Photochromism of double-bridged viologens in a polar polymer matrix

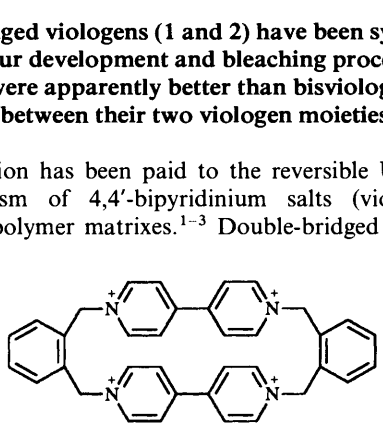
PERKIN 2

Xuehui Sun and Yu-kun Yang *

Institute of Chemistry, Academia Sinica, Beijing 100080, China

Double-bridged viologens (1 and 2) have been synthesized; in polar polymer films they displayed two distinct colour development and bleaching processes upon UV irradiation. Their photofatigue resistances were apparently better than bisviologens and benzylviologen due to particular intramolecular interactions between their two viologen moieties in the two photochromic stages.

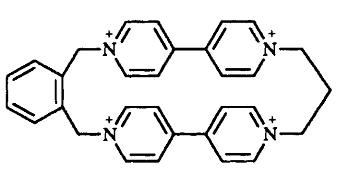
Much attention has been paid to the reversible UV-induced photochromism of 4,4′-bipyridinium salts (viologens) in solution or polymer matrixes.[1–3] Double-bridged viologen **1**, containing two parallel 4,4′-bipyridinium units, has been synthesized and its chromism induced by a chemical or electrochemical reductant in solution,[4] but the photochromism of a double-bridged viologen embedded in a polar polymer matrix has never been investigated. We describe in this paper, the preparation of double-bridged viologens **1** and **2** and their photochromism in polar polymer films. Their fascinating two stages of colour development has been observed and it has been found that there is a strong intramolecular interaction between the 4,4′-bipyridinium radical cation and 4,4′-bipyridinium dication in their first photoreduction stage as well as intramolecular pimerization between two 4,4′-bipyridinium radical cations in their second stage. Furthermore, the mechanism by which these special interactions in the two photoreduction stages influence the colour development, fading and photofatigue behaviour has also been investigated.



$4X^-$

1a; X = Br

1b; X = ClO_4



$4Br^-$

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Results and discussion

Preparation of double-bridged viologens and their photochromic behaviour

Double-bridged viologen **1a** was prepared by refluxing 4,4′-bipyridine and 1,2-bis(bromomethyl)benzene in water.[3] Viologen **1b** was obtained by anion exchange of **1a** with $HClO_4$ in water. The satisfactory elemental analysis data demonstrates that all of four Br^- of **1a** were replaced by ClO_4^-.

Viologens **1a** and **1b** can be well dispersed in PVP [poly(1-vinyl-2-pyrrolidone)] and in a mixture of PVP and MMA–HEMA (methyl methacrylate and hydroxyethylmethacrylate) copolymer to afford colourless or pale yellow coatings or films which are photochromic. The results shown in Fig. 1 indicate that double-bridged viologen **1b** in a polar polymer film undergoes two stages of colour development: first, **1b** is reduced to mono radical cation **1b′** with λ_{max} at 628 nm and the film becomes green; then mono radical cation **1b′** is further reduced to double radical cation **1b″** with λ_{max} at 536 nm and the film becomes violet. Upon standing in indoor lighting, the film exhibited a stable green colour with λ_{max} at 628 nm.

