ELSEVIER

Polymer 42 (2001) 9235–9241

polymer

www.elsevier.com/locate/polymer

Enhancement effects of L-tyrosine esters on photosensitized charge separation using ruthenium(II) complex- and viologen-containing polymers

Masahiro Suzuki[a,*], Mutsumi Kimura[b], Kenji Hanabusa[a], Hirofusa Shirai[b]

[a]*Graduate School of Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*
[b]*Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*

Received 23 April 2001; received in revised form 4 June 2001; accepted 15 June 2001

Abstract

Ruthenium(II) complex- and viologen-containing polymers, which consist of the bis(2,2′-bipyridine) ruthenium(II) complex coordinated with imidazolyl residues on poly(1-vinylimidazole) (RuVPIm) and partially quaternized poly(1-vinylimidazole) (RuVQPIm) and viologen covalently linking these polymers through a hexylene spacer, have been synthesized. These polymers have two kinds of ruthenium(II) complex residues, the ^{557}Ru(II) complex compartmentalized by the viologen residues and polymer backbone and a ^{640}Ru(II) complex exposed to the bulk solution, which show emission maxima at 557 and 640 nm, respectively. The influence of L-tyrosine esters with hexyl (C_6Tyr), octyl (C_8Tyr), and dodecyl (C_{12}Tyr) groups on the luminescence properties and photosensitized charge separation has been investigated in methanol. The luminescence intensities of these polymers decreased with the addition of the L-tyrosine esters, indicating that the quenching of the ruthenium(II) complex residues increased. The initial rates of the viologen radical formation was enhanced by the addition of the L-tyrosine esters. These results were attributed to a mediated effect of the L-tyrosine esters which acted as a mediator for photoinduced electron transfer from the photoexcited ruthenium(II) complex to viologen residue. Furthermore, the L-tyrosine esters undergoing interaction with a solvophobic domain where ^{557}Ru(II) complex residues were compartmentalized acted as the mediator for only the quenching reaction, while they undergo an interaction with the polymer backbone mediating both the quenching reaction and the back reaction in the photosensitized charge separation.

Keywords: Ruthenium; L-Tyrosine; Viologen

1. Introduction

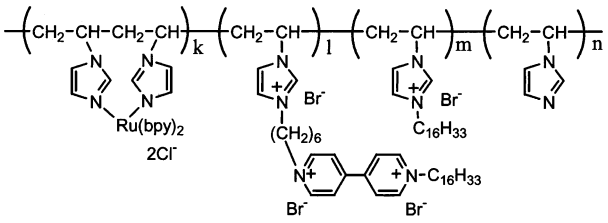
Many soluble polymers derivatized by the addition of polypyridine transition metal complexes have been employed for photoinduced electron- and energy transfer [1–12]. We have reported that the partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes (RuQPIms) have an excellent photosensitizing ability for quenching, photosensitized charge separation and photoinduced hydrogen generation reactions [13–16].

In biological systems, long-range electron transfer is achieved involving electron tunneling through polypeptides, and its kinetics and reaction mechanism have been investigated [17–18]. Many investigations have employed modified proteins and suggest that some amino acid residues in the proteins would participate in the electron transfer in biological systems [19–22]. For instance, in the photosynthesis of green plants, it has been reported that tyrosine residues participate in the photoinduced electron transfer [23].

On the other hand, the electron transfer in a natural polymer matrix and some synthetic polymers containing donors and acceptors as simple systems have been investigated [24–27]. For a long-range electron transfer in a synthetic system, the mediation effects of 3-methylindole as a tryptophan model compound on photoinduced electron transfer from the tris(2,2′-bipyridine)ruthenium(II) complex [$Ru(bpy)_3^{2+}$] to methylviologen (MV^{2+}) have been investigated in a polymer membrane [28]. This result indicated that the electron transfer distance doubled in the presence of 3-methylindole. Furthermore, it is reported that for electrochemical water oxidation in a polymer membrane, the

* Corresponding author. Fax: +81-268-24-7248.
E-mail address: msuzuki@giptc.shinshu-u.ac.jp (M. Suzuki).

