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Photosensitized charge separation using ruthenium(II) complex and viologen-containing polymers — effects of quaternization and length of alkyl side-chain

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Abstract

A series of the ruthenium(II) complex and viologen-containing partially quaternized poly(1-vinylimidazole)s with various degrees of quaternization (RuVQPIms) and various lengths of the alkyl side-chains [CnRuVQPIms:$n = 4$(butyl),8(octyl),12(dodecyl),16(hexadecyl)] have been synthesized and characterized using UV–Vis absorption and luminescence spectroscopies. The effects of quaternization and length of the alkyl side-chains on the photosensitized charge separation using these metallopolymers have been investigated in methanol. The photosensitized charge separation reaction took place through an intrapolymer process for all systems. In the cases of the RuVQPIms having a low degree of quaternization and short alkyl side-chain, the initial rate of the viologen radical formation linearly depended on the polymer concentration with two stages, while the RuVQPIm having a high degree of quaternization and long alkyl side-chain showed only one-stage dependence. Further, the rate of the second stage was larger than that of the first stage. The dependence with two stages would be caused by aggregation at a high polymer concentration through the interpolymer van der Waals interaction. The stronger interaction induced by increases in the number and length of the alkyl side-chains on the polymer backbone decreased the flexibility of the viologen residues; consequently, the enhancement of the rate in the second stage was not observed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photosensitized charge separation; Ruthenium(II) complex; Photosensitizer

1. Introduction

During natural photosynthesis [1,2], charge separation is a key process, and many synthetic systems have been proposed as functional mimics of the photosynthetic reaction center based on transition metal complexes [3–5] or porphyrins [6–10].

Transition metal complexes of ruthenium(II), osmium(II), rhenium(I), rhodium(III) and iridium(III) feature favorable electrochemical, photophysical, and photochemical properties [11–24]. Therefore, such complexes have been extensively used to construct polynuclear species, due to the relative ease of using a modular synthetic approach in coordination compounds [19–24]. In particular, the tris(2,2′-bipyridine)ruthenium(II) complex [$Ru(bpy)_3^{2+}$] has become one of the most studied photocatalysts for the chemical conversion of solar energy since it can thermodynamically photolyse water under visible light irradiation [12,25–29]. It has also been used as a probe molecule for investigating the interior structure of microheterogeneous systems such as micelles, liposomes and polymer systems [30–35].

Poly(1-vinylimidazole)-bound ruthenium(II) complexes were synthesized, and their photochemical, photophysical and electrochemical properties investigated [36–39]. These investigations suggested that the metallopolymers can be used as redox materials, photosensitizers and molecular diodes. Recently, we have reported that the partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes were used as a polymer photosensitizer, and these metallopolymers have excellent photosensitizing ability for photosensitized charge separation [40] and photoinduced hydrogen generation [41,42]. Quite recently, the synthesis and characterization of the ruthenium(II) complex and viologen-containing polymers based on the partially quaternized poly(1-vinylimidazole) [43] or poly(1-vinylimidazole) [44] have been reported. Further, the photosensitized charge separation using these polymers have been investigated and these metallopolymers provide efficient charge separation [45]. In the present article, we report the effects of quaternization and length of the alkyl side-chains on the photosensitized charge separation using the

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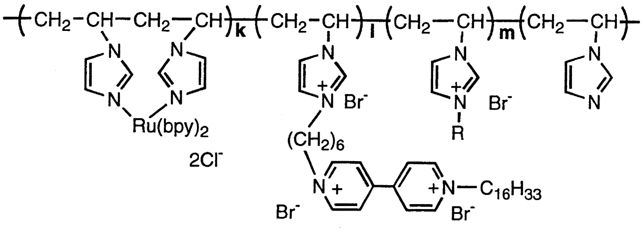


	R	k	l	m
RuVPIm-1		0.0041	0.0582	—
C_4RuVQPIm	C_4H_9	0.0041	0.0582	0.3422
C_8RuVQPIm	C_8H_{17}	0.0041	0.0582	0.3358
C_{12}RuVQPIm	$C_{12}H_{25}$	0.0041	0.0582	0.3438
C_{16}RuVQPIm	$C_{16}H_{33}$	0.0041	0.0582	0.3325
RuVPIm-2		0.0039	0.0512	—
RuVQPIm-1	$C_{16}H_{33}$	0.0039	0.0512	0.0733
RuVQPIm-2	$C_{16}H_{33}$	0.0039	0.0512	0.1311
RuVQPIm-3	$C_{16}H_{33}$	0.0039	0.0512	0.2431
RuVQPIm-4	$C_{16}H_{33}$	0.0039	0.0512	0.4822