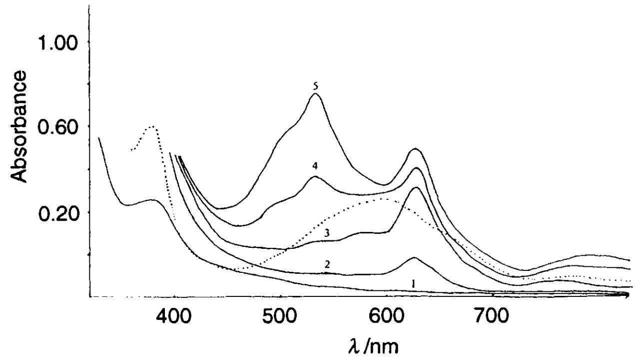
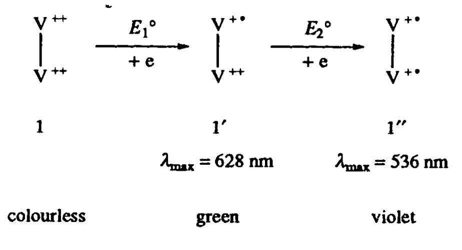


Fig. 1 Photochromism of **1b** in polar polymer film (——); visible absorption spectrum of reduced benzyl viologen (···): (1) before irradiation; (2) indoor sunlight; (3) UV light, 0.5 min; (4) UV light, 1.0 min; (5) UV light, 1.5 min



(1)

Compared with the radical cation of benzyl viologen with λ_{max} at 602 nm,[4] the maximum absorption of **1b′** has an obvious red shift which is characteristic of further delocalization of the radical's electron. This may be best explained by an intramolecular cross-ring interaction between the dipyridinium radical cation and unreduced dipyridinium within **1b′**. As may be deduced from a molecular model of **1**, two bipyridinium moieties are parallel to each other and the distance between them is only 2.9 Å.[5] It makes this special cross-ring interaction possible, thereby greatly stabilizing the mono radical cation **1b′**. As a result, its first reduction occurs more easily than its second reduction, *i.e.*, $E_1° > E_2°$.[5] This is also the reason that the film becomes green even under indoor sunlight, but that benzyl

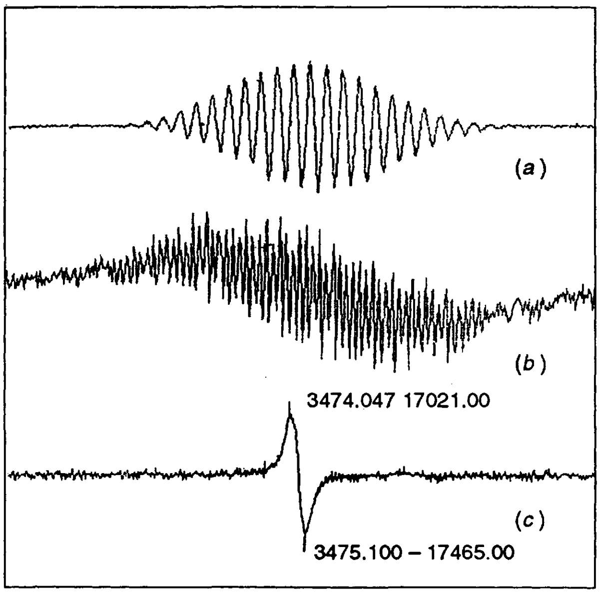
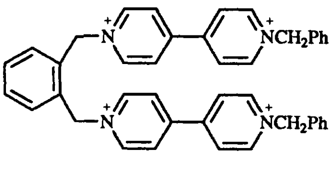


Fig. 2 EPR single given by benzy viologen bromide (*a*, $Q = 33.548$ Gs) and **1a** in its first (*b*, $Q = 25.936$ Gs) and second (*c*, $Q = 2.127$ Gs) reduction stages in aq. sodium sulfite

