Preparation and Photochemical Properties of Water-soluble Polymers with Pendant Tris(2,2′-bipyridyl)ruthenium(II) Groups. N-Ethylated Copolymers of Vinylpyridine and *cis*-Bis(2,2′-bipyridyl)(4-methyl-4′-vinyl-2,2′-bipyridyl)-ruthenium(II)

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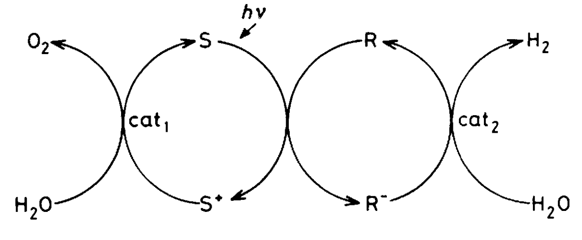
Copolymers (**1**) with pendant $[Ru(bipy)_3]^{2+}$-like centres (bipy = 2,2′-bipyridyl) were prepared by copolymerisation of 4-vinylpyridine (vp) and $[Ru(bipy)_2(mvbipy)]^{2+}$ (mvbipy = 4-methyl-4′-vinyl-2,2′-bipyridyl). By variation of the monomer feed ratios, copolymers with vp:Ru of 2:1, 11:1, and 66:1 were prepared. Quaternisation of the vinylpyridine groups of (**1**) with ethyl bromide yields water-soluble copolymers (**2**). Copolymers (**1**) and (**2**) were characterised by ^{1}H n.m.r., u.v.–visible, and atomic absorption spectroscopy. Fluorescence spectra and the lifetimes of copolymers (**2**) in aqueous solution and the quenching of the excited states by oxygen and methylviologen (1,1′-dimethyl-4,4′-bipyridinium) have been measured. These data indicate that the excited-state properties are only slightly affected by polymer-binding whereas the accessibility of the excited state to quenchers is substantially reduced. Rates for photoreduction of methylviologen in the presence of $N(CH_2CH_2OH)_3$ sensitised by copolymers (**2**) have been compared to that sensitised by $[Ru(bipy)_3]^{2+}$.

The photodissociation of water, based on a cyclic process such as that shown in Scheme 1, has been extensively discussed as a route to solar energy conversion and storage.[1–3] The photosensitised reduction of 4,4′-bipyridinium salts (viologens) by $[Ru(bipy)_3]^{2+}$-like complexes (bipy = 2,2′-bipyridyl) has been explored intensively as a key step in this process.[4,5] Polymer-bound complexes seem particularly appropriate for the fabrication of a device to utilise these photoreactions for solar energy conversion,[6–8] as by controlled synthesis it should be possible both to control the chemical reactivity of the reacting species and to prepare robust materials which can be incorporated into thin films, resins, or membranes required for the separate production of hydrogen and oxygen.[9]

Our initial report on ruthenium bipyridyl complexes covalently bound to a polymer indicated that a range of such materials could be prepared and that their chemical reactivity was affected by the polymer and the loading of the complex on the polymer chain.[10] The complexes prepared in that study were of the type $[Ru(bipy)_2(pvp)Cl]^+$ and $[Ru(bipy)_2(pvp)_2]^{2+}$ [pvp = poly(4-vinylpyridine)] and were found to undergo destructive photoanation particularly in non-aqueous solution.[11,12] Photo-induced electron transfer from polymer-bound ruthenium complexes to viologens was first demonstrated by Kaneko *et al.*[13,14] using bipyridylated polystyrene and since then such photo-induced electron-transfer reactions have been studied with ruthenium bipyridyl complexes bound to a number of functionalised polymers.[7,8,15,16] Of special interest are photostable polymers containing pendant 2,2′-bipyridyl, as the co-ordination sphere of these ruthenium complexes is then identical to that of the parent complex $[Ru(bipy)_3]^{2+}$. It has been found, however, that linking of the bipyridyl to the polymer chain must not be through the 6 position of the bipyridyl as the resulting steric hindrance has a very marked and deleterious effect on the photochemical and photophysical properties of the ruthenium centre.[17,18] Polymers derived from $[Ru(bipy)_2(mvbipy)]SO_4$ (mvbipy = 4-methyl-4′-vinyl-2,2′-bipyridyl) seem particularly useful and since the synthesis of the monomeric ligand was first reported[19] there have been a very substantial number of publications dealing with polymers of this compound.[20–22]



Scheme 1. Two-component system for the photoreduction of water by visible light; S = sensitiser; R = relay; cat = catalyst

The efficiency of the scheme for the photo-dissociation of water such as that shown in Scheme 1 depends on the quantum yield for electron-transfer products and the effectiveness of the reaction of these transient species with the catalysts. For the much discussed system $[Ru(bipy)_3]^{2+}$–methylviologen (1,1′-dimethyl-4,4′-bipyridinium, $dmbipy^{2+}$) the quantum yield of free $dmbipy^{\cdot+}$ is limited by the low yield of cage escape (*ca.* 25%)[23] because of rapid reverse electron transfer. Binding the $[Ru(bipy)_3]^{2+}$ group to the charged polymer might be expected to affect the rates of these reactions. We have therefore recently prepared a series of water-soluble copolymers of $[Ru(bipy)_2(mvbipy)]^{2+}$ in order to assess the effect of polymer binding on the yield of electron transfer.[22,24,25] In this paper we describe the preparation of a copolymer with a positively charged backbone where an enhanced yield of cage escape might be possible due to electrostatic repulsion of the $dmbipy^{\cdot+}$ away from the bound $[Ru(bipy)_3]^{3+}$-like centre.