Fig. 1. Chemical structure of a series of ruthenium(II) complex and viologen-containing polymers.

ruthenium(II) complex and viologen-containing polymers based on the partially quaternized poly(1-vinylimidazole).

2. Experimental

2.1. Materials

1-Vinylimidazole was purified by distillation under reduced pressure just before use. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization at 30°C. Alkyl bromides, 4,4′-bipyridine and 1,6-dibromohexane were of analytical grade and were used without further purification. 4-(4′-Pyridyl)-1-hexadecylpyridinium bromide and 1-(6-bromohexyl)-1′-hexadecyl-4,4′-bipyrinium dibromide were prepared by the methods described elsewhere [46,47]. *cis*-bis(2,2′-bipyridine)dichlororuthenium(II) was prepared according to the literature [48]. Poly(1-vinylimidazole) was prepared by a free-radical polymerization of 1-vinylimidazole with AIBN as the initiator in ethanol for 10 h. Ruthenium(II) complex-containing poly(1-vinylimidazole) (RuPIm) and the ruthenium(II) complex and viologen-containing poly(1-vinylimidazole)s (RuVPIms) were prepared by the previously reported methods [38,43]. The partially quaternized polymers were obtained from refluxing methanol of RuVPIms and alkyl bromide in methanol for 2 days. These polymers were identified by ^{1}H-NMR, UV–Vis absorption spectra and elemental analysis. The chemical structure of these metallopolymers, together with components of the ruthenium(II) complex, viologen and alkyl group, are shown in Fig. 1.

2.2. Measurements

UV–Vis absorption spectra were recorded using a JASCO V-570 UV/VIS/NIR spectrophotometer. Luminescence spectra were measured using a Hitachi 650-10S fluorescence spectrophotometer. The measurements of the Fourier-Transform Infrared (FTIR) spectra were performed using a JASCO FT/IR-400 FTIR spectrophotometer.

Photosensitized charge separation was performed at 25°C with light irradiation by a 300 W slide projector (ELMO Co., Ltd. S-300). The irradiation light at wavelengths less than 440 nm was cut off by a Toshiba Y-44 filter. A spectroscopic cell (1 × 1 cm) containing the metallopolymers and triethanolamine (TEOA) as a sacrificial electron donor in methanol was placed at a distance of 10 cm from the light source. Before the measurements, oxygen was expelled by bubbling argon gas into the sample solution for 20 min. The formation of the viologen radical calculated from the absorbance of the solution at 605 nm corresponding to the maximum wavelength of the viologen radical ($\epsilon_{605} = 13\,400\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$) was monitored as a function of irradiation time. The initial rates of viologen radical formation were calculated from the initial slope of a plot of the concentration of the viologen radical formed versus irradiation time. In all systems, the experimental errors are within ± 0.05.

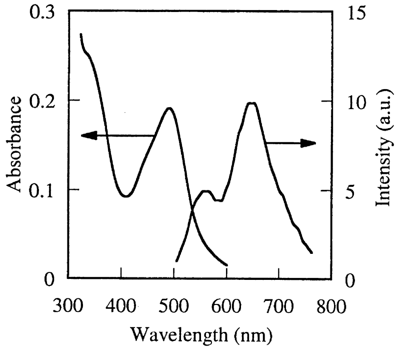


Fig. 2. Absorption and luminescence spectra of C_8RuQPIm at [Ru(II)] = 2.0×10^{-5} mol dm^{-3} in methanol.