0032-3861/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00471-2

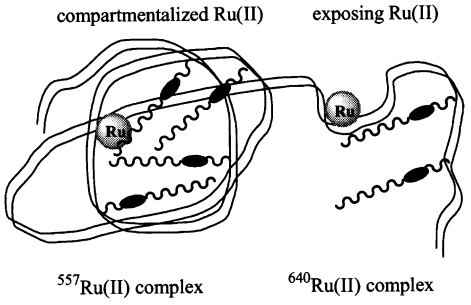


	k	l	m	n
RuVPIm	0.004	0.113	—	0.883
RuVQPIm	0.004	0.113	0.134	0.749

Fig. 1. Chemical structure of RuVPIm and RuVQPIm.

charge transfer distance between reactive centers increases in the presence of *p*-cresol from 1.28 to 2.25 nm, indicating that the *p*-cresol functions as a mediator for the charge transport [29,30].

Recently, we have reported that the L-tyrosine esters enhance the quenching efficiency in RuQPIms/viologens systems [31,32]. Furthermore, the effects of the L-tyrosine esters on the photosensitized charge separation reaction for RuQPIms/viologens/triethanolamine systems have been investigated [33]. In this paper, we describe the effects of L-tyrosine esters on the luminescence properties of the polymer-bound ruthenium(II) complex and viologen based on poly(1-vinylimidazole) (RuVPIm) and partially quaternized poly(1-vinylimidazole) (RuVQPIm), and the photosensitized charge separation reaction using these polymers in methanol (see Fig. 1 showing the chemical structure of RuVPIm and RuVQPIm). These polymers can achieve the photosensitized charge separation more efficiently than the RuQPIm/viologen systems because they have electron-donating [ruthenium(II) complexes] and electron-accepting (viologen residues) sites on the same polymer backbone [34,35]. These polymers have two emission maxima of 557 (^{557}Ru(II) complex residue) and 640 nm (^{640}Ru(II) complex residue) at a 488 nm excitation wavelength, corresponding to the ruthenium(II) complex residues compartmentalized by viologen residues and alkyl side chains and exposed to the bulk solution, respectively (Scheme 1) [36].



Scheme 1.

2. Experimental

2.1. Materials

L-Tyrosine, alkyl alcohols, and other reagents (commercially available guaranteed reagents) were used without further purification. Poly(1-vinylimidazole) or partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complex and viologen (RuVPIm or RuVQPIm) were prepared by a method described elsewhere [34]. The L-tyrosine esters with hexyl (C_6Tyr), octyl (C_8Tyr) and dodecyl (C_{12}Tyr) groups were prepared according to the literature [32].

2.2. Measurements

UV–Vis spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. Luminescence spectra were measured using a JASCO FP-750 spectrofluorometer.

Photosensitized charge separation reactions were carried out in methanol solutions containing 3.0×10^{-5} M RuVPIm or RuVQPIm, 0.1 M triethanolamine (TEOA) and various concentrations of L-tyrosine esters at 25°C under an argon atmosphere. A spectroscopic cell (1×1 cm^2) containing RuVPIms, TEOA and L-tyrosine esters in methanol was irradiated using a 300 W slide projector (CABIN Industry Co., Ltd, PROCABIN 67-Z) equipped with a UV cutoff filter ($\lambda > 440$ nm). The absorbance of the solution at 605 nm, which corresponds to the absorption maximum of the viologen radical ($\epsilon_{605} = 13400\ M^{-1}\ cm^{-1}$), was monitored as a function of the irradiation time. The initial rate of the viologen radical formation was calculated from the initial linear portion in the plot of the concentration of the viologen radical versus irradiation time. In all systems, experimental errors are within ± 0.05.

3. Results

3.1. Absorption and emission spectra

UV–Vis absorption spectrum measurements show that these polymers have an absorption maximum at 488 nm, which is a metal-to-ligand charge transfer (MLCT) band. As shown in Fig. 2, the luminescence properties of these polymer photosensitizers are hardly affected by quaternization because the quaternary degree of RuVQPIm is low.

3.2. Influence of L-tyrosine esters on luminescence properties

Fig. 3 shows the change in the luminescence intensity (I/I_0) at 557 (A) and 640 nm (B) with increasing concentration of the L-tyrosine esters. Here, I_0 and I represent the luminescence intensities in the absence and in the presence of the L-tyrosine esters, respectively. With the increasing concentration of the L-tyrosine esters, the luminescence