Results and Discussion

Preparation of Poly{*4-vinylpyridine*–co-$[Ru(bipy)_2(mvbipy)]^{2+}$} (**1**) *and their N-Ethylated Derivatives* (**2**).—Copolymers (**1**) were prepared by azobisisobutyronitrile (aibn)-initiated polymerisation of $[Ru(bipy)_2(mvbipy)]SO_4$[19] and 4-vinylpyri-

Table 1. Reaction feed ratios and analyses of copolymers (**1a**)—(**1c**) of 4-vinylpyridine and $[Ru(bipy)_2(mvbipy)]^{2+}$ and their ethylated derivatives (**2a**)—(**2c**)

Copolymer	vp:Ru Reaction feed ratio	Analyses[a] ^1H n.m.r.	visible	a.a.	Copolymer	Percentage quaternisation[b]
(**1a**)	2.03	1.8	1.9	1.7	(**2a**)	88
(**1b**)	9.9	10.8	11.2	11.5	(**2b**)	90
(**1c**)	99.7	—	—	66	(**2c**)	92

[a] vp:Ru molar ratio (x) determined prior to quaternisation. [b] Estimated by ^1H n.m.r. and u.v. spectroscopy.

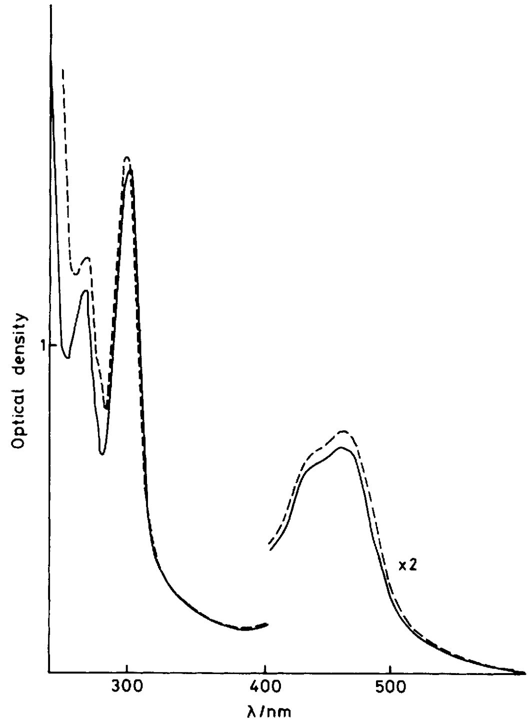


Figure 1. U.v.–visible absorption spectra of the '11:1' copolymers (**1b**) (——) and (**2b**) (– – – –) in aerobic aqueous solution at pH 8.9 (0.05 mol dm^{-3} borax buffer)

dine (vp). The amount of the ruthenium complex on the polymer chain was controlled by using different reaction feed ratios of the two polymerisable reactants $[Ru(bipy)_2(mvbipy)]SO_4$ and vp (Table 1). The samples were purified by repeated precipitation from dichloromethane with n-hexane and were isolated as orange solids. The u.v.–visible spectra of copolymers (**1**) in aqueous buffer (pH 8.9) show a band at 456 nm but none at about 340 nm (Figure 1), which would have been expected had a pvp-bound complex been formed.[11] This indicates that migration of the $[Ru(bipy)_2]^{2+}$ group from mvbipy to pvp does not occur during copolymerisation. Copolymers (**1a**) and (**1b**) were found to be sparingly soluble in water while (**1c**) was totally insoluble. However upon protonation of the pyridine functions at pH < 3 all samples dissolved in aqueous solution.[26]

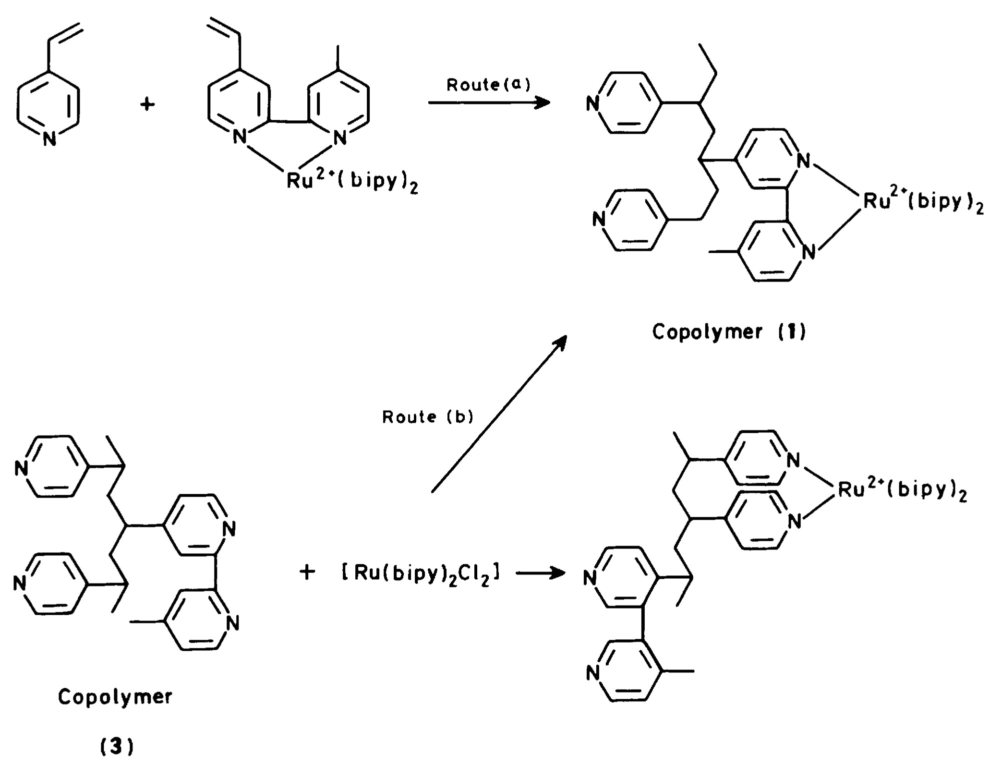
The pvp-based metallopolymers and the pvp homopolymer were quaternised by treatment with excess of bromoethane in sulpholane (tetrahydrothiophene 1,1-dioxide) and the water-soluble products (**2**) were isolated as hygroscopic solids after repeated dissolution in methanol and precipitation with diethyl ether.