viologen does not. Under further UV irradiation, the film of **1b** becomes violet ($\lambda_{max} = 536$ nm) while benzyl viologen remains blue ($\lambda_{max} = 602$ nm) under the same conditions. This suggests an intramolecular bipyridinium radical pimer (π-associated dimer) formed in the second photochromic stage of **1b**, just like the pimer produced from **1a** reduced by sodium dithionite in aqueous solution.[5] We discovered that the aqueous solution of **1a** also underwent the same colour development stages as the film of **1b** under UV light when **1a** was reduced by Na_2SO_3. Both of these two stages give the EPR signals shown in Fig. 2, which is characteristic of a free radical. In the first reduction stage the EPR spectrum of mono radical cation [Fig. 2(*b*)] has more fine structure than that of benzylviologen [Fig. 2(*a*)]. This indicates that there are more H atoms anticipating splitting in **1a′**, which is a reasonable result of intramolecular cross-ring interaction between a dipyridinium radical cation and unreduced dipyridinium within **1a′**. The experimental result in the second reduction stage is significantly different from that described in ref. 6 where it was considered that such associated radical cations should give no EPR signal. In our experiment the EPR signal of **1a″** was obtained with a large spectral line width and no fine structure [Fig. 2(*c*)]. This may be attributed to the pimerization of two radicals in **1a″** which makes radicals more localized. This is also the reason for the blue shift of λ_{max} in UV–VIS spectra of **1a″**.

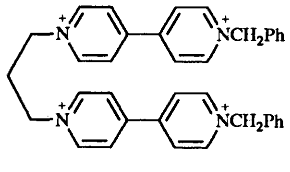
Model compounds **2**, **3** and **4** were prepared and their photochromic behaviour in polar polymer matrixes were also studied. Double-bridged viologen **2** is a new compound and was synthesized by refluxing 1,1″-propane-1,3-diylbis(4,4′-bipyridin-1-ium) dibromide and 1,2-bis(bromomethyl)benzene in water. Because of strong intramolecular strain in **2**, the formation of the cyclic molecule is very difficult and the yield is only 10%. Compounds **3a** and **4a** were prepared by treating 1,2-bis(bromomethyl)benzene and 1,3-dibromopropane respectively, with 1-benzyl-4-(4′-pyridyl)pyridinium bromide in acetonitrile. Compared to the synthetic route in ref. 5, our route is relatively simple and with high yields. Compounds **3a** and **4a** were anion exchanged with $HClO_4$ in water to produce **3b** and **4b** quantitatively.

The photochromism data of double-bridged viologens **1** and **2** as well as bisviologens **3** and **4** in polar polymer matrix are listed in Table 1. It can be observed from this Table that the double-bridged viologen **1a** and **2** in PVP film is green ($\lambda_{max} = 628$ nm) under indoor sunlight and becomes violet ($\lambda_{max} = 536$ nm) after irradiation by UV light, just as for compound **1b**. Although bisviologens **3** and **4** cannot change their colour whether in PVP or in a mixture of MMA–HEMA copolymer and PVP under indoor light, they can develop colour under UV light with two maximum absorption peaks at 602 and 536 nm appearing simultaneously, which are characteristic of mono radical cations of viologens.[5] After further irradiation by UV light, the ratio of the two absorbances A_{536}/A_{602} exhibit no apparent changes. Therefore, no obvious two colour development stages can be observed. The fact that the λ_{max} value of the bisviologen's mono radical cations are still located at 602 nm illustrates that there is no special intramolecular interaction between mono radical cations and unreduced bipyridinium cation in bisviologen **3** and **4**, but the inter- or intra-molecular association of two radicals can occur with $\lambda_{max} = 536$ nm.



$4X^-$

3a; X = Br
3b; X = ClO_4

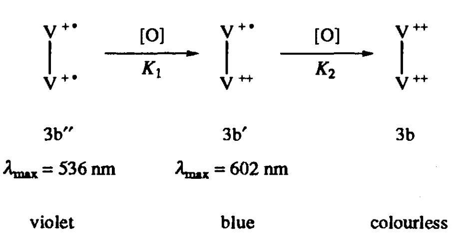


$4X^-$

4a; X = Br
4b; X = ClO_4

Fading behaviour of bisviologens and double-bridged viologens in polar polymer films induced by oxidation