3. Results and discussion

3.1. Spectroscopic properties

The absorption and luminescence spectra of the methanol solution of C_8RuQPIm at [Ru(II)] = 2.0×10^{-5} mol dm^{-3} are shown in Fig. 2. and the spectroscopic data for all metallopolymers are summarized in Table 1. The shapes of the absorption and luminescence spectra, showing one absorption peak in the visible region and two emitting peaks at 560 and 650 nm, respectively, were independent of the quaternization and length of the alkyl side-chains. Here, the two peaks at 560 and 650 nm are emissions from the ruthenium(II) complexes which are compartmentalized by the viologen residues and alkyl side-chains and exposed to the bulk solution, respectively [43]. Although the absorption maxima in the visible region, due to the metal-to-ligand charge transfer (MLCT) bands, were also independent of length of the alkyl side-chains, they significantly depend on the degree of quaternization. However, the luminescence intensities at two emitting peaks significantly depend on the degree of quaternization and the length of the alkyl side-chains. These results indicate that the absorption maxima depend on only the positively charged density on the polymer backbone and the luminescence intensity is affected by both the positively charge density and the length of the alkyl side-chains. We reported that the absorption maxima of a series of partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes slightly shifted to the longer wavelengths with increasing degree of quaternization [40]. This result led us to conclude that the excited state of the ruthenium(II) complex residue was slightly stabilized by the positive charge. Considering this result, in the present system, the shift in the absorption maxima is caused by stabilization of the ruthenium(II) complex residue. In contrast, the luminescence intensities at two peaks, 560 and 650 nm, have the minimum values depending on the degree of quaternization and length of the alkyl side-chains dependencies; these values are a degree of quaternization of ca. 0.24 and an eight carbon number. These results indicate that two kinds of ruthenium(II) complex residues are the most readily quenched by the viologen residues at ca. 0.24 degree of quaternization and 8 carbon number in the alkyl side-chain. Such dependencies would be caused by some factors that include an electrostatic effect (repulsion), van der Waals interaction of the alkyl side-chains and steric hindrance of the alkyl side-chains. The electrostatic repulsion between the positively charged groups induced by an increase in the degree of quaternization loosens the entwined polymer chains and increases the degree of freedom of the viologen residue, leading to acceleration of the quenching of the ruthenium(II) complex residue with the viologen. In contrast, the increase in the degree of quaternization also increases the van der Waals interaction between the alkyl side-chains which restricts loosening of the polymer chains and degree of freedom of the viologen residue, which leads to restriction of the quenching reaction. Further, the van der Waals interaction increases when the alkyl side-chain lengthens. The balance of electrostatic repulsion and van der Waals interaction is of importance. In Fig. 3A, the quenching of the ruthenium(II) complex is accelerated up to ca. 0.24 for the degree of quaternization, and then it is restricted. This is attributed to the fact that the effect of electrostatic repulsion on the quenching is dominated until ca. 0.24 degree of quaternization, and then the van der

Table 1
Spectroscopic data of all metallopolymers in methanol

	Absorption λ_{max} (nm)	Luminescence intensity	
		560 nm	650 nm
RuVPIm-1	488	17.0	21.9
C_4RuQPIm	490	7.5	12.1
C_8RuQPIm	490	5.1	10.3
C_{12}RuQPIm	490	7.5	14.5
C_{16}RuQPIm	490	11.5	20.0
RuVPIm-2	488	13.0	21.5
RuVQPIm-1	488	11.8	20.4
RuVQPIm-2	489	9.5	18.2
RuVQPIm-3	490	2.0	12.3
RuVQPIm-4	492	4.3	15.3

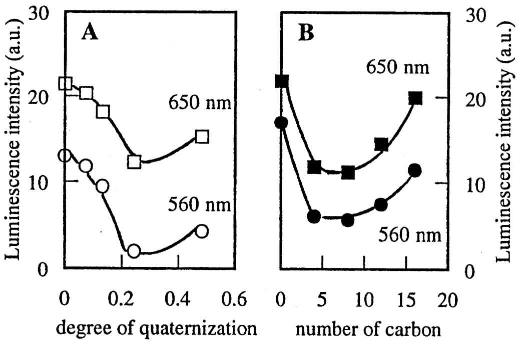


Fig. 3. Dependence of luminescence intensities at 560 and 650 nm on degree of quaternization (A) and number of carbon in the alkyl side-chain (B).