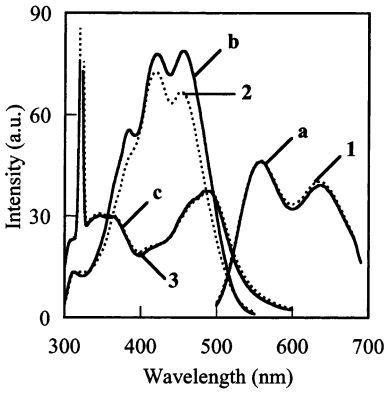


Fig. 2. Luminescence and excitation spectra of RuVPIm (solid lines: a, b, and c) and RuVQPIm (dotted lines: 1, 2, and 3) at ca. 3.0×10^{-5} mol dm^{-3} in the absence of L-tyrosine esters in methanol. (a and 1): Luminescence spectra at an excitation wavelength of 488 nm; (b and 2): excitation spectra for emission at 557 nm; (c and 3): excitation spectra for emission at 640 nm.

intensities decreased. Although these L-tyrosine esters interact with the polymers, they do not quench the ruthenium(II) complex residues [31,32]. Therefore, the ruthenium(II) complex residues with emissions at 557 (^{557}Ru(II) complex residue) and 640 nm (^{640}Ru(II) complex residue) are quenched by the viologen residues through the L-tyrosine esters; namely, the L-tyrosine esters mediate quenching of these ruthenium(II) complex residues with the viologen residue. The luminescence intensity of ^{560}Ru(II) complex residues decreased, while that of the ^{640}Ru(II) complex residues increased with increasing length of the alkyl groups in the L-tyrosine esters. These results indicate that the increase in the alkyl chain length of the L-tyrosine esters enhances the quenching of the ^{557}Ru(II) complex residues, while it decreases the quenching of ^{640}Ru(II) complex residues.

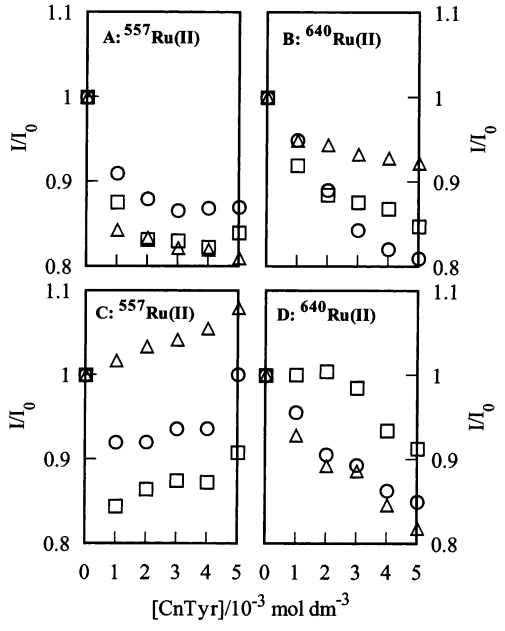


Fig. 3. Changes in luminescence intensity (I/I_0: I_0 and I are the luminescence intensities in the absence and in the presence of L-tyrosine ester) at 557 and 640 nm with increasing concentration of the L-tyrosine esters for RuVPIm (A, B) and RuVQPIm (C, D): (○): C_6Tyr; (□): C_8Tyr; (△): C_{12}Tyr.

As shown in Fig. 3, the luminescence of the ^{640}Ru(II) complex residue decreased with increasing concentration of the L-tyrosine ester for all the L-tyrosine esters. In contrast, the luminescence of the ^{557}Ru(II) complex residue decreased and then increased for the C_6Tyr and C_8Tyr systems, while it increased for the C_{12}Tyr system. Furthermore, the luminescence intensities of the ^{557}Ru(II) complex residues and ^{640}Ru(II) complex residues were in the order of C_{12}Tyr > C_6Tyr > C_8Tyr and C_8Tyr > C_6Tyr > C_{12}Tyr, respectively.

Compared with both the polymer systems, the luminescence intensities of the ^{557}Ru(II) and ^{640}Ru(II) complex residues on the RuVPIm were smaller than those on the RuVQPIm for all the L-tyrosine ester systems except the ^{640}Ru(II) complex/C_{12}Tyr system. This fact indicates that the quenching of the ruthenium(II) complex is restricted by quaternization. In contrast, the quenching of the ^{640}Ru(II) complex residue is accelerated by quaternization.