An alternative route to copolymers (**1**) would appear to be the reaction of a vp–mvbipy copolymer with $[Ru(bipy)_2Cl_2]$[11] [route (b) of Scheme 2]. The aibn–radical-initiated polymerisation of mvbipy and vp yielded a polymer (**3**) containing both monodentate vp and bidentate (mvbipy) co-ordination sites. Copolymer (**3**) was allowed to react with $[Ru(bipy)_2Cl_2]$ in water–methanol (40:60 v/v) at 60 °C and the reaction course monitored spectrophotometrically. Before heating, the absorption spectra showed two bands at 351 and 503 nm (optical density ratio = 0.8), expected for the $[Ru(bipy)_2(H_2O)Cl]^+$ complex. Upon reaction these bands shift initially to 340 and 490 nm but after heating for 1 d the main bands appear at 343 and 456 nm (optical density ratio = 1.5), the characteristic absorptions of $[Ru(bipy)_2]^{2+}$ bound to two pyridine ligands,[10–12] suggesting that the polymer-bound $[Ru(bipy)_2(pvp)_2]^{2+}$ complex is the predominant product. Polymer-bound centres of the $[Ru(bipy)_3]^{2+}$ type would not be expected to show the strong band at 343 nm. These results therefore illustrate that this method is unsatisfactory for the preparation of poly{vp–co-$[Ru(bipy)_2(mvbipy)]^{2+}$}.

Characterisation of Copolymers (**1**) *and* (**2**).—The quantity of ruthenium in the copolymers (**1a**)—(**1c**) was assayed by atomic absorption, and the concentration of the '$[Ru(bipy)_3]^{2+}$' centre on the polymer backbone and the extent of quaternisation of the pendant pyridyl groups were estimated by ^1H n.m.r. and u.v.–visible spectroscopy.

^1H *N.m.r.* Spectra of the homopolymers (pvp and its N-ethylated derivative) and metallopolymers were obtained in a variety of solvents. Resonances from the chain-end isobutyronitrile groups derived from the aibn initiator were not observed, reflecting the long-chain nature of the polymer. The spectra of the '66:1' copolymer (**1c**) were very similar to the spectra of the homopolymer (pvp), the signals due to the bipyridyl protons being too weak to be detected. For the '2:1' and the '11:1' polymers (**1a**) and (**1b**) the resonances due to the bipyridyl protons were observed in addition to those of the pvp backbone (Figure 2): as expected these signals are considerably broadened relative to those of the complex $[Ru(bipy)_3]^{2+}$. The resonances due to the pvp occur in two distinct regions; at high field a broad resonance arising from the aliphatic protons (H_α,H_β) of the backbone, and at low field two broad resonances due to the aromatic protons of the pendant pyridyl unit (H_AH_B). The resonances originating from the polymer-bound $[Ru(bipy)_3]^{2+}$ unit (22 protons) also occur at low field and overlap with the signals arising from the pvp backbone. The resonances resulting from the aromatic protons H_B ($2x$) of the pvp unit occur slightly upfield of the aromatic protons of the bipyridyl ligands and H_A of the pvp system ($22 + 2x$ protons). Thus from integration an estimate of the loading x may be obtained for polymers (**1a**) and (**1b**).

The ^1H n.m.r. spectra of the 'quaternised polymers' (**2a**)—(**2c**) were recorded in D_2O, CD_3OD, or CF_3CO_2D solution. It was observed that quaternisation causes the aromatic resonances to be shifted downfield. In CF_3CO_2D solutions resonances arising from the quaternary methylene protons, centred at 4.7 p.p.m., are clearly defined and provide a good method of determining the degree of quaternisation of the sample (Table 1).



Scheme 2. Preparation of copolymers (**1a**)—(**1c**)

Table 2. Emission properties of metallopolymer complexes (**2a**)—(**2c**) in aqueous solution

Complex	$\lambda_{max.}$[a]/nm	Relative intensity[b]	τ/ns *b*	 *c*
$[Ru(bipy)_3]^{2+}$	612	1	600[d,e]	410[d,e]
(**2a**)	615	0.84	490[e]	430[e]
(**2b**)	617	0.95	565[d,e]	420[d,e]
(**2c**)	618	0.95	560[d,e]	420[d,e]

[a] Uncorrected for response of R928 photomultiplier. [b] Anaerobic aqueous solution. [c] Air-saturated aqueous solution. [d,e] Lifetimes were obtained by time-correlated single-photon counting (±15%) and single-shot dye-laser excitation ($\lambda_{max.}$ = 460 nm)(±5%), respectively, and the results found to be consistent.

U.v.–visible spectra. In the region 300—500 nm the polymeric $[Ru(bipy)_3]^{2+}$ complexes (**1**) and (**2**) exhibit very similar absorption spectra to $[Ru(bipy)_3]^{2+}$ the metal-to-ligand charge-transfer (m.l.c.t.) band {$\lambda_{max.}$ at 452 nm for $[Ru(bipy)_3]^{2+}$ in water} undergoing a slight red shift and broadening. The ruthenium content of the copolymers may be determined by quantitative analysis of the visible spectrum if it is assumed that the absorption coefficient for the polymer-bound ruthenium centre is the same as that for $[Ru(bipy)_3]^{2+}$. The values so calculated are given in Table 1 and are seen to be in good agreement with those obtained from ^1H n.m.r. and atomic absorption spectroscopy.

