Kinetic Study on Electron-Transfer Quenching of a Photoexcited Ruthenium Complex in Polyelectrolyte Solutions

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ABSTRACT: The dynamics of the quenching reactions of photoexcited $Ru(bpy)_3^{2+}$ (tris(2,2′-bipyridine)-ruthenium(II)) by methylviologen quencher in poly(styrenesulfonate) (PSS) and the copolymers with butyl methacrylate aqueous solutions was investigated by means of laser flash photolysis and steady-state emission spectra. The emission of $Ru(bpy)_3^{2+*}$ was effectively quenched by the quencher in the polyelectrolyte aqueous solutions. The time-resolved emission decays in the presence of the quencher could be fitted to a nonexponential kinetics. The analysis equation for the emission decays was derived on the basis of a Poisson kinetic model analogous to that obtained in micellar systems. The validity of the equation was checked by quenching under a variety of conditions: changing the quencher concentration, the polymer concentration, the molecular weight of PSS, and the composition of copolymer. It can be concluded that a microdomain consisting of ca. 43 styrenesulfonate monomer units is formed around the ruthenium complex on the polymer chain just like a micelle domain and the effective quenching occurs by concentrating the viologen into this small domain. The numbers of styrenesulfonate monomer units forming the microdomain were nearly constant irrespective of the polymer concentration, the molecular weight of PSS used, and the copolymer composition in the PSS copolymers. Kinetic parameters are also discussed in comparison with the results in SDS micellar systems.

Introduction

Recently, photoinduced electron-transfer reactions in molecular assemblies such as micelles,[1] microemulsions,[2] vesicles,[3] and amphiphilic polymers[4] have received much attention and have been extensively investigated. The molecular assemblies have provided new environments where photoreactions frequently proceed with consequences different from those observed in a homogeneous solution.[1b,5] Especially, the kinetic behavior is characterized by a Poisson distribution of the substrates in the microheterogeneous domains offered by the molecular assembly in aqueous solution.[6-11] We have studied the kinetics of quenching of photoexcited ruthenium complexes in SDS micellar solution and showed that the quenching kinetics can be described by a micellar-like kinetics.[1c-e]

On the other hand, emission quenching techniques have been often employed to examine aggregation parameters for molecular assemblies (e.g., critical micellar concentration and aggregation number in a micellar system) and the partition of solutes between the microdomains and aqueous phases.[11-15] In this paper, we study the quenching of a photoexcited tris(2,2′-bipyridine)ruthenium complex ($Ru(bpy)_3^{2+*}$) by methylviologen quencher (MV^{2+}) in poly(styrenesulfonate) and the copolymers with butyl methacrylate aqueous solutions. It is shown that the kinetic behavior of the quenching can be analyzed by a micellar-like kinetic model. The properties of the microdomain and quenching reactivity in the polymer domain are also discussed.

Experimental Section

Materials. Poly(sodium styrenesulfonates) (PSS-1, -2, and -3) were prepared by free-radical polymerization with potassium persulfate as thermal initiator in water at 50 °C. Poly(sodium styrenesulfonate) copolymers (PSS-BM-1 and -2) were prepared by free-radical copolymerization of styrenesulfonate (SS) with butyl methacrylate (BMA) in a mixture of water and dimethylformamide (DMF). The polymers were purified by ion exchanging with cation (Dowex 50W-X8) and anion (Amberlite IRA-40) exchange resins, followed by ultrafiltration (Toyo ultrafilter UH-1). The average molecular weights of PSS-1, -2, and -3 were obtained by their intrinsic viscosities to be 1.1×10^6, 3.5×10^5, and 6.34×10^4, respectively. The copolymer compositions were determined by elemental analysis (PSS-BM-1: BMA/SS = 1; PSS-BM-2: BMA/SS = 2). $Ru(bpy)_3Cl_2 \cdot 6H_2O$ was synthesized according to published procedures.[16,17] Commercially available *N*,*N*′-dimethyl-4,4′-bipyridinium chloride was purified by recrystallization.