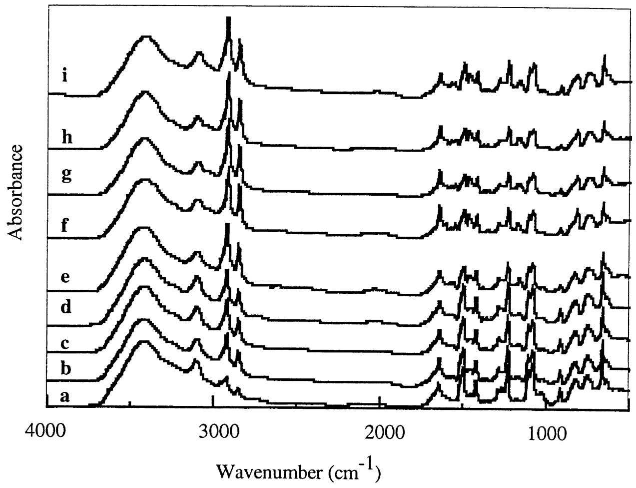


Fig. 4. FTIR spectra of a series of ruthenium(II) complex and viologen-containing polymers.

Waals interaction dominates above it. In Fig. 3B, since the effect of electrostatic repulsion on the quenching of the ruthenium(II) complex is almost equal among these systems, the luminescence intensity is dominated by only the strength of the van der Waals interaction. In the cases of alkyl chain lengths of 4 and 8, the quenching of the ruthenium(II) complex residue is accelerated by the increase in the degree of freedom of the viologen residues and is barely affected by the van der Waals interaction. With lengthening of the alkyl side-chain, the van der Waals interaction increases and the degree of freedom of the viologen residues is restricted; consequently, the luminescence intensity increases.

Fig. 4 shows the FTIR spectra of these metallopolymers. The absorption band around 3400 cm^{-1} is assigned to water which is adsorbed on the polymers through hydrogen bonding with the imidazolyl and/or imidazolium residues. The absorption bands at ca. 1650 cm^{-1} and 1500 cm^{-1} arise from the ring stretch of the imidazolyl residue [49]. The bands at ca. 2920 cm^{-1} and 2850 cm^{-1} arising from the C–H stretching vibration of the alkyl side-chains increase with increasing degree of quaternization and length of the alkyl side-chains. This result corresponds to the increases in the length of the alkyl side-chain and degree of quaternization.

3.2. Photosensitized charge separation

When a methanol solution of these metallopolymers and triethanolamine (TEOA) as a sacrificial electron donor was irradiated by visible light ($\lambda > 440$ nm), the absorbance at 605 nm, corresponding to the absorption maximum of the viologen radical, increases, indicating that charge separation was achieved. In the present systems, at least three processes can be proposed for the charge separation reaction; intrapolymer, interpolymer and both of them. The concentration of the ruthenium(II) complex residue increases with a concomitant increase in that of the viologen; namely, it corresponds to an increase in the number of polymer chains. In the case of the intrapolymer process, the initial rates of the viologen radical formation depends on the number of ruthenium(II) complex residues and the viologen residues on the same polymer backbone, but not on the number of redox centers in the solution. Therefore, the initial rate shows the first-order dependence for the initial concentration of the ruthenium(II) complex and viologen residue. In contrast, the initial rate for the interpolymer process depends on the concentration of the ruthenium(II) complex and the viologen in the solution, because the interpolymer reaction proceeds through a bimolecular process. The initial rate shows the second-order dependence for the number of polymer chains. Further, the dependence of the initial rate occurring through both the intra- and interpolymer processes on the number of the polymer chains would be very complicated.

3.2.1. Effects of the degree of quaternization

Fig. 5. shows the dependence of the initial rates of the viologen radical formation on the concentration of the ruthenium(II) complex for RuVPIm-2 and a series of RuVQPIms. These metallopolymers also have the viologen species with a constant ratio of [Ru(II)]/[Viologen]. The same dependence for the concentration of the viologen was observed. Although all systems have the induced concentration region up to ca. 2.0 × 10^{-5} mol dm^{-3} of