In the u.v. spectral region (200—300 nm) bands due to the pvp and the ligand-localised band of $[Ru(bipy)_2(mvbipy)]^{2+}$ centre may be observed. For the quaternised polymers (**2a**)—(**2c**) it was found that the spectrum was essentially the same at pH 2 or 9. At pH 2 any unquaternised pvp should protonate (pK_a = 3.25 at I = 0, 3.95 at I = 0.05 mol dm^{-3}).[26] At 225 nm, Hpvp$^+$ absorbs more strongly than pvp and therefore it is expected that the absorption spectra of a partially quaternised sample at pH 2 and at pH 9 should be different.[27,28] The absence of any such difference confirms that the samples are substantially quaternised (>85%) (Table 1).

Photochemical and Photophysical Properties.—Emission from the ethylated copolymers (**2a**)—(**2c**) was observed following excitation (λ = 455 nm) into the m.l.c.t. absorption band of their $[Ru(bipy)_3]^{2+}$-like centres. The spectra recorded in air-saturated solutions are very similar to that of $[Ru(bipy)_3]^{2+}$ but are slightly red shifted and broadened (Table 2). It may also be seen that increasing the loading of the ruthenium centre on the polymer backbone causes a decrease in quantum yield.

In deaerated solutions the fluorescence decays of copolymers (**2a**)—(**2c**) follow a single exponential (Figure 3). The luminescence lifetimes of (**2b**) and (**2c**) are slightly shorter than that of $[Ru(bipy)_3]^{2+}$ under the same conditions whereas that of (**2a**), the 2:1 copolymer, is significantly less (Table 2). This may indicate that self-quenching of the excited state is important when the reaction centres are in close proximity. In air-equilibrated solutions the lifetimes of the complexes (**2**) are slightly longer than that of $[Ru(bipy)_3]^{2+}$ (Table 2), indicating that the rate constants for the quenching by O_2 of the $[Ru(bipy)_3]^{2+}$-like centre are less for these polymers than for $[Ru(bipy)_3]^{2+}$ (Table 3). This is presumably a result of lower accessibility to the excited state due to polymer coiling.

Quenching of the emission by methylviologen (dmbipy^{2+}). The quenching of the $[Ru(bipy)_3]^{2+}$-like luminescence by dmbipy^{2+} was examined in air-saturated solutions at 25 °C. Stern–Volmer plots of the relative fluorescence intensity in the absence (I_0) and in the presence (I) of quencher were found to be non-linear (Figure 4) at the higher concentrations of 1,1′-dimethyl-4,4′-bipyridinium dichloride employed. This non-linearity may be attributed in part to the increase in the ionic strength of the

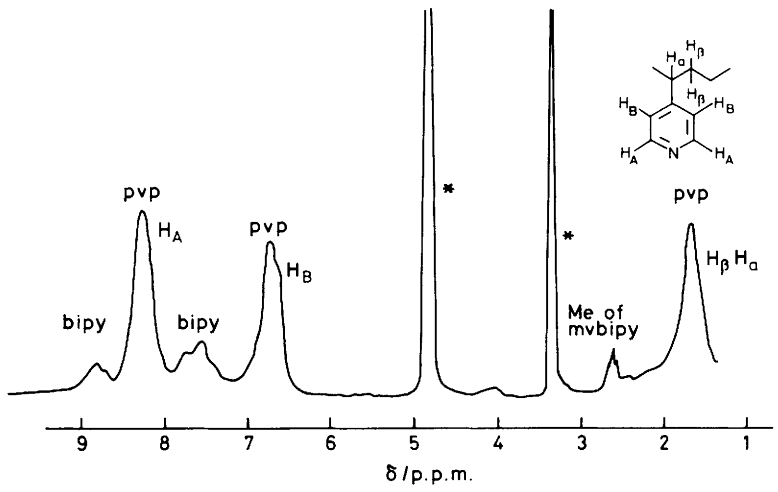


Figure 2. 80 MHz ^1H N.m.r. spectrum of copolymer (**1b**) in CD_3OD. Solvent peaks indicated by asterisks

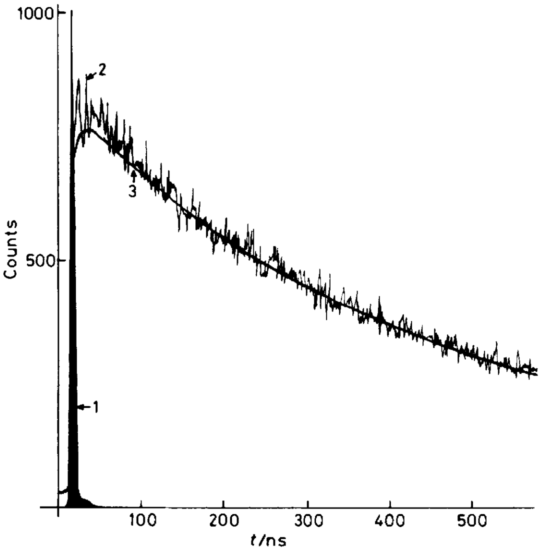


Figure 3. Fluorescence decay of copolymer (**2c**) in anaerobic aqueous solution: 1, excitation profile; 2, decay profile; and 3, best fit for single exponential decay

Table 3. Rate constants for quenching of the $[Ru(bipy)_3]^{2+}$-like excited state of copolymers (**2a**)—(**2c**) by oxygen (O_2) and methylviologen(dmbipy^{2+})[a]

	For O_2	For dmbipy^{2+}	
Complex	$10^{-8}\,k_{q(O_2)}$[b]/ dm^3 mol^{-1} s^{-1}	K_{SV}[c]/ dm^3 mol^{-1}	$10^{-7}\,k_q$/ dm^3 mol^{-1} s^{-1}
$[Ru(bipy)_3]^{2+}$	26 ± 4	182 ± 10	45 ± 5
(**2a**)	9 ± 3	18 ± 1	4.2 ± 0.4
(**2b**)	20 ± 5	22 ± 1	5.2 ± 0.4
(**2c**)	20 ± 5	44 ± 2	10 ± 1

[a] In aqueous air-saturated solution at room temperature. [b] Determined from excited-state lifetimes in degassed and air-saturated solution at 18 °C; $[O_2]$ taken to be 3×10^{-4} mol dm^{-3}. [c] Determined from the initial slope for air-saturated solutions at room temperature (18 ± 2 °C): $k_q = K_{SV}/\tau_{O_2}$.