3.3. Photosensitized charge separation

With the visible light irradiation ($\lambda > 440$ nm) of a methanol solution containing the polymer and triethanolamine (TEOA) under an argon atmosphere, the absorbance at 605 nm, corresponding to the absorption maximum of the viologen radical species, increased. Furthermore, the initial rates of the viologen radical formation linearly depended on the concentration of the ruthenium(II) complex residues. Therefore, this reaction proceeds through an intra-polymer process.[1]

Fig. 4 shows the dependence of the initial rate of the viologen radical formation on the concentration of the L-tyrosine esters for RuVPIm (A) and RuVQPIm (B). For the RuVPIm system, the initial rate of the viologen radical formation was increased by the addition of the L-tyrosine esters, and decreased with increasing concentration of the L-tyrosine esters. Furthermore, the initial rate decreased with increasing length of the alkyl group in the L-tyrosine esters. This behavior was similar to the luminescence intensity of the ^{557}Ru(II) complex residue and the contradictory behavior for that of the ^{640}Ru(II) complex residue.

For the RuVQPIm system, the initial rate was also increased by the addition of the L-tyrosine esters, and

[1] In these systems, the initial rates of the viologen radical formation revealed linear dependence on the concentrations of ruthenium(II) complex residue. With increasing concentration of the ruthenium(II) complex residue, that of the viologen residues also increases because these polymers have both ruthenium(II) complex and viologen on the same polymer backbone. The reaction rate of inter-polymer (bimolecular) process reveals a second-order dependence on the ruthenium(II) complex concentration. Therefore, these systems proceed through intra-polymer (unimolecular) process.

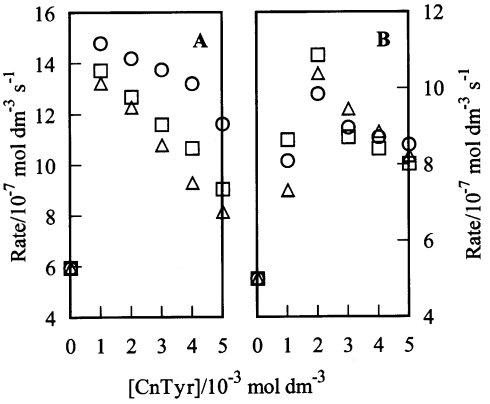
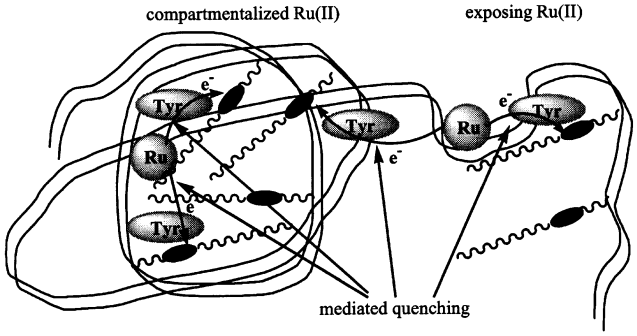


Fig. 4. Dependence of the initial rate for the viologen radical formation on concentration of the L-tyrosine ester for RuVPIm (A) and RuVQPIm (B): C_6Tyr:(○); C_8Tyr:(□); C_{12}Tyr:(△).



Scheme 2.

decreased with increasing concentration of the L-tyrosine esters. The length of the alkyl group in the L-tyrosine esters slightly affected the initial rate in a high concentration range of the L-tyrosine ester in the order of C_8Tyr < C_6Tyr < C_{12}Tyr. At a low L-tyrosine ester concentration, however, the initial rate depended on the length of the alkyl side chain in the order of C_{12}Tyr < C_6Tyr < C_8Tyr. In a low L-tyrosine ester concentration, the order of the initial rate was similar to that of the luminescence intensity of the ^{557}Ru(II) complex residue. In contrast, the order for the high concentration was similar to that of the ^{640}Ru(II) complex residue, although the difference was very small. Compared with these polymers, the initial rate of the viologen radical formation for the RuVPIm system was larger than that for RuVQPIm system, having the same behavior for the luminescence.

4. Discussion

4.1. Luminescence properties of RuVPIm

These polymers have two ruthenium(II) complex residues with emission maxima at 557 and 640 nm, which are the compartmentalized species and exposed one, respectively. Furthermore, it is well-known that these L-tyrosine esters interact with the ruthenium(II) complex containing poly(1-vinylimidazole) and partially quaternized poly(1-vinylimidazole) [31,32]. Considering these facts, the L-tyrosine esters undergo interaction with these polymers in the present system. This is supported by the enhancement of quenching induced by the addition of the L-tyrosine esters (Scheme 2). For the low concentration of the L-tyrosine esters, most of the L-tyrosine esters interact with a solvophobic domain where the viologen residues and the polymer backbone closely aggregate and compartmentalize the ^{557}Ru(II) complex residues.