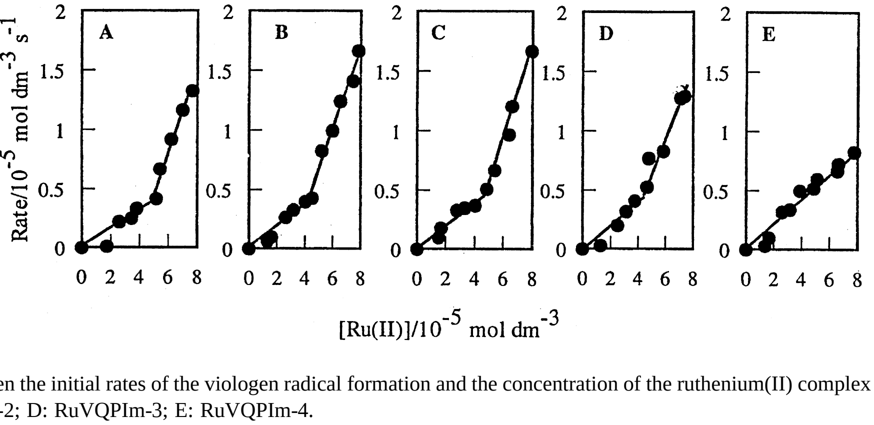


Fig. 5. Relationships between the initial rates of the viologen radical formation and the concentration of the ruthenium(II) complex residue: A: RuVPIm-2; B: RuVQPIm-1; C: RuVQPIm-2; D: RuVQPIm-3; E: RuVQPIm-4.

Table 2
Kinetic parameters for RuVPIm-2 and a series of RuVQPIms

	First slope		Second slope	
	k_{Ru} (s^{-1})	k_{V} (s^{-1})	k'_{Ru} (s^{-1})	k'_{V} (s^{-1})
RuVPIm-2	8.11×10^{-2}	5.95×10^{-3}	2.97×10^{-1}	2.18×10^{-2}
RuVQPIm-1	1.05×10^{-1}	7.11×10^{-3}	3.06×10^{-1}	2.24×10^{-2}
RuVQPIm-2	1.04×10^{-1}	7.64×10^{-3}	3.81×10^{-1}	2.78×10^{-2}
RuVQPIm-3	1.06×10^{-1}	7.61×10^{-3}	3.21×10^{-1}	2.34×10^{-2}
RuVQPIm-4	1.04×10^{-1}	7.66×10^{-3}	—	—

the ruthenium(II) complex, they do not have the induced concentration region for the viologen concentration. The initial rates linearly increased with increasing concentration of the ruthenium(II) complex in two stages, while the rate for RuVQPIm-4 shows a one-step dependence. This result indicates that the photosensitized charge separation reaction takes place through the intrapolymer process, and the reaction is accelerated at a high concentration of the ruthenium(II) complex for the metallopolymer systems except for the RuVQPIm-4 system. Based on these results, the rate law of the photosensitized charge separation reactions can be expressed by Eqs. (1) and (2):

$$\mathrm{Rate} = k_{\mathrm{Ru}}[\mathrm{Ru(II)}], \quad (1)$$

$$\mathrm{Rate} = k_{\mathrm{V}}[\mathrm{Viologen}], \quad (2)$$

where k_{Ru} and k_{V} are the first-order rate constants. As these metallopolymers have a constant ratio of [Viologen]/[Ru(II)] = 13.13, Eq. (2) is converted to Eq. (3):

$$\mathrm{Rate} = 13.13 k_{\mathrm{V}}[\mathrm{Ru(II)}]. \quad (3)$$

Consequently, relationship between k_{Ru} and k_{V} is expressed by Eq. (4).

$$k_{\mathrm{Ru}} = 13.13 k_{\mathrm{V}}. \quad (4)$$

The kinetic parameters obtained from Fig. 5 are summarized in Table 2. The k_{Ru} values for all systems almost satisfy Eq. (4). Therefore, it is evident that the rate law for these systems is expressed by Eq. (3).