Measurements. The ruthenium complex was solubilized into freshly prepared aqueous polymer solutions. All of the sample solutions were sonicated and degassed under vacuum (5×10^{-5} Torr) by successive freeze-pump-thaw cycles. Laser photolysis experiments for emission decays were carried out with a Q-switched ruby laser; $Ru(bpy)_3^{2+}$ was excited with 347.1-nm photons (a laser pulse width of 18 ns), and the emission signal through a grating monochromator was monitored with a Sony-Tektronix 7844 oscilloscope. The computer fitting for emission decays was carried out by a program using a simplex method. For the emission quenching, the weighed quencher (MV^{2+}), which was sealed in a glass tube equipped with a break seal under vacuum, was added to the solution by breaking the seal. The steady-state fluorescence intensity was measured with a Shimadzu RF 503A spectrofluorometer.

Results and Discussion

Emission Properties of $Ru(bpy)_3^{2+*}$ in PSS Aqueous Solutions. The wavelengths of the emission maxima (uncorrected) and the lifetimes of $Ru(bpy)_3^{2+*}$ in various microheterogeneous environments are shown in Table I. Hydrophobic environments (SDS, PSS-1, and PSS-BM-1) result in a red shift in the emission maximum and a lengthening of the lifetime. It is reported that the hydrophobic interaction between PSS and the ligand of the ruthenium complexes leads to the enhancement of the emission intensity, which is accompanied by a lengthening of the lifetime.[18] The emission intensity and the lifetime

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Table I
Emission Maxima and Lifetimes for Ru(bpy)$_3^{2+*}$ in Various Molecular Assemblies

	H$_2$O	PSS-1	PSS-BM-1	SDS[a]	PMA[b]
emission,[c] nm	585	590	590	605	585
lifetime, s	0.6	0.8	0.8	0.8	0.63

[a] Sodium dodecyl sulfate. [b] Poly(methacrylic acid). [c] Uncorrected values.

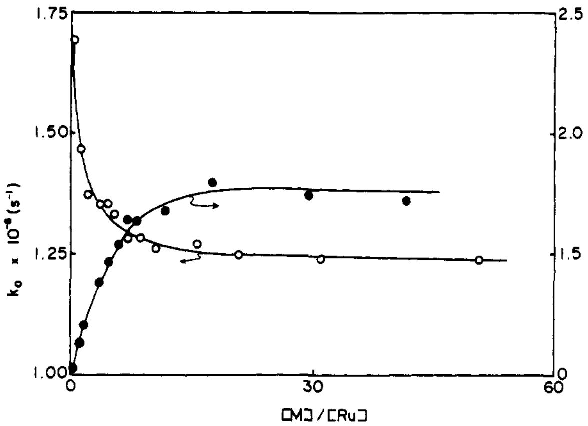

Figure 1. Emission intensity and lifetime of Ru(bpy)$_3^{2+*}$ at various PSS concentrations ([Ru] = 2 × 10^{-5} M (constant), [M] = concentration of styrenesulfonate monomer unit).

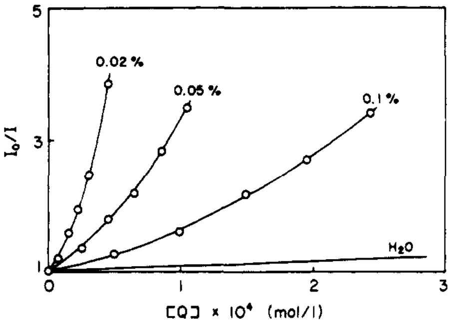

Figure 2. Stern–Volmer plots for the quenching of Ru(bpy)$_3^{2+*}$ by methylviologen at various PSS concentrations (weight percent).

