Anomalous Luminescence and Emission Quenching Behaviors of Tris(2,2'-bipyridine)Ruthenium(II) in Poly(methacrylic acid) Solutions[1]

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The luminescence spectra of $Ru(bpy)_3^{2+}$ in poly(methacrylic acid) (PMA) solutions varied sensitively with pH. At pH<5.5, the emission intensity increased with pH up to 4 times, while it decreased with pH beyond the pH. The enhanced emission intensity was accompanied by blue-shift of the emission maxima as much as 15 nm. The enhancement of emission intensity was attributed to the restricted rotational mobility of ligand of the cation bound to densely coiled PMA molecules at pH<5.5. The sharp decrease in emission intensity with increasing pH near pH 5.6 was accounted for conformational transition of the polymer to more extended structure, which was also revealed in viscosity measurement. The enhancement of emission intensity became higher as NaCl concentration of the solution increased. The binding constant of $Ru(bpy)_3^{2+}$ with two carboxylate groups of PMA was calculated as 2×10^5 M^{-1} in 0.1 M NaCl at pH 5.2. The pH dependence of luminescence quenching rate of $Ru(bpy)_3^{2+}$ by Cu^{++} also showed maximum near pH 5, and the rate was more than 10^3 times higher than that in water, whereas the maximum enhancement of quenching rate (about 20 times) in poly(acrylic acid) (PAA) solution occurred at pH4.5. On the other hand, the pH dependence for neutral water soluble nitrobenzene (NB) exhibited opposite trend to that of Cu^{++}. The quenching constant vs pH curve for MV^{++} was composite of those for Cu^{++} and NB. The anomalous high quenching rate for Cu^{++} in PMA solution at pH<5.5 was attributed to the binding of $Ru(bpy)_3^{2+}$ and Cu^{++} to the same region of PMA, when it conforms densely coiled structure in the pH range. The observation of minimum quenching rate for NB near pH 5.5 indicated that the $Ru(bpy)_3^{2+}$ bound to the densely coiled PMA is not accessible by NB, which is in bulk water phase. The composite nature of the pH dependence of quenching rate for MV^{++} in PMA solution was attributed to the smaller binding affinity of the cation to PMA, compared to that of Cu^{++}. The sharp, cooperative conformational transition with pH observed in PMA was not revealed in PAA. But, the pH dependence of quenching rates in this polymer reflected increased charge density and, thus, binding of cations to the polymer, and expansion of the polymer chain with pH.

Introduction

In recent years, the photochemistry and photophysics of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, have drawn increased amounts of interest. This is primarily due to the promise of using the complex cation in the conversion of solar energy into the stored chemical energy.[2] The conversion is achieved via electron transfer from photoexcited $Ru(bpy)_3^{2+}$ to an electron relay, which splits water to produce hydrogen. In views of catalytic action of polyelectrolytes on th chemical reactions between ionic species having opposite charge to a polyelectrolyte, the luminescence and luminescence quenching behaviors of $Ru(bpy)_3^{2+}$ in anionic polyelectrolyte solutions have been investigated.[3] The enhancement of the photochemical reaction rate between $Ru(bpy)_3^{2+}$ and cationic quenchers, such as methyl viologen(MV^{++}) and Cu^{++}, was mainly ascribed to the increased local concentrations of the reacting species in the polyanionic domains. Previously, we reported the enhanced luminescence emission intensity(I_E) of $Ru(bpy)_3^{2+}$, as well as increased quenching reaction rate with MV^{++} and Cu^{++}, by poly(styrenesulfonate), PSS, whereas no appreciable changes in I_E and much less enhancement of the quenching rate were observed by poly(vinylsulfonate), PVS.[4] These results were attributed to the strong binding of $Ru(bpy)_3^{2+}$ onto PSS due to the hydrophobic and electrostatic interactions. The enhanced emission intensity and thus, the increased excited life-time of $Ru(bpy)_3^{2+}$ were also found when the cation is adsorbed onto polymerized silica,[5] porous vycor glass,[6] PSS column,[7] and anionic polyelectrolytes bearing a number of phenyl groups.[8]