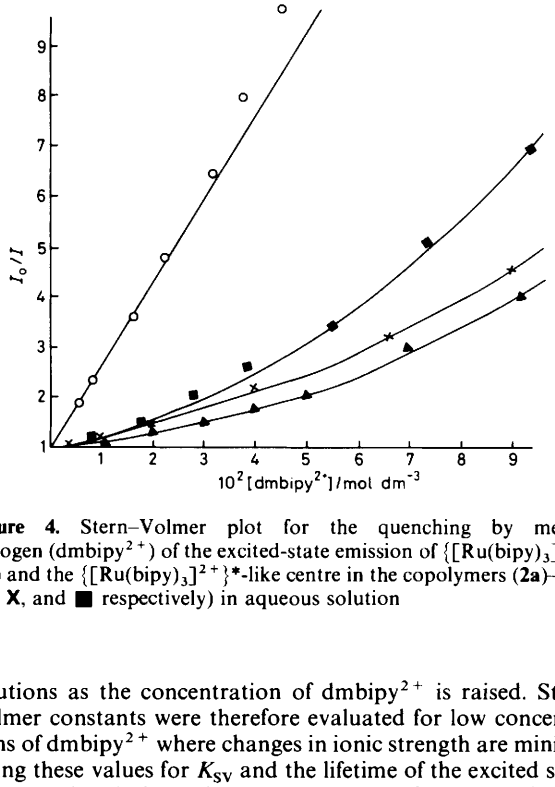


Figure 4. Stern–Volmer plot for the quenching by methylviologen (dmbipy^{2+}) of the excited-state emission of $\{[Ru(bipy)_3]^{2+}\}^*$ (○) and the $\{[Ru(bipy)_3]^{2+}\}^*$-like centre in the copolymers (**2a**)—(**2c**) (▲, X, and ■ respectively) in aqueous solution

solutions as the concentration of dmbipy^{2+} is raised. Stern–Volmer constants were therefore evaluated for low concentrations of dmbipy^{2+} where changes in ionic strength are minimal. Using these values for K_{SV} and the lifetime of the excited states in aerated solution, the rate constants for quenching by dmbipy^{2+} were evaluated (Table 3). Binding $[Ru(bipy)_3]^{2+}$ to the positively charged backbone substantially reduces the rate of quenching by dmbipy^{2+} and comparison with the results of oxygen quenching (Table 3) suggests that the effect is both one of reduced accessibility of the excited state and repulsion between the positively charged backbone and the quencher.

Photosensitised reduction of dmbipy^{2+} *by copolymers* (**2a**)—(**2c**). The efficiency of photo-induced electron transfer to dmbipy^{2+} from the copolymers (**2a**)—(**2c**) was compared to that from $[Ru(bipy)_3]^{2+}$ by monitoring spectrophotometrically the rate of production of the semi-reduced radical dmbipy$^{\cdot +}$ (λ_{max} = 605 nm, ε = 13 700 dm^3 mol^{-1} cm^{-1}) upon visible-light irradiation (λ = 436 nm) of the complexes at pH 8.9 in the presence of dmbipy^{2+} and triethanolamine (2,2′,2″-nitrilotriethanol). The latter was chosen in preference to ethylenediaminetetra-acetate as a sacrificial donor in order to avoid further

$$[\mathrm{Ru(bipy)_3}]^{2+} \xrightarrow{h\nu} \{[\mathrm{Ru(bipy)_3}]^{2+}\}^*$$

$$\begin{tikzcd} \{[\mathrm{Ru(bipy)_3}]^{2+}\}^* + \mathrm{dmbipy}^{2+} \arrow[r, "k_q"] & \{[\mathrm{Ru(bipy)_3}]^{3+}\cdot\mathrm{dmbipy}^{\cdot+}\} \arrow[r, "k_{cs}"] \arrow[d, "k_b"] & [\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{dmbipy}^{\cdot+} \\ & [\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{dmbipy}^{2+} & \end{tikzcd}$$

$$[\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{N(CH_2CH_2OH)_3} \xrightarrow{k_s} [\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{N(CH_2CH_2OH)_3}^{+}$$

Scheme 3. Photoreduction of $[Ru(bipy)_3]^{2+}$ by methylviologen in the presence of a sacrificial donor triethanolamine; $\alpha_{cs} = k_{cs}/(k_{cs} + k_b)$

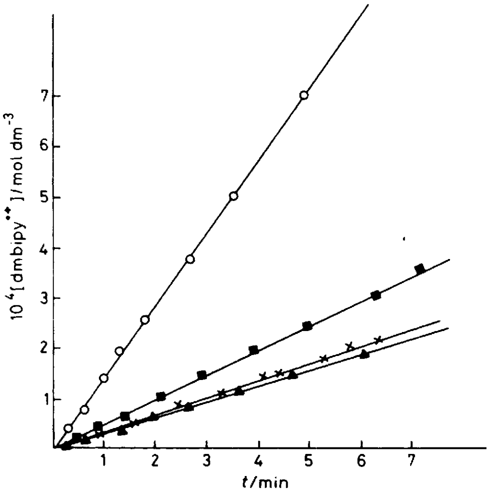


Figure 5. Relative rates of accumulation of the semireduced radical (dmbipy$^{\cdot+}$) upon irradiation of the $[Ru(bipy)_3]^{2+}$-like centre for $[Ru(bipy)_3]^{2+}$ (○) and copolymers (**2a**)—(**2c**) (▲, X, and ■ respectively) in a sacrificial system containing $[N(CH_2CH_2OH)_3]$ = 0.125 mol dm^{-3} and $[dmbipy^{2+}]$ = 0.02 mol dm^{-3} monitored at 605 nm. At least two separate runs with each sample were carried out using the $[Ru(bipy)_3]^{2+}$–dmbipy^{2+} system as an actinometer