In Fig. 5, the large rate constants are for high ruthenium(II) concentrations, although the rate law does not change. That is to say, the reaction rate is accelerated at the high ruthenium(II) complex concentration proceeding through the intrapolymer process. We reported that the partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complex and viologen underwent the interpolymer interaction between alkyl side-chains and formed a partial polymer aggregate [44]. Therefore, the enhancement in the rate of the viologen radical formation at high polymer concentration is caused by the interpolymer interaction as shown in Scheme 1. Since the interacted polymer chains can be regarded as one molecule, the reaction proceeds through an intrapolymer process, namely the intra-aggregate process. At a low polymer concentration, the intrapolymer process occurs in one polymer chain, while it occurs in the aggregate formed by a few polymer chains via the interpolymer interaction. Although the k_{Ru} and k_{V} obtained from the first slope are increased by quaternization, they are almost constant even when the degree of quaternization increases, indicating that the alkyl side-chains do not act as the steric hindrance. The k'_{Ru} and k'_{V} obtained from the second slope increase with increasing degree of quaternization, and then decrease via the maximum values at RuVQPIm-2. This phenomenon agrees with the result that the quenching efficiency of the RuVQPIm-2 is the largest as shown in Fig. 3. As already mentioned, the balance of the electrostatic repulsion and van der Waals interaction is an important factor for the charge separation reaction at high polymer concentrations. In addition, the number of ruthenium(II) complexes and viologen residues in one molecule becoming large by aggregation is also one of the factors. In contrast, the interpolymer interaction becomes strong with increasing degree of quaternization, and the strong interaction would bring about a decrease in the degree of freedom of the viologen segments, leading to a decrease in the rate constant. Particularly, for RuVQPIm-4 having a high degree of quaternization, the ruthenium(II) complex concentration dependence of the rate does not have the second slope. It is likely that the degree of freedom of the viologen segment is restricted by a strong van der Waals interaction (Scheme 2).

3.2.2. Effects of length of the alkyl side-chains

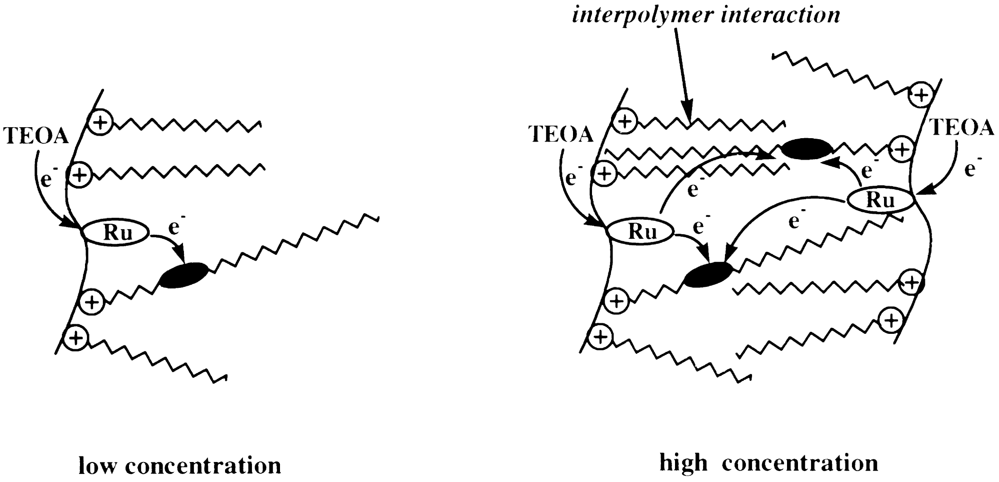
Fig. 6 shows the dependence of the initial rates of the viologen radical formation on the concentration of the ruthenium(II) complex for RuVPIm-1 and a series of CnRuVQPIms. The initial rates linearly depend on the concentration of the ruthenium(II) complex. The RuVPIm-1 and C_4RuVQPIm show the two-stage dependence, while the other systems show only a one-stage dependence. Therefore, the rate law in the systems can also be expressed by Eqs. (1) and (2). These metallopolymers have a constant ratio of [Viologen]/[Ru(II)] = 14.2, and Eq. (2) is converted to Eq. (5).

$$\mathrm{Rate} = 14.2 k_{\mathrm{V}}[\mathrm{Ru(II)}]. \quad (5)$$

Further, the relationship between k_{Ru} and k_{V} is expressed by Eq. (6).