The van der Waals interaction between the solvophobic domain and L-tyrosine ester becomes strong with increasing length of the alkyl group in the L-tyrosine esters, and the incorporation of the L-tyrosine ester into the solvophobic domain is facilitated. Some L-tyrosine esters incorporated into the solvophobic domain act as an electron pathway molecule (mediator); namely, the L-tyrosine esters mediate the intra-polymer quenching of the ^{557}Ru(II) complex residue with the viologen residue, leading to a decrease in the luminescence intensity. Furthermore, the amount of L-tyrosine esters incorporated into the solvophobic domain has a limitation (probably at 1.0×10^{-3} M of L-tyrosine esters), which brings about a slightly decreased or almost constant luminescence intensity in the high L-tyrosine ester concentration range (Fig. 3A). Therefore, the mediated effect on the quenching of the ^{577}Ru(II) complex residues is constant above 1.0×10^{-3} M of L-tyrosine esters.

The steric hindrance and van der Waals interaction between the L-tyrosine esters and the solvophobic domain increase with increasing length of the alkyl group in the L-tyrosine esters. The steric hindrance hardly affects the interaction with the solvophobic domain because the mediated effect of the L-tyrosine ester with a long alkyl group on the quenching is large. The molecular sizes of the L-tyrosine esters are an important factor. Although the L-tyrosine esters are fixed to the solvophobic domain to some extent through van der Waals interaction, the L-tyrosine ester with a large molecular size can flexibly move in the solvophobic domain. Consequently, the mediated effect on the quenching of the ^{557}Ru(II) complex residue increases.

Above 1.0×10^{-3} M of L-tyrosine esters, these L-tyrosine esters interact with the polymer backbone, and some L-tyrosine esters interacting with the polymer backbone mediate the quenching of the ^{640}Ru(II) complex residues with the viologen residues. The mediated effect, depending on the number of interacting L-tyrosine esters, increases with increasing L-tyrosine ester concentration. As mentioned above, both the steric hindrance and the van der Waals interaction increase with increasing length of the alkyl group in the L-tyrosine esters. The interaction of the L-tyrosine esters with the polymer backbone is relatively weak and the polymer backbone is flexible comparable to the solvophobic domain. This flexibility of the polymer backbone decreases the van der Waals interaction with the L-tyrosine

esters, which is more effective for the L-tyrosine ester with the large molecular size. Therefore, the mediated effect of the L-tyrosine esters on the quenching of the ^{640}Ru(II) complex residues is more effective for the L-tyrosine ester with a short alkyl group. It is noteworthy that the mediated effect on the quenching of the ^{557}Ru(II) complex residue (in the solvophobic domain) is more effective for the L-tyrosine ester with the long alkyl group, while that of the ^{640}Ru(II) complex residue is more effective for the L-tyrosine ester with the short alkyl group.

4.2. Luminescence properties of RuVQPIm

Though the luminescence properties of these polymers are hardly affected by quaternization, the influence of the L-tyrosine esters on the luminescence properties of these polymers differ dramatically. This could be attributed to the fact that a structurally different solvophobic domain is formed by quaternization. The C_6Tyr and C_8Tyr clearly demonstrate the mediated effect on quenching of the ^{557}Ru(II) complex residues, while the C_{12}Tyr does not have the mediated effect and enhances the luminescence intensity. In the high concentration range, however, C_6Tyr and C_8Tyr enhance the luminescence intensity. These facts suggest that the solvophobic domain on the RuVQPIm does not have a limitation for the number of L-tyrosine esters interacting with it. Although the largest mediated effect is demonstrated at a 1.0×10^{-3} M C_6Tyr and C_8Tyr concentration, further interaction of the L-tyrosine esters restricts the mediated effect. The C_{12}Tyr undergoes a relatively strong interaction with the solvophobic domain. The interaction restricts the thermal motion of the ^{557}Ru(II) complex residues leading to an increase in the luminescence intensity.