Table 4. Rates of reduction of methylviologen sensitised by copolymers (**2a**)—(**2c**) relative to $[Ru(bipy)_3]^{2+}$ at pH 8.9 in the presence of the sacrificial donor triethanolamine

Complex	Relative rate of formation of dmbipy$^{\cdot+}$, $\Phi_{(rel)}$	Relative extent of quenching, $\alpha_{q(rel)}$	Relative cage separation efficiency, $\alpha_{cs(rel)}$
$[Ru(bipy)_3]^{2+}$	1	1	1
(**2a**)	0.21 ± 0.02	0.57 ± 0.02	0.37 ± 0.05
(**2b**)	0.23 ± 0.02	0.41 ± 0.02	0.56 ± 0.08
(**2c**)	0.33 ± 0.03	0.36 ± 0.02	0.9 ± 0.1

Borax (disodium tetraborate) buffer (0.05 mol dm^{-3}), pH 8.9; $[N(CH_2CH_2OH)_3]$ = 0.125, $[dmbipy^{2+}]$ = 0.02 mol dm^{-3}

complications with coulombic effects. It scavenges any ruthenium(III) complex escaping from the solvent cage (Scheme 3).†

As shown in Figure 5 the rate of production of dmbipy$^{\cdot+}$ depends on the Ru : co-monomer ratio and in each case was found to be less than that observed for $[Ru(bipy)_3]^{2+}$. This reduced activity may be attributed to two main factors: the fraction of excited states quenched and the yield of dmbipy$^{\cdot+}$ escaping from the solvent cage. The extent of quenching of the excited state was determined fluorimetrically for each complex by comparing the emission intensity [in the presence of $N(CH_2CH_2OH)_3$] with and without 2×10^{-2} mol dm^{-3} dmbipy^{2+}. As shown in Table 4, it was found that the extent of quenching α_q is less for the polymer-bound complexes than for $[Ru(bipy)_3]^{2+}$. Using the values of α_q so determined, it is possible to evaluate the efficiency of cage escape (α_{cs}) using equation (1) and assuming that the quantum yield for formation

$$\alpha_{cs(rel)} = \Phi_{(rel)}/\alpha_{q(rel)} \qquad (1)$$

of the reactive excited state (α^*) and the efficiency of trapping (α_{tr}) of the ruthenium(III) complexes escaping from the cage are both unity {as for $[Ru(bipy)_3]^{2+}$}.[29] Here $\Phi_{(rel)}$ is the yield of dmbipy$^{\cdot+}$ and $\alpha_{q(rel)}$ is the fraction of excited states quenched both relative to that for $[Ru(bipy)_3]^{2+}$ under identical excitation conditions. Values for α_{cs} {relative to that of $[Ru(bipy)_3]^{2+}$} are given in Table 4 and in all cases are less than unity.

Conclusions

Water-soluble polymers containing $[Ru(bipy)_3]^{2+}$-like centres have been successfully prepared by the copolymerisation of $[Ru(bipy)_2(mvbipy)]^{2+}$ and 4-vinylpyridine followed by ethylation of the pendant pyridyl groups of the copolymer. This has been demonstrated by the u.v.–visible and fluorescence spectra and by the single exponential fluorescence decay. An attempt to prepare a similar copolymer by reaction of methylvinylbipyridyl–vinylpyridine copolymer (**3**) with $[Ru(bipy)_2Cl_2]$ (and subsequent quaternisation) was frustrated by the co-ordination of the ruthenium to the vinylpyridine. More generally, the reaction of mvbipy copolymers with $[Ru(bipy)_2Cl_2]$ will not be a satisfactory route to the preparation of $[Ru(bipy)_2(mvbipy)]^{2+}$ copolymers if the comonomer can also co-ordinate to ruthenium. This latter route was recently used by Hou *et al.*[30] It seems probable that in their case too a substantial fraction of the ruthenium centres were bound to the vinylpyridine and this would explain the multisite emission reported.

The photophysical properties of the $[Ru(bipy)_2(mvbipy)]^{2+}$ copolymers (**2a**)—(**2c**) are very similar to those found for $[Ru(bipy)_3]^{2+}$. The slight red-shifting of both the absorption and emission bands is consistent with that expected for a 4,4′-disubstituted bipyridyl complex.[31,32] Possibly changes in the environment of the emitting complex caused by the partial replacement of solvent water by charged organic polymer groups would also have a similar effect.[33] The lifetime of the highly loaded material (**2a**) (pvp:Ru *ca.* 2) is about 13% less than that of the less highly loaded samples (**2b**), (**2c**). This small reduction in lifetime may be attributed to some self-quenching by the $[Ru(bipy)_3]^{2+}$ as has previously been reported for related materials.[17]

The rate constants for the quenching of the excited states of copolymers (**2a**)—(**2c**) by oxygen are slightly less than that for $[Ru(bipy)_3]^{2+}$ under similar conditions. This small effect may be ascribed to some difficulty of access by the oxygen to the $[Ru(bipy)_3]^{2+}$-like centre because of coiling of the polymer. A similar explanation is also applicable for the reduced rate of

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† No evidence was found for reductive quenching by $N(CH_2CH_2OH)_3$ of the excited state of $[Ru(bipy)_3]^{2+}$ or of the copolymers (**2b**) and (**2c**). Indeed the lifetime in the pH 9 buffer–$N(CH_2CH_2OH)_3$ mixture was found to be 2—5% longer than in aqueous solution.

quenching by methylviologen of the polymer-bound excited species, although repulsion between the dmbipy^{2+} and the ethylpyridinium groups of the polymer is probably more important. As expected this rate of quenching is markedly sensitive to the ionic strength of the medium both because of a primary kinetic salt effect and possibly because of increased polymer coiling. This matter is being studied in detail and will be the subject of a subsequent publication.