A UV–VIS spectrometer was used to record the fading process of bisviologen **3b** and double-bridged viologen **1b** in films of the mixture of PVP and MMA–HEMA copolymer in the dark at room temperature after irradiation by UV light. The results are shown in Fig. 3 and Fig. 4. The fading of bisviologen **3b** in polymer film is achieved through the following two consecutive oxidation reactions of cation radicals (2).



$$\begin{matrix} V^{+\bullet} \\ | \\ V^{+\bullet} \end{matrix} \xrightarrow[K_1]{[O]} \begin{matrix} V^{+\bullet} \\ | \\ V^{++} \end{matrix} \xrightarrow[K_2]{[O]} \begin{matrix} V^{++} \\ | \\ V^{++} \end{matrix} \qquad (2)$$

3b″ 3b′ 3b

$\lambda_{max} = 536$ nm $\lambda_{max} = 602$ nm

violet blue colourless

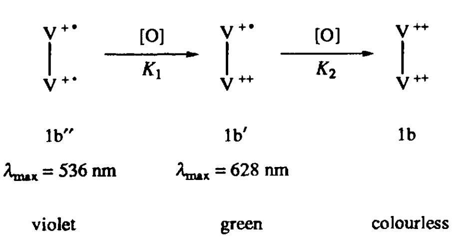
It can be recognized from Fig. 3 that the falling of the absorbance at $\lambda_{max} = 536$ nm which belongs to **3b″** is a first order dynamic process (curve 1). Its apparent fading rate constant obtained from the slope of curve 1 is 1.71×10^{-4} s^{-1}. The shape of curve 2 conforms to the dynamic characteristic of two consecutive reactions with $k_2 > k_1$. This can be well explained by the fact that the associated radical cations **3b″** is more stable than unassociated **3b′**.

The fading process of double-bridged viologen **1b** in polymer film is very different from that of **3b**. It exhibits two distinct colour stages: from violet to green, finally to its original colourless or pale yellow. The fading process of its two absorption bands at 536 and 628 nm described in Fig. 4 are also

Table 1 Photochromic behaviour of double-bridged viologens (**1**, **2**) and bisviologens (**3**, **4**) in polar polymer films

			Under *indoor* indoor light		Under UV irradiation[b]					
					30 s			120 s		
	Polymer matrix film[a]	λ_{max}/nm	A	Colour	A	A_{536}/A_{626}	Colour	A	A_{536}/A_{626}	Colour
1a	PVP	628	0.204	Green	0.265	0.88	Blue–Violet	0.332	2.39	Violet
		536	—		0.234			0.790		
1b	P(MMA–HEMA)–PVP	628	0.200	Green	0.210	0.88	Blue–Violet	0.283	1.50	Violet
		536	—		0.185			0.425		
2	PVP	628	0.235	Green	0.450	0.89	Blue–Violet	0.550	2.22	Violet
		536	—		0.401			1.220		
3a	PVP	602	—	Colourless	0.185	1.92[c]	Violet	0.370	2.54[c]	Red
		536	—		0.355			0.940		
3b	P(MMA–HEMA)–PVP	602	—	Colourless	0.080	1.43[c]	Red	0.235	1.62[c]	Pale-violet
		536	—		0.114			0.380		
4a	PVP	602	—	Colourless	0.330	1.00[c]	Pale-violet	0.646	0.97[c]	Pale-violet
		536	—		0.330			0.624		
4b	P(MMA–HEMA)–PVP	602	—	Colourless	0.073	0.63[c]	Pale-violet	0.239	0.86[c]	Pale-violet
		536	—		0.043			0.206		

[a] PVP = polyvinylpyrrolidone, P(MMA–HEMA)–PVP means a mixture of PVP and copolymer of methyl methacrylate and hydroxyethyl methacrylate (weight ratio 1 : 9). Thickness of film: 25–30 μm. [b] Light source was a 10 W high pressure mercury lamp and the light strength measured at the sample was 2500 μW cm^{-2}. [c] Value of A_{536}/A_{602}.