The quaternization with long alkyl groups (hexadecyl) forms the optimized place in the solvophobic domain to incorporate the C_8Tyr. Namely, the solvophobic domain is able to incorporate the C_8Tyr into the place where the C_8Tyr species can effectively mediate the quenching. Although this place would be able to incorporate more C_6Tyr species than C_8Tyr due to its small molecular size and the C_6Tyr also demonstrates the mediated effect, the efficiency of the mediated effect is small. In contrast, the mediated effect of C_8Tyr on the quenching of the ^{640}Ru(II) complex residue is small. This is the reason why the number of C_8Tyr species interacting with the polymer backbone is less than the other L-tyrosine esters because the C_8Tyr species predominantly undergo an interaction with the solvophobic domain. The C_6Tyr and C_{12}Tyr undergo an interaction with the polymer backbone, thus leading to the effective mediated effect.

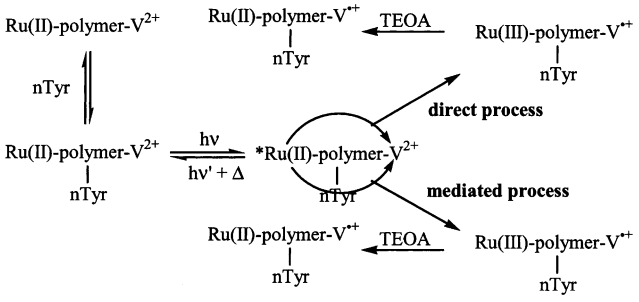
4.3. Photosensitized charge separation

Since the quenching reaction proceeds through two processes which are mediated by the L-tyrosine esters and not mediated, the photosensitized charge separation reaction also takes place through two processes as shown in Scheme 3.

Here, these processes, which are mediated by the L-tyrosine and proceed through direct electron transfer to the viologen residue, are abbreviated as the mediated process and the direct one, respectively. For both polymer systems, the initial rates of the viologen radical formation are increased by the addition of the L-tyrosine esters. This is clearly attributed to the mediated effect of the L-tyrosine esters.

4.3.1. RuVPIm system

The sharp enhancement of the initial rate induced by the addition of 1.0×10^{-3} M L-tyrosine ester corresponds to the sharp decrease in the luminescence intensity of the ^{557}Ru(II) complex residues (the enhancement of quenching). The decrease in the initial rate with increasing concentration of the L-tyrosine ester is similar to the behavior of the luminescence intensity of the ^{640}Ru(II) complex residues. At 1.0×10^{-3} M L-tyrosine ester, most of the L-tyrosine esters is incorporated into the solvophobic domain, and some L-tyrosine esters mediate the quenching of the ^{557}Ru(II) complex residue. In addition, the L-tyrosine esters barely interact with the polymer backbone at this concentration. Above 1.0×10^{-3} M L-tyrosine ester, the added L-tyrosine esters predominantly undergo an interaction with the polymer backbone because many L-tyrosine esters already interact with the solvophobic domain. Therefore, the photosensitized charge separation reaction in the solvophobic domain [^{557}Ru(II) complex residues] proceeds through only the mediated process, while the reaction of the ^{640}Ru(II) complex residues proceeds through both the processes. For the reaction of the ^{640}Ru(II) complex residue, the direct process decreases and the mediated one increases with increasing L-tyrosine ester concentration. The result obtained from the luminescence studies reveals that, above 1.0×10^{-3} M L-tyrosine esters, the mediated effect in the solvophobic domain is almost constant (or slightly decreased) and that of the ^{640}Ru(II) complex residue increases with increasing concentration of the L-tyrosine esters. Considering this result, it appears that the initial rate is enhanced by the mediated process in the solvophobic domain, and the decrease in the initial rate with increasing L-tyrosine ester concentration is caused by the mediated



Scheme 3.

process of the ^{640}Ru(II) complex residues. That is to say, the mediated effect in the solvophobic domain enhances the initial rate, while that of the ^{640}Ru(II) complex residues decreases. It is likely that the mediated effect of the L-tyrosine esters on the photosensitized charge separation reaction of the ^{640}Ru(II) complex residue accelerates not only quenching reaction but also back reaction. The L-tyrosine esters interacting with the polymer backbone can move to some extent due to the flexibility of the polymer backbone. Consequently, the flexible motion of the L-tyrosine esters allows them to act as the mediator molecules for both the quenching and back reactions. On the other hand, the mediated effect in the solvophobic domain only has acceleration of quenching. Probably, the L-tyrosine esters are fixed at a particular location in the solvophobic domain, where the L-tyrosine esters act as a mediator molecule (electron pathway molecule) for the quenching reaction only. In the mediated process, the L-tyrosine esters would always exist near the electron donor molecules. If the L-tyrosine esters exist near the electron acceptor, the electron transfer between the donor and acceptor is not necessarily mediated. Namely, in the presence of L-tyrosine esters near the donor, the electron transports to the acceptor through the L-tyrosine esters, while, in that near the acceptor, the electron transfer do not necessarily take place through the mediator molecule (the direct electron transfer to the acceptor also occurs). Since the mediated process only proceeds in the solvophobic domain and quenching reaction is mediated by the L-tyrosine esters, it is assumed that the L-tyrosine esters fixed to the domain exist near the Ru(II) complex residues. In contrast, the electron donor is the viologen radical species in the back reaction. The fixed L-tyrosine esters cannot move towards the viologen radical species.