Each of the copolymers sensitise the reduction of dmbipy^{2+} to dmbipy$^{\bullet+}$ in a sacrificial system although the yield is significantly lower than that for [Ru(bipy)$_3$]$^{2+}$. This decrease may be attributed principally to the expected reduced extent of quenching, but analysis also suggests that the extent of escape of the electron-transfer products is also less in the case of the polymers. This presumably implies (at least at the ionic strength of the solutions used) that the dmbipy$^{\bullet+}$ is hindered by the polymer chain from escaping from the ruthenium(III) centre and that this factor dominates any increase in escape yield due to repulsion of dmbipy$^{\bullet+}$ from the positively charged chain. It is to be expected that the extent of escape of dmbipy$^{\bullet+}$ will also be dependent on the ionic strength of the medium and it is hoped in the near future to carry out the direct determination of the dmbipy$^{\bullet+}$ yield by dye-laser excitation of the m.l.c.t. band of [Ru(bipy)$_3$]$^{2+}$ in the absence of scavengers such as triethanolamine.

Experimental

The compounds [Ru(bipy)$_2$Cl$_2$]$\cdot$2H$_2$O,[34] [Ru(bipy)$_2$(mvbipy)]Cl$_2$,[19] and 4-methyl-4′-vinyl-2,2′-bipyridyl (mvbipy)[19] were prepared by literature methods. The salt [Ru(bipy)$_2$(mvbipy)]PF$_6$ was purified by column chromatography on neutral alumina, eluting with acetone. The red crystalline product was characterised by u.v.–visible, ^{1}H n.m.r. spectroscopy, and elemental analysis. The sulphate salt was obtained by anion metathesis using Amberlite resin IRA-400(Cl) which had previously been converted into the sulphate form.

4-Vinylpyridine (vp) (Aldrich) was vacuum distilled and kept at −20 °C until required. Azobisisobutyronitrile (aibn) was recrystallised from chloroform. Atactic pvp was prepared by aibn-initiated bulk polymerisation of vp at 75 °C and the polymer was purified by repeated dissolution in methanol and precipitation with diethyl ether. The molecular weight was estimated from viscosity measurements in ethyl methyl ketone–2-propanol (84:14 v/v) at 25 °C using the Mark–Houwink equation $[\eta] = 3.8 \times 10^{-4}\ \bar{M}_V{}^{0.575}$, giving $\bar{M}_V = 23\,000$. Reagent grade solvents were purified by standard procedures and were fractionally distilled before use. Hydrated RuCl$_3$ was a loan from Johnson-Matthey and Co. Other chemicals employed were reagent grade and were used as received.

Copolymerisation of [Ru(bipy)$_2$(mvbipy)]SO$_4$ *and* 4-*Vinylpyridine*.—The required quantities of the ruthenium complex and distilled vp (Table 1) were placed in a tube and dissolved in the minimum of methanol; aibn (0.1 g per g monomer) was added and the resultant mixture was heated at 70 °C for 1 h. Purification of the resultant copolymers (**1a**)—(**1c**) was effected by dissolution in CH$_2$Cl$_2$ and reprecipitation with n-hexane. Copolymer (**1a**) was further purified by redissolving in methanol and precipitating into diethyl ether. The resultant orange powders were vacuum dried. Reaction feed ratios, [Ru(bipy)$_2$(mvbipy)]SO$_4$ in g (mmol): 4-vinylpyridine in cm^3 (mmol), were 0.649 (0.92):0.20 (1.9), 0.332 (0.47):0.50 (4.7), and 0.066 (0.094):1.0 (9.3) for (**1a**)—(**1c**) respectively. ^{1}H N.m.r. (CD$_3$OD): (**1a**), δ 1.5—2.3 (br, 5.4 H), 2.5—2.6 (br, 3 H), 6.65—6.75 (br, 3.6 H), 7.5—9.0 (br, 25.6 H); (**1b**) 1.5—2.3 (br, 32.4 H), 2.5—2.6 (br, 3 H), 6.65—6.75 (br, 21.6 H), 7.5—9.0 (br, 43.6); (**1c**), 1.5—2 (br, 3 H), 6.65—6.75 (br, 2 H), and 7.5—9.0 (br, 2 H) (for assignments see Figure 3).

Quaternisation of Poly-4-*vinylpyridine*.—Excess of bromoethane (1 cm^3) was added to a solution of pvp (0.500 g) in sulpholane (15 cm^3) and was stirred at 75 °C for 2 d. The product was isolated by precipitation with acetone and purified by dissolution in methanol and repeated precipitation with acetone to yield a white hygroscopic solid.