For efficient photoinduced electron transfer from $Ru(bpy)_3^{2+}$ to a quencher, both longer life-time of the photosensitizer and higher local concentrations of the reacting pair are desirable. It is well known that poly(methacrylic acid), PMA, exhibits a conformational transition, when degree of neutralization is about 0.2, from the densely coiled conformation to the more extended one as pH is raised.[9-13] It is expected that the conformations of PMA could exert profound effects on the luminescing behaviors of $Ru(bpy)_3^{2+}$. Also, emission quenching rate with a quencher would be very high, provided that a quencher binds to PMA by chelation to carboxylate groups of the polymer in the coiled conformation. In this communication, we report the pH dependent emitting and emission quenching properties of $Ru(bpy)_3^{2+}$ with Cu^{++}, MV^{++} and nitrobenzene in PMA solutions. These are compared to those in poly(acrylic acid), PAA, solutions.[14]

Experimental

$Ru(bpy)_3(ClO_4)_2$ was prepared by reacting $RuCl_3\bullet xH_2O$ and 2,2' bipyridine in ethanol, followed by the reduction with Zn amalgam and then precipitation with aqueous $NaClO_4$. IR, UV-Vis and luminescence spectra of this sample were indentical to those of commercial sample from Aldrich. PMA and PAA were obtained from Polyscience and converted to their salt forms by neutralization with NaOH. The salts were dissolved in water and then precipitated with ethanol. The preparation of methyl viologen was described previously.[4] These chemicals were dried in a vacuum oven at 50°C over 24 hours before using. Other chemicals were commercially available reagent grade and used as received.

Solutions were prepared with deionized distilled water and contained 0.1 M NaCl, unless otherwise specified. The concentrations of $Ru(bpy)_3^{2+}$ and nitrobenzene were determined from absorbance values using $\varepsilon_{453} = 14000$ for $Ru(bpy)_3^{2+}$ and $\varepsilon_{264}^{EtOH} = 8800$ M^{-1} cm^{-1} for nitrobenzene. Concentrations of

PMA and PAA are expressed in terms of monomeric units based on the dried weight. Luminescence spectra(uncorrected) were recorded on a Hitachi 650-10S fluorimeter at 25°C at excitation wavelength of 450 nm as have been described previously.[4] Viscosity measurments were carried out using an Ubbelohde type viscometer at 25°C.

Results and Discussion

Luminescence in PMA and PAA Solutions. The absorption and emission spectra of $Ru(bpy)_3^{2+}$ in PMA solutions were essentially the same as those obtained in the absence of PMA, when pH of the solutions is lower than 3. The maxima of the spectra were shown at 453 and 600 nm, respectively. Unlike in water, the emission spectra in PMA solutions showed a remarkable pH dependence as shown in Figure 1. The emission intensity increased as much as 4 times at about pH 5, and the enhanced emission was always accompanied by the blue shift of the emission maximum up to 15 nm. Both the intensity and maximum of the emission spectrum above pH 7 were also very similar to those in water. Figure 2 shows the pH dependence of the emission intensity of photoexcited $Ru(bpy)_3^{2+}$ in PMA solutions and compared the same in PAA solutions at various concentration of NaCl. The curves for PMA solutions exhibit maxima near pH 5, at which it is known that PMA molecules undergo conformational transition.[8-12]

To correlate the pH dependence of the emission spectra of $Ru(bpy)_3^{2+}$ in PMA solutions to the conformation of the polymer, the variation of specific viscosity ($\eta_{sp} = \eta_{soln}/\eta_{solv} - 1$) of PMA solutions with pH was investigated. The results were plotted in Figure 3. The sharp increase in η_{sp} of 8 mM PMA solutons near pH 5.7 in 0.01 M NaCl is in good agreement with changes in emission intensity and maxima of $Ru(bpy)_3^{2+}$ in the solution. The titration of PMA solutions with NaOH revealed that the degree of neutralization of PMA is about 0.2 at the pH value.