(3)

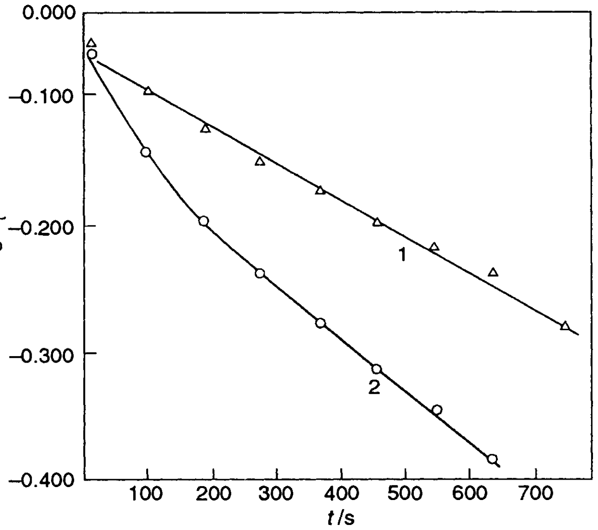


Fig. 3 Fading of bisviologen **3b** in polymer matrix in air: (○) 602; (△) 536 nm

different from each other. Although the fading of a double-bridged viologen is the result of two consecutive oxidation reactions in reaction (3) the decline of the absorbance at λ_{max} = 536 nm (curve 2) is much faster than that of the absorbance at λ_{max} = 628 nm (curve 1). The apparent fading rate constant of **1b**″ (k_1) obtained from the slope of curve 2 is 5.76 × 10^{-4} s^{-1}. However, curve 1 hardly decreases initially. Only after a large part of **1b**″ has disappeared, does curve 1 begin to fall obviously. In this section A_{628} is much larger than A_{536} and the polymer film becomes green. The apparent fading rate constant of mono radical cation **1b**′ (k_2) which can be obtained from the slope of the final section of curve 1 is 2.97 × 10^{-4} s^{-1} and it is evidently smaller than k_1. The decrease of k_2 is a direct result of stabilization of dipyridinium radical cation in **1b**′ by the intramolecular cross-ring interaction of another unreduced dipyridinium cation. The decrease of apparent fading constant k_2 is also the reason for double-bridged viologen **1b** having two distinctive fading stages.

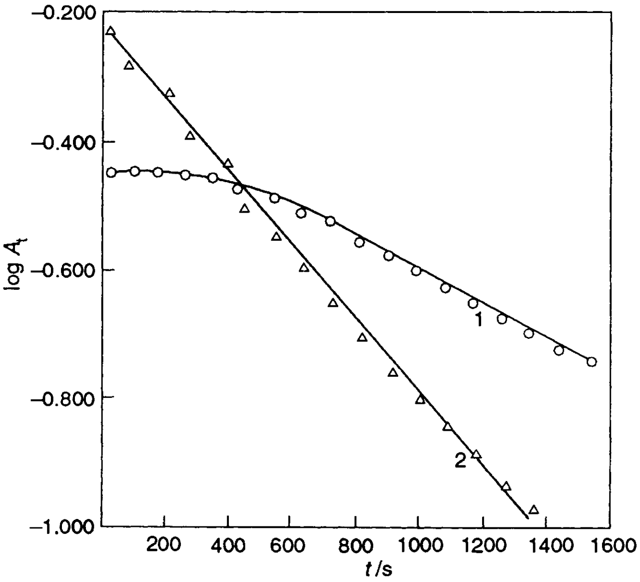


Fig. 4 Fading of double-bridged viologen **1b** in polymer matrix in air: (○) 628; (△) 536 nm

Photofatigue of double-bridged viologen in polar polymer film

In order to measure and compare photofatigue performance of a double-bridged viologen in polymer film, **1b**, **3b**, **4b** and benzylviologen perchlorate **5** in the polymer film which consists of PVP and HEMA–MMA copolymer underwent several cycles of UV irradiation for 2 min and fading in the dark in air. The absorbance at monitored wavenumbers was recorded immediately after irradiation. Their photofatigue performance can be determined by comparing the ratio of absorbance A_n/A_1. From Table 2, although degrees of photofatigue of double-bridged viologen **1b** as well as model compounds bisviologen **3b** and **4b** for their two absorption bands are different, all of them are more durable than benzyl viologen **5**. As discussed above, the mono radical cation of **1b** (λ_{max} = 628 nm) can be stablilized by the special intramolecular cross-ring interaction of another