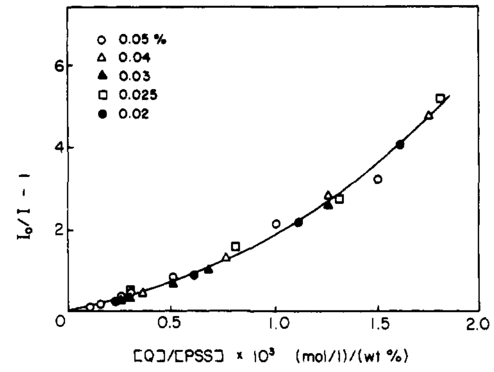

Figure 3. Plots of $I_0/I - 1$ against [Q]/[PSS].

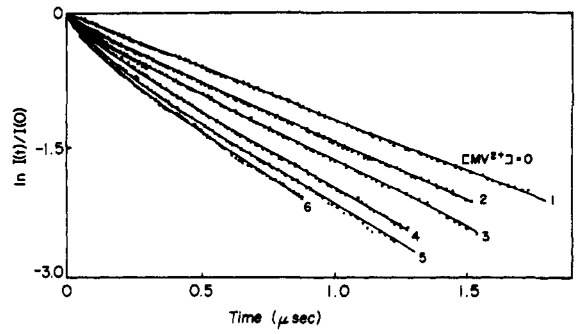

Figure 4. Emission decay of Ru(bpy)$_3^{2+*}$ in the quenching by methylviologen in 0.05% PSS aqueous solution at 22 °C ([MV^{2+}] (10^{-5} M): curve 1, 0; curve 2, 0.51; curve 3, 1.01; curve 4, 2.03; curve 5, 2.54; curve 6, 3.05). (—) Calculated. (···) Experimental.

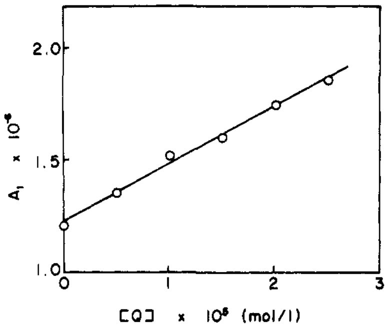

Figure 5. Dependence of A_1 upon [Q] for the quenching in 0.05% PSS solution.

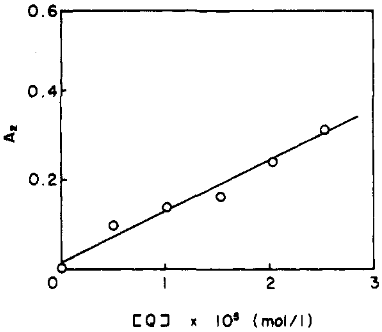

Figure 6. Dependence of A_2 upon [Q] for the quenching in 0.05% PSS solution.

of Ru(bpy)$_3^{2+*}$ were measured as a function of PSS concentration (Figure 1). The emission intensity increases and the lifetime lengthens with increasing PSS concentration. Under the condition where the concentration of PSS monomer unit is about 10 times larger than that of the ruthenium, both the emission intensity and the lifetime are approaching the respective constant values. It is supported that Ru(bpy)$_3^{2+}$ is solubilized and distributed homogeneously into the PSS polymer domain at the molar ratios, [PSS monomer unit]/[Ru(bpy)$_3^{2+}$] > 10. The subsequent quenching experiments of Ru(bpy)$_3^{2+}$ were carried out at molar ratios > 10.