Quaternisation of Poly{vp–co-[Ru(bipy)$_2$(mvbipy)]$^{2+}$} (**1**).—Copolymers (**1a**)—(**1c**) were dissolved in sulpholane (15 cm^3) and excess of bromoethane (1 cm^3) was added. The resultant mixtures were stirred at 75 °C for 2 d. The products were isolated by precipitation with diethyl ether followed by dissolution in methanol and further precipitation with ether several times. The orange hygroscopic solids (**2a**)—(**2c**) were stored *in vacuo*. The degree of quaternisation was estimated to be greater than 85%. ^{1}H N.m.r. (CF$_3$CO$_2$D): (**2a**), δ 1.5—3.0 (br, 10.5 H), 4.7—4.8 (br, 3.45 H), 7.5—9.0 (br, 29.2 H); (**2b**), 1.5—3.0 (br, 61.9 H), 4.7—4.8 (br, 19.74 H), 7.5—9.0 (br, 65.2 H); (**2c**), 1.5—3.0 (br, 5.6 H), 4.7—4.8 (br, 1.74 H), and 7.5—9.0 (br, 4 H).

Copolymerisation of 4-*Methyl*-4′-*vinyl*-2,2′-*bipyridyl with* 4-*Vinylpyridine*.—To mvbipy (46.4 mg, 0.236 mmol) dissolved in acetone (0.5 cm^3) was added vp (0.5 cm^3, 4.66 mmol) and aibn (0.029 g); the mixture was heated at 70 °C for 1 h. The product [poly(mvbipy–co-vp)] (**3**) was purified by dissolution in CH$_2$Cl$_2$ and reprecipitation with n-hexane to give a white powder.

Reaction of [Ru(bipy)$_2$Cl$_2$]$\cdot$2H$_2$O *with Poly*(mvbipy–co-vp).—The complex [Ru(bipy)$_2$Cl$_2$]$\cdot$2H$_2$O (7.9 mg, 0.0152 mmol) and poly(mvbipy–co-vp) (vp:mvbipy = 19.7:1) (62.7 mg, 0.0276 mmol of mvbipy groups) were dissolved in methanol–water (60:40 v/v) (50 cm^3). A 5-cm^3 aliquot was immediately placed in a stemmed cuvette and the absorption spectrum recorded. The cuvette was immersed in a bath of refluxing methanol–water (60:40 v/v) in the dark and spectra were recorded at intervals.

Instrumentation.—Steady-state absorption spectra and optical densities were recorded on a Pye-Unicam SP8-200 spectrophotometer. Luminescence spectra were obtained on a Perkin-Elmer MPF 44B spectrofluorimeter equipped with a R928 photomultiplier, and were not corrected for instrumental response. Excitation was at 455 nm and emission was measured at 615 nm. Optically dilute solutions were employed. Proton n.m.r. spectra were recorded on a Bruker WP-80 80-MHz Fourier-transform instrument. Chemical shifts are measured relative to an internal standard [SiMe$_4$ for organic solvents and sodium 3-(trimethylsilyl)propanesulphonate for water and trifluoroacetic acid]. Atomic absorption determination of ruthenium in polymers was made by measuring the absorption at 349.9 nm for homogeneous 5% HCl solutions using an Instrumentation Lab a.a./a.e. spectrometer 257 using [Ru(bipy)$_2$(mvbipy)]SO$_4$ as a standard.

Photochemical and Photophysical Procedures.—Quenching efficiencies for the systems used for the photo-induced electron transfer were determined by measuring the relative emission intensities in the presence (I) and absence (I_0) of methylviologen. Samples had an optical density of *ca.* 0.1 at the excitation wavelength of 455 nm.

Luminescence lifetimes were determined in two ways: (*a*) on time-correlated single-photon counting equipment (Applied Photophysics) using a nitrogen-filled lamp (pulse width *ca.* 3 ns), a Philips XP2233B stop photomultiplier, ORTEC EEG

474, 473A, and 457 signal-processing modules, and a Canberra series 30 multichannel analyser; (*b*) by monitoring the fluorescence decay after excitation by a coumarin 1 dye laser (λ = 460 nm) (Oxford lasers EDL 1) pumped by a Lambda Physik EMG-50 XeCl laser (pulse width *ca.* 15 ns, pulse energy 20—40 mJ). Fluorescence decays were observed along a 1-cm optical path in a crossed-beam arrangement, detected on a R928 photomultiplier, and recorded on a 125-MHz digital oscilloscope (Philips PM 3311C).

Photoreduction Procedure.—Solutions for study of photo-induced electron transfer contained *ca.* 3.3 × 10^{-5} mol dm^{-3} ruthenium complex as sensitiser, 0.02 mol dm^{-3} methylviologen (dmbipy^{2+}), and 0.125 mol dm^{-3} triethanolamine in pH 8.9 borate buffer (0.025 mol dm^{-3}). For polymer-bound derivatives (**2a**)—(**2c**) the concentration was such that the optical density at $\lambda_{max.}$ (m.l.c.t.) was the same as that for 3.3 × 10^{-5} mol dm^{-3} [Ru(bipy)$_3$]$^{2+}$. Blank experiments were also carried out in the absence of a sensitiser where it was confirmed that no semireduced radical was produced. Aliquots (4 cm^3) were rigorously degassed (three freeze–pump–thaw cycles) and irradiated with light from an MED 250W medium-pressure mercury lamp monochromated at 436 nm. Solutions were shaken to ensure homogeneity. Values of Φ(dmbipy$^{\bullet +}$) relative to that using [Ru(bipy)$_3$]$^{2+}$ as the sensitiser were determined from the initial linear growth of [dmbipy$^{\bullet +}$] as a function of time; [dmbipy$^{\bullet +}$] was established from the absorbance of the solution at 605 nm (ε = 1.37 × 10^4 dm^3 mol^{-1} cm^{-1}).[35]

Acknowledgements

The authors are grateful to Dr. M. J. Murphy, Mr. W. J. M. van der Putten, and Dr. P. Brint (University College Cork) for their help with luminescence lifetime measurements, the National Board for Science and Technology and the EEC Solar Energy Programme Project for financial support, and to Trinity College Dublin, the Department of Education, and Dublin County Council for support (to P. M. E. and C. M. O'C.).

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Received 10th December 1985; Paper 5/2168