With the increasing length of the alkyl groups in the L-tyrosine esters, the mediated effect in the solvophobic domain increases and that of the ^{640}Ru(II) complex residue decreases. This fact indicates that the mediated effect of the ^{640}Ru(II) complex residue contributes to the initial rate of the viologen radical formation, which can be explained as already mentioned.

4.3.2. RuVQPIm system

The initial rate of the viologen radical formation reveals a maximum value at 2.0×10^{-3} M of the L-tyrosine esters. For a low concentration of L-tyrosine esters, the mediated effect in the solvophobic domain contributes to the initial rate, which leads to an increase in the initial rate in the order of C_8Tyr > C_6Tyr > C_{12}Tyr. However, the initial rate is affected by the mediated effect of the ^{640}Ru(II) complex residue (C_{12}Tyr > C_6Tyr > C_8Tyr) in the high concentration range. For C_8Tyr and C_6Tyr, since the mediated effect of the ^{640}Ru(II) complex residue decreases the initial rate, the L-tyrosine esters undergoing an interaction with the polymer backbone act as a mediator for both the forward and back reactions. In addition, the restriction of the mediated effect in the solvophobic domain is also one of the factors that decreases the initial rate. On the other hand, the enhancement in the initial rate induced by the addition of the C_{12}Tyr is caused only by the mediated effect of ^{640}Ru(II) complex residue.

Comparing both the polymer systems, in the absence and in the presence of L-tyrosine esters, the initial rate in the RuVQPIm system is smaller than that in the RuVPIm system, which is attributable to the steric hindrance of the long alkyl side chains on the polymers. Although the initial rates for the RuVPIm system decrease with increasing molecular size of the L-tyrosine esters, those for RuVQPIm system show a maximum value for C_8Tyr at a low concentration. This is the reason why the solvophobic domain on RuVQPIm has a size-specificity for C_8Tyr to some extent and allows the C_8Tyr place on the site where it mediates only the quenching reaction.

5. Conclusion

We have revealed the effects of the L-tyrosine esters on the luminescence properties and photosensitized charge separation using RuVPIm and RuVQPIm having two kinds of ruthenium(II) complex residues on the same polymer backbone: one is a ^{557}Ru(II) complex residue compartmentalized into the solvophobic domain, the other is a ^{640}Ru(II) complex residue exposing to the bulk. The L-tyrosine esters act as mediators for electron transfer from the photoexcited ruthenium(II) complex to viologen residue. The photosensitized charge separation proceeds through direct and mediated processes for ^{640}Ru(II) complexes and only mediated process for ^{577}Ru(II) complexes. The mediated effect significantly depends on the length of the alkyl groups in the L-tyrosine esters and quaternization, which is explained by various effects such as the interaction of the L-tyrosine esters with these polymers, molecular sizes (alkyl chain length), and steric hindrance. In the solvophobic domain [^{557}Ru(II) complex residues], the L-tyrosine esters mediate the quenching reaction and make the initial rate of viologen radical formation increase. In contrast, the L-tyrosine esters mediate both the quenching and back reactions in the bulk [^{640}Ru(II) complex residues], which leads to decrease the initial rate. The initial rate strongly depends on the concentration of the L-tyrosine esters and the solvophobic domain has a limitation for the amount of the L-tyrosine esters that can incorporate; as a result, the initial rate relatively decreases at high concentration of the L-tyrosine esters because the mediated process through the ^{640}Ru(II) complex residues increases. Furthermore, it is found that the special site, where the C_8Tyr demonstrates the most effective mediated effect among these L-tyrosine esters, is formed by quaternization with hexadecyl groups. This result suggests that the domain, having a size-specificity for the L-tyrosine esters, can be formed by changing the degree of quaternization and the length of the quaternized alkyl side chains.