Emission Quenching of Ru(bpy)$_3^{2+*}$ with MV^{2+}. The quenching reaction of Ru(bpy)$_3^{2+*}$ emission by MV^{2+} can be expressed by

$$\mathrm{Ru(bpy)_3}^{2+*} + \mathrm{MV}^{2+} \rightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{MV}^{+} \quad (1)$$

The steady-state emission quenchings in various PSS concentrations are shown in Figure 2. It is clear that compared to the bulk water, the quenching is more efficient in the presence of PSS, and for a given concentration of quencher the quenching is more efficient in more dilute PSS solutions. The enhancement in the apparent quenching efficiency (increase in the slope of Figure 2) can be attributed to the concentrating of both the ruthenium complex and quencher cations into the anion polymer (PSS) domain due to electrostatic and/or hydrophobic interactions. The Stern–Volmer plots of $(I_0/I - 1)$ against [Q]/[PSS], the ratio of the quencher concentration to the polymer concentration, were on the same line (Figure 3) irrespective of the PSS concentration, indicating that the quenching reaction occurs in the polymer phase.

In order to clarify the quenching mechanism, a kinetic analysis of the time-resolved emission decays in the presence of the quencher in PSS aqueous solutions was carried out. The emission decays in the presence of the quencher are nonexponential; that is, they consist of a rapid decay at initial stage and the subsequent slower decay (Figure 4). The emission decay can be analyzed by the equation which also is applicable in analysis of fluorescence decays in micellar systems:[6-9]

$$\ln (I(t)/I(0)) = -A_1 t - A_2(1 - \exp(-A_3 t)) \quad (2)$$

$I(0)$ and $I(t)$ are the emission intensities of $Ru(bpy)_3^{2+*}$ at $t = 0$ and t, respectively. A_1, A_2, and A_3 are expressed as the following kinetic model.

(a) Kinetic Model. Consider a quenching scheme similar to that in a micellar solution:

Quenching in domain

$$D_n^* \underset{h\nu}{\overset{k_0+nk_r}{\rightleftharpoons}} D_n$$

Exchange of quenchers between aqueous phase and domain

$$D_{n-1}^* + Q_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} D_n^*$$

Exchange of quenchers between domains

$$D_n^* + D_m \underset{(m+1)k_e}{\overset{nk_e}{\rightleftharpoons}} D_{n-1}^* + D_{m+1}$$

where Q_{aq} is a quencher in the aqueous phase and D_n is a domain containing the excited ruthenium complex and n quenchers. k_0 is the rate constant for the emission decay of $Ru(bpy)_3^{2+*}$ in the absence of quencher, k_r is the intradomain quenching rate constant, and k_f and k_b are the rate constants for the entrance and the exit of quencher between the aqueous phase and the micellar phase, respectively. It is assumed that the distribution of quencher and ruthenium complex per domain obeys Poisson statistics (K is the association constant = k_f/k_b) and that the photoexcited $Ru(bpy)_3^{2+}$ is quenched by MV^{2+} in the microdomain formed on the PSS polymer chains with a quenching rate constant k_r. We can obtain the equations for A_1 to A_3:

$$A_1 = k_0 + k_r K(1 - a_r)[Q]/(1 + K[D]) = k_0 + S_1[Q] \quad (3)$$

$$A_2 = K[Q]a_r^2/(1 + K[D]) = S_2[Q] \quad (4)$$

$$A_3 = k_r + k_b + k_e[D] \quad (5)$$

where a_r is the quenching efficiency ($=k_r/(k_r + k_b + k_e[D])$). [Q] and [D] represent the total concentration of quencher and microdomain, respectively. We consider that a microdomain is analogous to a micelle and consists of m monomer (SS) units; that is, the value m just corresponds to the aggregation number in micellar system. [D] is expressed by $[M]/m$; [M] is the total concentration of SS monomer units.