$$k_{\mathrm{Ru}} = 14.2 k_{\mathrm{V}}. \quad (6)$$

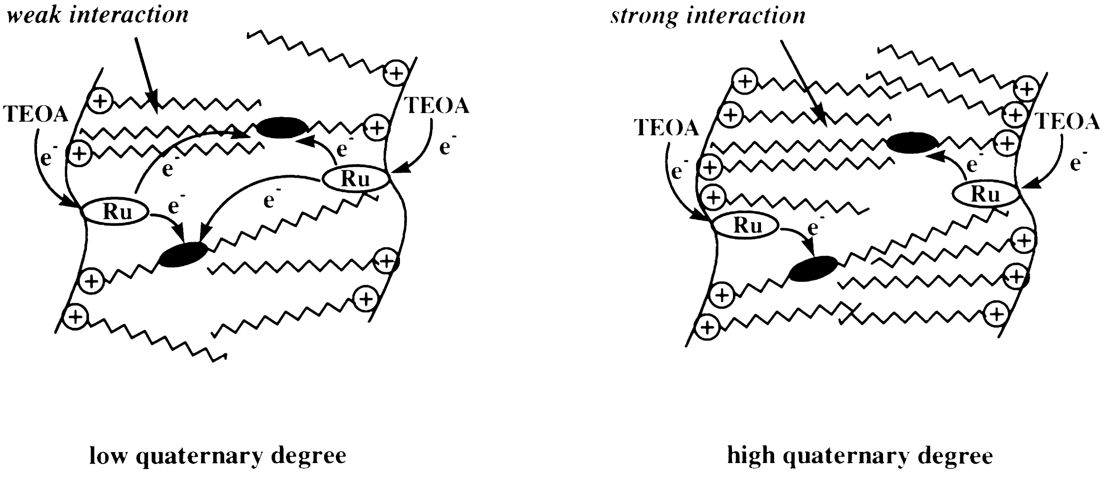
For RuVPIm-1 and C_4RuVQPIm, the two-stage dependence



Scheme 1.

can be explained by the same reason as that of the balance of the electrostatic repulsion and van der Waals interaction changes with increasing polymer concentration as already mentioned. It is surprising that C_4RuVQPIm having a short alkyl side-chain undergoes interpolymer interaction at a high polymer concentration. These rate constants satisfy Eq. (6). By quaternization, the rate constants obtained from the first and second slopes decrease and increase, respectively. The enhancement of the k'_{Ru} and k'_V is caused by an increase in the number of ruthenium(II) complexes and viologen residues induced by aggregation of the polymer chains through the interpolymer interaction. With increasing length of the alkyl side-chains, the interpolymer van der Waals interaction increases and the degree of freedom of the viologen residues is restricted. Consequently, the second slope does not appear for C_8RuVQPIm, C_{12}RuVQPIm and C_{16}RuVQPIm.

The k_{Ru} and k_V slightly increase with increasing length of the alkyl side-chain. Further, it is noteworthy that the rate constants obtained from the first slope do not agree with Eq. (6) with increasing length of the alkyl side-chains. Clearly, the k_{Ru} values obtained from the theoretical calculation [Eq.(6)] are smaller than those obtained from Fig. 6 for C_8RuVQPIm, C_{12}RuVQPIm and C_{16}RuVQPIm. Further, the degree of restriction of the viologen residues slightly decreases with increasing length of the alkyl side-chains, although the interpolymer interaction increases. These results suggest a contribution of the electrostatic repulsion between the viologen and ruthenium(II) complex as well as viologen and polymer backbone. The electrostatic repulsion becomes small with increasing length of the alkyl side-chains. Although the viologen residues are restricted by an interpolymer interaction, the electrostatic repulsion in the aggregate decreases with increasing length of the alkyl side-chains, consequently leading to enhancement of the rate. As summarized in Table 3, however, the contribution is slight. A tentative illustration of the reaction mechanism for the systems is shown in Scheme 3.



Scheme 2.