Table 2 Photofatigue behaviour of various viologens

Viologen	λ/nm	A_n/A_1 $n = 1$	2	3	4	5	6	7	8	9	10
1b	628	1.00	0.982	0.966	0.938	0.928	0.895	0.844	0.828	0.770	0.717
	536	1.00	0.966	0.919	0.795	0.674	0.635	0.578	0.525	0.493	0.453
3b	602	1.00	0.930	0.867	0.773	0.748	0.696	0.612	0.605	0.550	0.506
	540	1.00	0.874	0.762	0.678	0.641	0.589	0.523	0.432	0.421	0.376
4b	604	1.00	0.899	0.835	0.744	0.700	0.656	0.579	0.559	0.526	0.500
	544	1.00	0.815	0.670	0.567	0.528	0.509	0.466	—	—	—
5	602	1.00	0.819	0.617	0.555	0.431	0.399	—	—	0.380	0.320

unreduced dipyridinium cation and the bis radical cation of **1b** (λ_{max} = 536 nm) can be stabilized by the formation of intramolecular radical pimer. The radical cation of **3b** and **4b** can also be stabilized by association of radicals. These may be the main reasons why they, especially double-bridged viologen **1b**, have better photofatigue resistance than benzylviologen **5**.

Experimental

UV–VIS, ^{1}H NMR and EPR spectra were recorded on Hitachi 340, JNM-FX100 and Bruker ESR-300 spectrometers, respectively. Elemental analyses were measured by the elemental analyses division of the Institute of Chemistry, Academia Sinica.

4,9(1,2)-Dibenzena-1,6(1,4),2,7(4,1)-tetrapyridinacyclodecaphanetetraium tetrakisperchlorate 1b

Following the method described in ref. 4, a suspension of 1,2-bis(bromomethyl)benzene (9.4 g, 35.5 mmol) in an acetonitrile solution of 4,4′-bipyridine (4 g, 25.6 mmol; 132 cm^3) was stirred at reflux temperature for 10 h. The resulting yellow precipitate **1a** (6.2 g) was recrystallized twice (water) to afford a yellow powder in a 58% yield. Elemental and ^{1}H NMR analyses were satisfactory. Compound **1b** was prepared by adding aq. $HClO_4$ (20%; 20 cm^3) to aq. **1a** (1 g; 35 cm^3). A white deposit was separated in a 90% yield (Calc. for $C_{36}H_{32}Cl_4N_4O_{16}$: C, 47.16; H, 3.49; N, 6.11. Found: C, 47.7; H, 3.6; N, 6.2%); mp > 360 °C (decomp. in air).

4(1,2)-Benzena-1,6(1,4),2,7(4,1)-tetrapyridinacyclodecaphanetetraium tetrakisbromide 2

1,1″-Propane-1,3-diylbis(4,4′-bipyridin-1-ium) dibromide (1.5 g, 3.0 mmol) [synthesized by refluxing 1,3-dibromopropane (2.0 g, 9.9 mmol) and excess 4,4′-bipyridine (4.6 g, 30 mmol) in acetonitrile for 11 h] and 1,2-bis(bromomethyl)benzene (1 equiv.) were refluxed in water for 6 h. After removing some of the solvent, some needle crystals grew in two days in a refrigerator (5 °C); these were washed with acetone. Compound **2** was obtained in 9% yield; δ_H(D_2O, ref. dioxane, 3.27 (m, 2 H, $-CH_2-CH_2-CH_2-$), 5.27 (m, 4 H, $-CH_2-CH_2-CH_2-$), 6.26 (d, 2 H, J = 18 Hz, Ar–CH_2–$N^+ \leqslant$), 6.44 (d, 2 H, J = 18 Hz, phenyl–CH_2–$N^+ \leqslant$), 8.99 (s, 4 H, CoH$_4$), 8.53 (m, 8 H, β-Py-H) and 9.27 (m, 8 H, α-Py–H) (Calc. for $C_{31}H_{30}Br_4N_4 \cdot 5H_2O$: C, 42.88; H, 4.61; N, 6.45. Found: C, 42.6; H, 4.4; N, 6.3%).