The curves in Figure 3 can be interpreted in terms of neutralization of PMA, and subsequent binding of $Ru(bpy)_3^{2+}$ cation on the polymer and conformational transition of the polymer. At pH<3, PMA is not ionized and binding of $Ru(bpy)_3^{2+}$ to the polymer is negligible. Thus, the spectral properties of the cation are identical with those observed in water. Raising pH from this value neutralizes the PMA, and $Ru(bpy)_3^{2+}$ binds to the ionized polymer by electrostatic interaction. Even though the PMA swells as carboxylic group is ionized, it still exists as compact, densely coiled structure. The $Ru(bpy)_3^{2+}$ bound on this structure feels restricted rotational mobility of ligand around the metal, and excited life-time, which is parallel to the emission intensity, is increased. This interpretation accords well with the observed enhancement of emission intensity and excited life-time of the cation bound on rigid matrix. [4-8,16] The binding of $Ru(bpy)_3^{2+}$ to PMA increases with pH as evidenced from the increasing emission intensity with pH. The highest enhancement, four-fold, was observed at pH 5.2 in 0.1 M NaCl. This pH is about 0.5 pH unit lower than the pH value at which conformational transition of PMA is revealed in viscosity measurement. This implies that binding of $Ru(bpy)_3^{2+}$ (10 μM) to PMA (8 mM) is virtually completed at about pH 5.2. The sharp increase in η_{sp} at pH 5.7 reflects the conformational transition of PMA to more extended structure. In this structure, the bound $Ru(bpy)_3^{2+}$ regains the mobility of ligand and the emission spectra of the complex cation becomes the same as that in water.

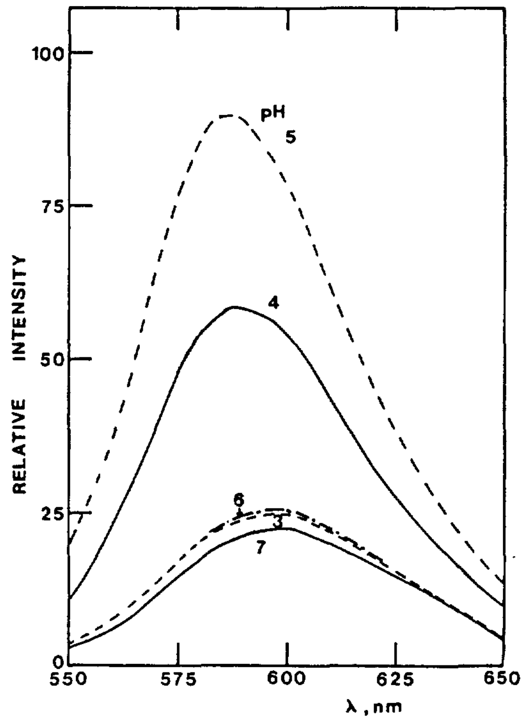

Figure 1. The pH dependence of emission spectra of 1x10^{-5} M $Ru(bpy)_3^{2+}$ in 8 mM PMA solutions containing 0.1 M NaCl at 25°C. Excitation wavelength was 450 nm.

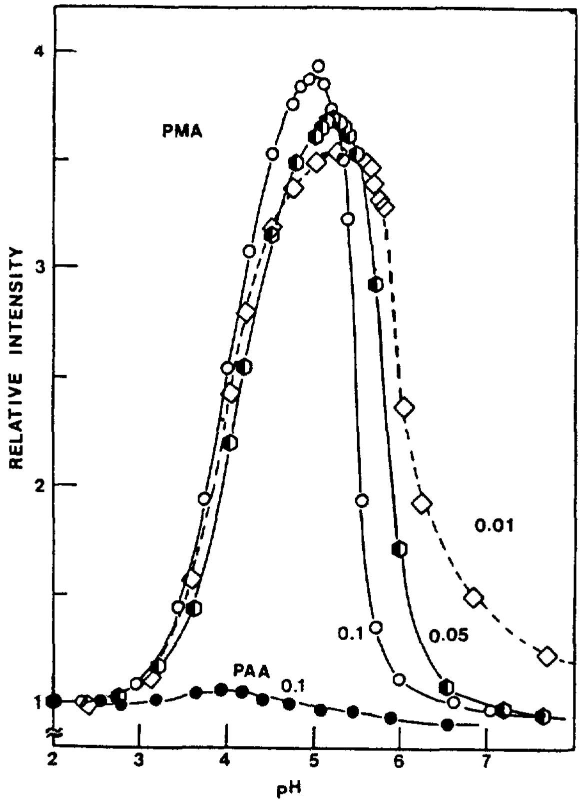

Figure 2. Relative changes of emission intensity of $Ru(bpy)_3^{2+}$ as function of pH in 8 mM PMA and PAA solutions. Salt concentrations are given in the Figure. Other conditions are the same as in Figure 1.