At first we analyzed the emission decays using eq 2 and determined the unknown parameters of A_1, A_2, and A_3 at various quencher concentrations by a computer-fitting method (the solid lines in Figure 4 are the fitted results). The plots of A_1 and A_2 against the quencher concentration gave straight lines (Figures 5 and 6) and satisfy eqs 3 and 4. A_3 was independent of [Q]. Moreover, the following relationships are derived from eqs 3 and 4:

$$1/S_1 = 1/Kk_r(1 - a_r) + [M]/mk_b a_r \quad (6)$$

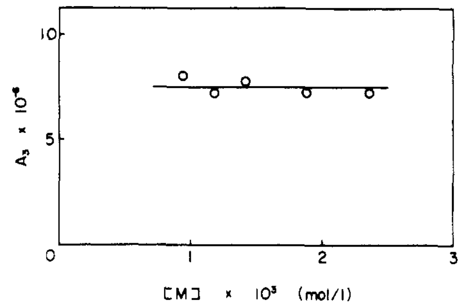

Figure 7. Dependence of A_3 upon [M] for the quenching in 0.05% PSS solution.

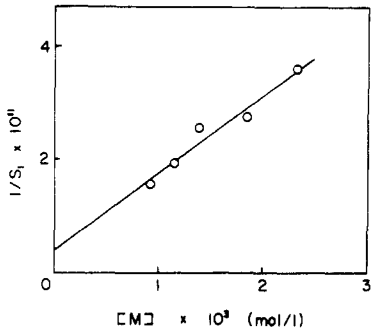

Figure 8. Plots of $1/S_1$ vs [M] (see text).

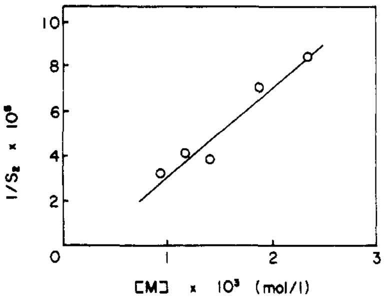

Figure 9. Plots of $1/S_2$ vs [M] (see text).

$$1/S_2 = 1/Ka_r^2 + [M]/ma_r^2 \quad (7)$$

The relationships in eqs 5–7 were confirmed by the quenching experiments with varying PSS concentration. A_3 does not change widely at various PSS concentrations (Figure 7), indicating that the exchange process of quenchers between microdomains during the lifetime of the excited ruthenium complex, which is considered in a micellar solution,[8] is negligible in the present experimental conditions. S_1 values were obtained from the slope of similar plots with Figure 5 at various PSS concentrations, and $1/S_1$ was plotted against [M] (Figure 8), giving a good linear relationship. A similar plot was obtained for S_2 (Figure 9). This clearly indicates that the time-resolved emission decays of $Ru(bpy)_3^{2+*}$ in the presence of MV^{2+} quencher in PSS aqueous solution can be analyzed by eqs 2–5.

(b) Quenching Parameters. Kinetic parameters based on the quenching processes in PSS aqueous solutions were evaluated from the analysis of the emission decay by the equations described above. The association constant (K) for methylviologen with the microdomain was estimated to be 1.8×10^5 M^{-1}, which is slightly less than that with SDS micelle (10^6 M^{-1}).[1c] This may be due to the difference in hydrophobicity between SDS micelle and PSS. The intradomain quenching rate constant (k_r) was determined to be 6.2×10^6 s^{-1}, and the quenching efficiency (a_r) was 0.79.

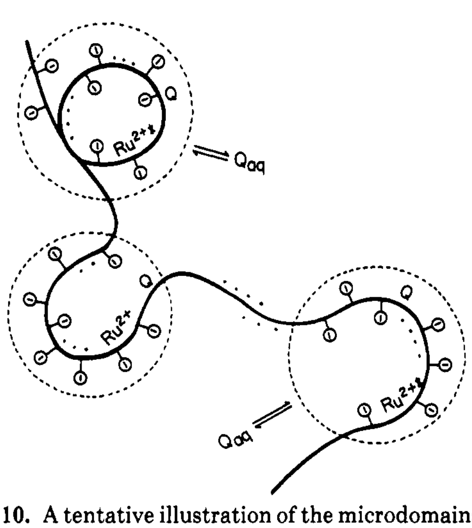

Figure 10. A tentative illustration of the microdomains formed on a PSS polymer chain.