1,11(1),6(1,2)-Tribenzena-3,8(1,4),4,9(4,1)-tetrapyridinaundecaphanetetraium tetrakisperchlorate 3b

1,2-Bis(bromomethyl)benzene (0.32 g, 1.2 mmol) and 1-benzyl-4-(4′-pyridyl)pyridinium bromide (1.0 g, 3.1 mmol) [which was prepared by refluxing benzyl bromide (3.0 g, 17.5 mmol) and 4,4′-bipyridine (4.1 g, 26.3 mmol) in ethyl acetate (30 cm^3) for 6 h] were refluxed in dry acetonitrile for 18 h, the precipitated **3a** (1.1 g) was separated in 80% yield. Bisviologen **3b** was prepared from aq. **3a** (0.9 g, 0.98 mmol), which was added to excess aq. $HClO_4$ (3.1 g, 35%) at room temperature. The orange powder was separated and washed thoroughly (water) and dried (95% yield) (Calc. for $C_{42}H_{38}Cl_4N_4O_{16} \cdot 2H_2O$. C, 48.85; N, 5.43. Found: C, 48.7; H, 3.85; N, 5.35%).

1,11-Dibenzena-3,8(1,4),4,9(4,1)-tetrapyridinaundecaphanetetraium tetrakisperchlorate 4b

A mixture of 1,3-dibromopropane (0.2 g, 1.1 mmol) and excess 1-benzyl-4-(4′-pyridyl)pyridinium bromide (1.1 g, 3.3 mmol) was refluxed in dried acetonitrile for 20 h. The product **4a** (0.45 g) was obtained in 48% yield. Compound **4b** was prepared by adding aq. **4a** (0.5 g, 35 cm^3) to excess aq. $HClO_4$ (*ca.* 35%) at room temperature. The resulting orange powder was filtered, washed (water) and dried (92% yield) (Calc. for $C_{37}H_{36}Cl_4N_4O_{16} \cdot 3/2H_2O$: C, 46.21; H, 4.06; N, 5.83. Found: C, 46.2; H, 3.8; N, 5.8%).

1,1′-Dibenzyl-4,4′-bipyridinium bisperchlorate

Compound 5 was prepared following the method described in ref. 7; its elemental analysis was satisfactory.

MMA–HEMA copolymer

MMA (70 g, 0.7 mol) was treated with HEMA (30 g, 0.23 mol) for 4 h at 80 °C in ethyl acetate–toluene (256 g, 20 : 1, v/v) with benzoyl peroxide as the initiator. The resulting solution contained (39% copolymer and its M_n measured by vapour phase osmometer was 1470.

Preparation of films containing various viologens

The polymer matrix films were prepared by dissolving viologen, PVP and a solution of MMA–HEMA copolymer in DMF, the solvent was then evaporated on a $SiCl_4$-treated glass surface at 40 °C. The films contained 0.1 mmol viologen in 1 g dried polymer mixture with 10% PVP by weight. The thickness of films was controlled by the solution concentration and casting area. The films were maintained at 20 °C, 70% relative humidity before measurement.

UV–VIS spectra

The irradiation was carried out with a 10 W high pressure Hg lamp and the light intensity upon samples was *ca.* 2500 μW cm^{-2}. The UV–VIS spectra were recorded 10s after irradiation stopped.

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Paper 5/04128G
Received 26*th June* 1995
Accepted 1*st September* 1995