Acknowledgements

This work was supported by a Grant-in-Aid for COE research (10CE2003) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] Kurimura Y, Shinozaki M, Ito F, Uratani Y, Shigehara K, Tsuchida E, Kaneko M, Yamada A. Bull Chem Soc Jpn 1982;55:380.
[2] Sassoon RE, Rabani J. J Phys Chem 1985;89:5500.
[3] Ennis PM, Kelly JM, O'Connell CM. J Chem Soc, Dalton Trans 1986:2485.
[4] Kaneko M, Nakamura H. Macromolecules 1987;20:2265.
[5] Ennis PM, Kelly JM. J Phys Chem 1989;93:5735.
[6] Forster RJ, Vos JG. Macromolecules 1990;23:4372.
[7] Worl LA, Strouse GF, Younathan JN, Baxter SM, Meyer TJ. J Am Chem Soc 1990;112:7571.
[8] Younathan JN, Jones Jr WE, Meyer TJ. J Phys Chem 1991;95:448.
[9] Baxter SM, Jones Jr WE, Danielson E, Worl LA, Strouse GF, Younathan JN, Meyer TJ. Coord Chem Rev 1991;111:47.
[10] Jones Jr WE, Baxter SM, Strouse GF, Meyer TJ. J Am Chem Soc 1993;115:7363.
[11] Leasure RM, Kajita T, Meyer TJ. Inorg Chem 1996;35:5962.
[12] Dupray LM, Meyer TJ. Inorg Chem 1996;35:6299.
[13] Suzuki M, Mori Y, Kimura M, Hanabusa K, Shirai H. J Chem Soc, Faraday Trans 1996;92:3599.
[14] Suzuki M, Yokoyama N, Mori Y, Kimura M, Hanabusa K, Shirai H. Macromol Chem Phys 1997;198:959.
[15] Suzuki M, Kobayashi S, Kimura M, Hanabusa K, Shirai H. Chem Commun 1997:227.
[16] Suzuki M, Kimura M, Hanabusa K, Shirai H. Macromol Chem Phys 1998;199:945.
[17] Palmer G, editor. Long range electron transfer in biology Structure and bonding, vol. 75. Berlin: Springer, 1991.
[18] Bolton JR, Mataga N, MacLendon G, editors. Electron transfer in inorganic, organic and biological systems ACS advances in chemistry series no. 228Washington, DC: American Chemical Society, 1991.
[19] Axup AW, Albin M, Mayo SL, Crutchley RJ, Gray HB. J Am Chem Soc 1988;110:435.
[20] Bowler BE, Meade TJ, Mayo SL, Richards JH, Gray HB. J Am Chem Soc 1989;111:8757.
[21] Beratan DN, Onuchic JN, Betts JN, Bowler BE, Gray HB. J Am Chem Soc 1990;112:7915.
[22] Farver O, Pecht I. J Am Chem Soc 1992;114:5764.
[23] Siddarth P, Marcus RA. J Phys Chem 1993;97:2400.
[24] Barry BA. Photochem Photobiol 1993;57:179.
[25] Kaneko M, Moriyoshi J, Yamada A. Nature 1980;285:468.
[26] Milosavljevic BH, Thomas JK. J Phys Chem 1985;89:1830.
[27] Colon J, Yang CY, Clearfield A, Martin CR. J Phys Chem 1990;94:874.
[28] Nagai K, Tsukamoto J, Takamiya N, Kaneko M. J Phys Chem 1995;99:6648.
[29] Yagi M, Kinoshita K, Kaneko M. J Phys Chem B 1997;101:3957.
[30] Kinoshita K, Yagi M, Kaneko M. Macromolecules 1998;31:6042.
[31] Suzuki M, Sano M, Kimura M, Hanabusa K, Shirai H. New J Chem 1998:1431.
[32] Suzuki M, Sano M, Kimura M, Hanabusa K, Shirai H. Eur Polym J 1999;35:221.
[33] Suzuki M, Sano M, Kimura M, Hanabusa K, Shirai H. J Polym Sci Part A, Polym Chem 1999;37:4360.
[34] Suzuki M, Kimura M, Hanabusa K, Shirai H. Acta Polym 1999; 50:45.
[35] Suzuki M, Yokoyama N, Kimura M, Hanabusa K, Shirai H. Eur Polym J 1999;35:1057.
[36] Suzuki M, Kobayashi S, Uchida S, Kimura M, Hanabusa K, Shirai H. Macromol Chem Phys 1998;199:937.