Similar abrupt decrease in emission intensity and red shift of emission maxima, when pH was raised through pH 5, were observed in the fluorescence of diphenylanthracene copolymerized with PMA.[16] This was also attributed to the conformational transition of PMA.

In contrast to PMA solutions, the pH dependence of luminescence spectra of Ru(bpy)$_3^{2+}$ in PAA solutions was very small (Figure 2). In these solutions, the maximum enhancement of emission intensity was only 6% at pH 4. Above this pH, the intensity decreased with increasing pH over wide pH range without noticeable change in emission maximum, 600 nm. The latter behavior is nearly identical to that observed in PAA-pendent Ru(bpy)$_3^{2+}$.[17] This result indicates that the conformational transition observed in PMA is minimized in PAA, and the decrease in emission intensity at pH>4 mainly arises from expansion of the polymer as degree of neutralization increases.

As can be seen in Figures 1 and 3, the increased emission intensity of Ru(bpy)$_3^{2+}$ in PMA solutions was accompanied by the blue shift of the spectra. This correlation between I_E and λ_{max} was also reported for the cation incorporated in polymerized silica by Wheeler and Thomas: they found a 27 nm blue shift of emission maximum and about sixfold increase in emission intensity.[5] However, the enhancement of emission intensity is not always parallel to the shift of emission maximum. In some systems, red shift are observed.[4] And no spectral shift are shown in other systems.[6,16] Unlike the emission spectra, the absorption spectra of Ru(bpy)$_3^{2+}$ in PMA solutions did not depend on pH. This implies that the ground state of Ru(bpy)$_3^{2+}$ are identical in free and bound states, whereas the emitting excited triplet states differ. The energy of this state may be determined by the microenvironment of the cation, rather than the flexibility of ligand which is related to the emission intensity.

Binding Constant of Ru(bpy)$_3^{2+}$ on PMA. The pH dependence of emission intensity at pH<5.5 in PMA solutions reflects the pH dependence of degree of binding of Ru(bpy)$_3^{2+}$ on the coiled PMA. At a given pH(for example, 5.2) the binding increases with concentration of PMA, which manifests as enhanced emission and blue-shift of the emission maxima. Figure 4 shows the results at pH 5.2. If we assume that the relative increase in the emission intensity is directly proportional to the fraction(f) of Ru(bpy)$_3^{2+}$ bound to PMA, the apparent binding constant(K) can be evaluated from Equation 1, as described previously.[4]

$$\log (f/(1-f)) = \log K + n(\log[PMA] - \log 2) \qquad (1)$$

This equation is for 1:2 binding and assumes that all carboxylic groups are available for binding of Ru(bpy)$_3^{2+}$. n is an empirical parameter. The fractions(f) of Ru(bpy)$_3^{2+}$ bound on the PMA were calculated from the emission intensity vs [PMA] curve. The results were plotted according to Equation 1 in inset of the Figure. The log K and n values were 4.6 and 1.4, respectively. Since Ru(bpy)$_3^{2+}$ does not bind to PMA at low pH, the binding of the cation to PMA is electrostatic in origin. In this case, the apparent binding constant K should be corrected by the degree of neutralization of PMA, 0.2, at the pH, 5.2. This correction can be made by division of the K value by 0.2. The corrected apparent binding constant was 2x10^5 M^{-1}. This value is about three times higher than the binding constant of the cation on PSS.[4] This difference can not be explained by considering only electrostatic interaction. Previously, we attributed the much higher binding constant of Ru(bpy)$_3^{2+}$ on PSS than that on PVS to contribution of hydrophobic effect on the former interaction. The same explanation can be given to the high binding affinity of the cation on PMA.