Table II
Kinetic Parameters for the Quenching of $Ru(bpy)_3^{2+*}$ by Methylviologen in Poly(styrenesulfonates) and the Copolymers

polymer	k_r, 10^6 s^{-1}	monomer units/domain	a_r
PSS-1	6.2	43 ± 4	0.79
PSS-1 (0.1M NaCl)	6.7	41	0.78
PSS-2	6.8	42 ± 4	0.85
PSS-3	6.2	43 ± 5	0.80
PSS-BM-1	8.1	81 ± 11	0.86
PSS-BM-2	7.6	103 ± 10	0.88

In SDS micellar solutions,[1c,d] we have reported that the intramicellar quenching rate constants for various alkylviologens were 10^5–10^6 s^{-1}, which could be determined by using longer lifetime ruthenium complexes: $Ru(dpphen)_3^{2+}$ (dpphen = 4,7-diphenyl-1,10-phenanthroline, $k_0 = 1.6 \times 10^5$ s^{-1}) and $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline, $k_0 = 4.4 \times 10^5$ s^{-1}). When $Ru(bpy)_3^{2+}$ ($k_0 = 1.25 \times 10^6$ s^{-1}) was used as an emission probe in SDS micellar solution, the emission decay in the presence of methylviologen quencher showed a single-exponential decay. The rapid decay at short times due to the effective quenching becomes less remarkable when k_0 is comparable to k_r and the emission decay is nearly single exponential.[10,19] In the present PSS systems, an initial rapid emission decay was observed (Figure 4), indicating that the quenching in PSS systems is more effective than that in SDS and the value $k_r = 6.2 \times 10^6$ s^{-1}, which is larger than k_0 ($=1.25 \times 10^6$ s^{-1}), is reasonable.

Interesting information on the microdomain formed on the PSS chains can be obtained from the above analysis. The m value is the number of monomer units forming the microdomain. The analysis of the quenching in PSS-1 aqueous solution in the range of 0.02–0.05% polymer concentration indicates that 43 ± 4 monomer units form the microdomain. Although the structural features of the domain are not determined from the present work, the following picture can be considered: The styrenesulfonate anion groups gather around $Ru(bpy)_3^{2+*}$ by electrostatic binding and π-electron overlap interactions, forming a microdomain. A pictorial representation is shown in Figure 10, though no direct evidence of such as a micelle exists at present. The number of monomer units forming the microdomain does not change with dilution of the polymer nor with addition of NaCl (0.1 M) (Table II). Some amphiphilic polymers have been reported to form a similar hydrophobic microdomain, and the monomer units per domain have varied according to the amphiphilic polymers employed.[20-26] Recently, Sawaki et al. have reported the formation of organic cation–PSS polymer anion micelle-like clusters.[25] Hydrophobic microdomains consisting of 20–30 monomer units are reported in amphiphilic polymers having aromatic pendant groups.[20,21] Moreover, there are some reports that ionic polymers form clusters with 50–100 ionic groups.[22,23] The cluster in a Nafion membrane is formed of 67 ionic head groups (SO_3).[24]

We determined the m values in aqueous solutions of PSS having various molecular weights (1.1×10^6, 3.5×10^5, and 6.3×10^4) (Table II). The number of monomer units per microdomain did not change with the molecular weight of PSS. This means that a steady microdomain with a similar size is formed in the different polymer chain lengths. The microdomain is likely destroyed and reformed during polymer chain movements; however, the microdomain offers a steady reaction environment at least during the lifetime of excited $Ru(bpy)_3^{2+}$. The excited ruthenium probe in the microdomain is quenched by a methylviologen quencher in the same domain analogous to an SDS micelle.