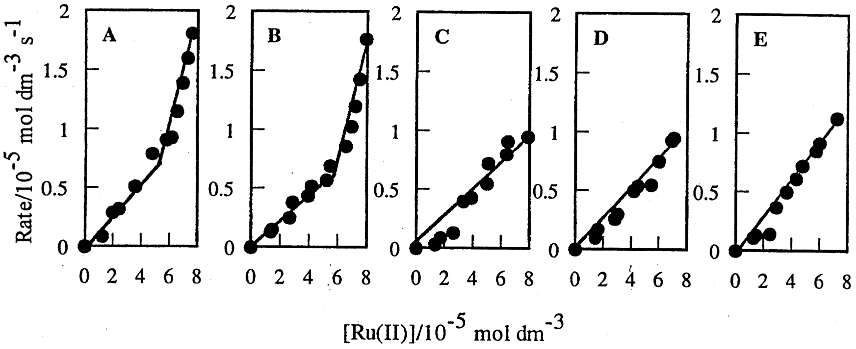
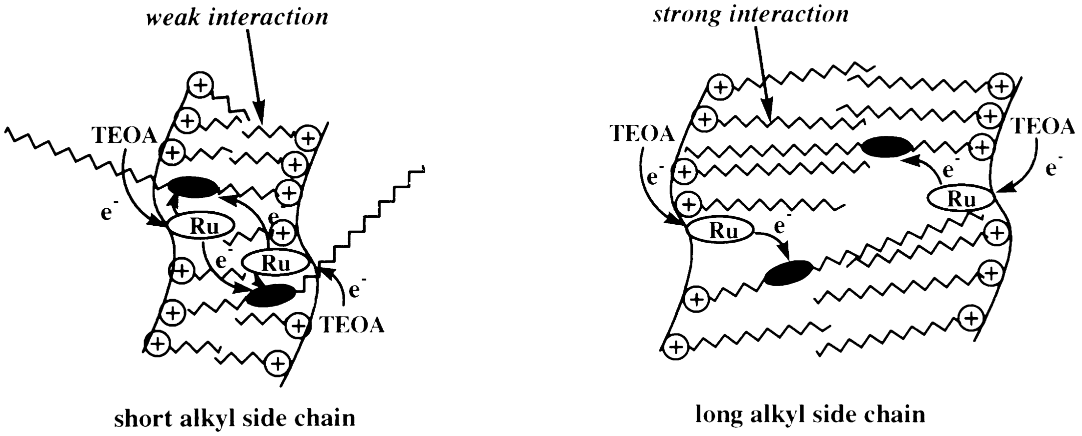


Fig. 6. Relationships between the initial rates of the viologen radical formation and the concentration of the ruthenium(II) complex residue: A: RuVPIm-1; B: C_4RuVQPIm; C: C_8RuVQPIm; D: C_{12}RuVQPIm; E: C_{16}RuVQPIm.

Table 3
Kinetic parameters for RuVPIm-1 and a series of CnRuVQPIms

	First slope k_{Ru}(s^{-1})	k_V(s^{-1})	Second slope k'_{Ru}(s^{-1})	k'_V(s^{-1})
RuVPIm-1	1.64×10^{-1}	1.16×10^{-2}	6.05×10^{-1}	4.32×10^{-2}
C_4RuQPIm	1.22×10^{-1}	8.58×10^{-3}	7.32×10^{-1}	5.09×10^{-2}
C_8RuQPIm	1.28×10^{-1}	9.43×10^{-3}	—	—
C_{12}RuQPIm	1.31×10^{-1}	1.02×10^{-3}	—	—
C_{16}RuQPIm	1.35×10^{-1}	1.12×10^{-2}	—	—



Scheme 3.

4. Conclusions

We revealed the spectroscopic properties of a series of ruthenium(II) complex and viologen-containing polymers based on poly(1-vinylimidazole) with various degree of quaternization and length of the alkyl side-chains, and studied the photosensitized charge separation reaction using these metallopolymers. Absorption spectrum measurements indicate that the absorption maxima depend on only the positively charged density on the polymer backbone. Further, luminescence spectrum measurements demonstrate that the luminescence properties of these metallopolymers are affected by some effects such as electrostatic repulsion, van der Waals interaction and steric hindrance. During photosensitized charge separation, the initial rates of the viologen radical formation linearly depend on the concentration of the ruthenium(II) complex, namely, the polymer chain with two stages. In the cases of the long alkyl side-chain and high degree of quaternization, however, a one-step dependence is observed. These results indicate that the photosensitized charge separation reaction proceeds through the intrapolymer process and the rates depend on the degree of freedom of the viologen which is determined by strength of interpolymer van der Waals interaction. Further, it was found that the rate law for the present systems can be simply explained by Eqs. (1) and (2).

Acknowledgements

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