3	PVA modified with 4
0.50	13	Washed out
1.00	15	10/11
1.25	19	11/12
1.50	19	13/14
1.75	20	15
2.00	20	15

[a] 200 light units exposure.

Table 5
Decrease in fluorescence intensity of PVA films modified with 3 and 4 on exposure to light [a]

	PVA modified with 3 (mol.%)			PVA modified with 4 (mol.%)		
	0.5	1.00	1.50	0.5	1.00	1.50
Wavelength [b] of fluorescence before irradiation (nm)	420	445	455	410–415	420	445
Wavelength [b] of fluorescence after irradiation (nm)	415	420–425	420	410	410	415
Decrease (%) in fluorescence intensity	60	61	74	54	53	70

[a] Refers to 10 passes under the Colordry unit.
[b] Position of wavelength maximum.

than 4 and that the crosslinking efficiency increases with concentration.

4. Discussion

In the seminal work by Quina and Whitten [5], compounds similar to 1 and 2 were studied, with the main difference being that their compounds possessed long-chain alkyl groups attached to nitrogen rather than *N*-methyl groups. The long-chain alkyl groups facilitated aggregation and, not surprisingly, these compounds formed monolayers which exhibited excimer emission.

From Table 1, it appears that 1 and 2 show some degree of aggregation in aqueous solution, as judged by the bathochromic shift of the UV absorption maximum with an increase in concentration. The fluorescence spectrum of 1 (Fig. 1) exhibits a λ_{max} value at 430 nm, which is well to the blue of the maximum expected for an excimer (e.g. 450–500 nm). However, on increasing the concentration, some structure is lost suggesting that complex formation may be taking place. The structureless nature of the fluorescence from 2 coupled with the bathochromic shift in the maximum wavelength of fluorescence with increasing concentration (Fig. 2) is a good indication that emission is emanating from a complex such as an excimer. The spectra shown in Figs. 3 and 4 reveal, surprisingly, that PVA does not have a strong influence on the association of 1 and 2, but causes, in both cases, a hypsochromic shift (approximately 20 nm).

Modification of PVA with 3 and 4 leads to an increase in viscosity, with the 4-substituted compound 3 having the greatest effect (Table 2). Association of the styrylpyridinium compounds would be expected to cause the linear polymeric chains to interact, thereby increasing the viscosity. Therefore these results indicate that 3 leads to association to the greatest extent. The bathochromic shift in the position of the maximum absorption as the concentration of the styrylpyridinium groups is increased (Table 3) also points to the association of the pendant groups. These measurements, however, do not reveal the degree of association: fluorescence spectroscopy provides further evidence for association and its role in the crosslinking process. From Table 5, it can be seen that, as the level of PVA modification with styrylpyridinium groups is increased, the wavelength of maximum fluorescence shows a bathochromic shift. Dilution of the modified PVA solutions causes a hypsochromic shift in the wavelength of maximum fluorescence (Figs. 5 and 6). Additional evidence for association comes from the observation that the excitation fluorescence spectra of the modified PVAs show maxima that are red shifted from the UV absorption maxima (Table 3). The maxima recorded in this way may not be true maxima due to the influence of inner filter effects, but given that this is not serious, the excitation spectra suggest that the aggregates give rise to new absorption bands. These aggregates probably give rise to new fluorescence bands which will contribute to, if not dominate, the so-called emission bands.

Of particular importance is the finding that PVA modified with 3 shows a much higher quantum yield for excimer (or excited complex?) fluorescence compared with PVA modified with 4 at the same concentration (Fig. 7). This result suggests that either the pendant groups are less associated in PVA modified with 4 than with 3 or association of the pendant groups leads to more efficient non-radiative decay for 4 than for 3. The viscosity measurements (Table 2) provide evidence that the pendant groups derived from 4 are less efficient at associating than those derived from 3. Consequently, the high quantum yield of fluorescence for PVA modified with 3 most probably reflects the greater degree of association of these pendant groups. However, if a substantial portion of pendant groups derived from 4 are not associated, we would expect to see some contribution in the fluorescence spectrum from the monomeric species (at $\lambda_{max} = 420$ nm). This clearly is not the case, and so it seems that the nature of the aggregates derived from the pendant groups 3 and 4 is different. Such differences may be due to the relative dispositions of the styrylpyridinium groups (distance between and relative orientation of the groups) or may reflect a different size distribution of the aggregates. There is much evidence from the work on excited complexes, including excimers [11], that the distance between partners and their relative orientation affect both the efficiency of non-radiative decay and the wavelength of maximum fluorescence. Given that the pendant groups derived from 3 and 4 associate in different ways, the efficiency of crosslinking will not be the same. In addition, 2- and 4-styrylpyridinium compounds may intrinsically cyclodimerize with different quantum efficiencies.

The results given in Table 5 show quite clearly that PVA modified with 3 photocrosslinks with greater efficiency than that modified with 4. These findings are backed up by the data given in Table 4, which show that PVA modified with 3 needs less light to be rendered water insoluble than PVA modified with 4. Previously, we have presented evidence and arguments in favour of the cyclodimerization occurring via an excimer [9]. Consequently, the data in Table 5 are worthy of further inspection. Given that the samples were exposed to a similar degree of illumination, the greater the degree of association (as monitored by the wavelength of maximum fluorescence), the more effective the crosslinking (as measured by the percentage drop in fluorescence after irradiation). The less effective association of PVA modified with 4 compared with 3 clearly leads to less efficient crosslinking (as monitored by the percentage fluorescence decrease after irradiation). The results are supported by those shown in Table 4, in which it can be seen that PVA modified with 4, which shows little excimer formation, undergoes crosslinking relatively inefficiently as judged by the stepwedge results.

5. Conclusions

From the study of the model compounds 1 and 2, it has been shown that simple styrylpyridinium compounds can associate, albeit weakly, in aqueous solution. The pendant groups obtained by reacting 3 and 4 with PVA become associated, but with differing efficiency, and this in turn affects the photophysical and photochemical properties. The association of the pendant groups derived from 3 favours the cyclodimerization reaction which is at the heart of the imaging process originally described by Ichimura [7,8].

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