The emission decays for the quenching in the PSS copolymers with butyl methacrylate (PSS-BM-1 and -2) were analyzed with the same method. A good fitting of the emission decay was obtained with eq 2. The obtained A_1–A_3 parameters satisfied the relationships expressed in eqs 3–5. The quenching rate constants and the quenching efficiencies were nearly equal to those in PSS (Table II). The number (m) of monomer units forming the microdomain increases with decreasing styrenesulfonate content in the copolymers. However, the number of styrenesulfonate anion groups forming a microdomain was nearly constant (about 40 units). The fraction of butyl methacrylate comonomer increases the m value. Further studies varying copolymer composition are necessary to gain more insight into the characteristics of the microdomain.

In conclusion, the emission decay for the quenching in poly(styrenesulfonate) aqueous solutions could be analyzed with a kinetic model analogous to that for micellar systems; a microdomain consisting of ca. 43 monomer units is formed on the polymer chains, and the effective quenching takes place by concentrating the ruthenium and the quencher into the small microdomain. The quenchings in PSS copolymer with butyl methacrylate were also analyzed with same kinetic model.

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References and Notes

(1) (a) Thomas, J. K.; Almgren, M. *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 2, p 559. (b) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982. (c) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529. (d) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1985**, *89*, 497. (e) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1989**, *93, 1426.

(2) (a) Yamaguchi, Y.; Miyashita, T.; Matsuda, M. *J. Phys. Chem.* **1981**, *85*, 1369. (b) Almgren, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.

(3) Nomura, T.; Escabi-Perez, J. R.; Sunamoto, J.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1484.

(4) (a) Miyashita, T.; Ohsawa, M.; Matsuda, M. *Macromolecules* **1986**, *19*, 585. (b) Meisel, D.; Matheson, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6577. (c) Meyerstein, D.; Rabani, J.; Matheson, M. S.; Meisel, D. *J. Phys. Chem.* **1978**, *82*, 1879. (d) Jonah, C. D.; Mahteson, M. S.; Meisel, D. *J. Phys. Chem.* **1979**, *83*, 257.

(5) Freeman, G. R. *Kinetics of Nonhomogeneous Processes*; Wiley: New York, 1987.

(6) Infelta, P. P.; Gratzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190.
(7) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289.
(8) Dederen, J. C.; Van der Auweraer, M.; De Schryver, F. C. *Chem. Phys. Lett*, **1979**, *68*, 451.
(9) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1978**, *53*, 165.
(10) Thomas, J. K. *J. Phys. Chem.* **1987**, *91*, 267.
(11) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3550.
(12) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.
(13) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543.
(14) Dederen, J. C.; De Schryver, F. C. *J. Phys. Chem.* **1981**, *85*, 1198.
(15) Almgren, M.; Swarup, S. J. *J. Phys. Chem.* **1983**, *87*, 876.
(16) Fujita, I.; Kobayashi, H. *Ber. Bunsen*-Ges. *Phys. Chem.* **1979**, *76*, 115.
(17) Plamer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.
(18) Duveneck, G. L.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *J. Phys. Chem.* **1988**, *92*, 2028.
(19) Rodgers, M. A.; Becker, J. C. *J. Phys. Chem.* **1980**, *84*, 2762.
(20) Morishima, Y.; Itoh, Y.; Nozakura, S. *Chem. Phys. Lett.* **1982**, 258.
(21) Kobayashi, K.; Sumitomo, H. *Macromolecules* **1980**, *13*, 234.
(22) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(23) Forsman, W. C. *Macromolecules* **1982**, *15*, 1032.
(24) Lee, P. C.; Meisel, D. *J. Am Chem. Soc.* **1980**, *102*, 5477.
(25) Takagi, K.; Fukaya, H.; Sawaki, Y. *J. Am. Chem. Soc.* **1988**, *110*, 7469.
(26) Miyashita, T.; Matsuda, M. *Polym. Commun.* **1984**, *25*, 138.

Registry No. MV^{2+}, 1910-42-5; PSS, 62744-35-8; (SS)(BMA) (copolymer), 131237-12-2; $Ru(bpy)_3Cl_2$, 74391-32-5.