Luminescence Quenching in PMA and PAA Solutions.

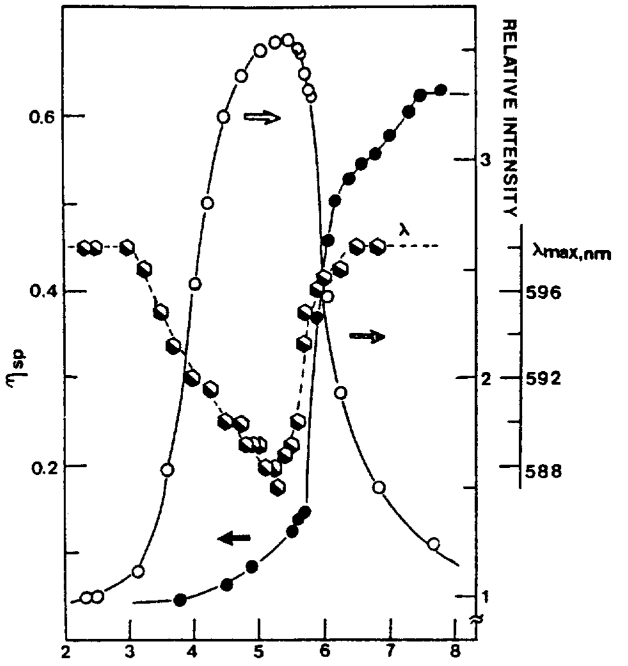

Figure 3. The pH dependences of emission intensity at peak(○), and of wavelength of emission maxima(◐) in 8 mM PMA solutions. (●) is variation of specific viscosity of the PMA solutions with pH.

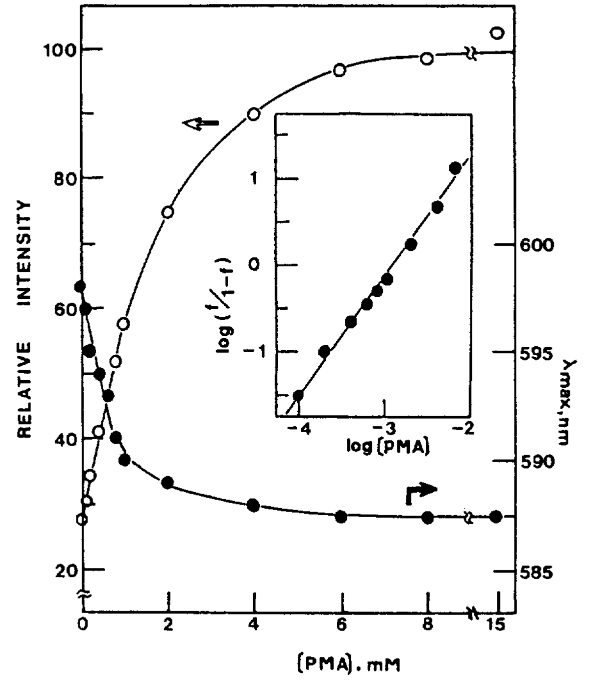

Figure 4. Variations of emission intensity(○) and emission maxima(●) with concentrations of PMA at pH 5.2 in 0.1 M NaCl solutions. Inset is the plot of emission intensity data according to Equation 1.

The luminescence quenching of $Ru(bpy)_3^{2+}$ in PMA solutions by methyl viologen(MV^{++}), Cu^{++}, and nitrobenzene(NB) were investigated by varying pH of the solutions at fixed concentration of the polymer, 8 mM. The results were compared with those in PAA solutions. The quenching data were analyzed by using Stern-Volmer Equation.

$$I_0/I = 1 + K_{SV}[Q] \qquad (2)$$

I_0 and I denote the emission intensity in the absence and presence of a quencher Q. The Stern-Volmer constant, K_{SV} is related to the luminescence life-time(τ_E) and the bimolecular rate constant(kq) for the quenching reaction by $K_{SV} = \tau_E$ kq.

The quenching of $Ru(bpy)_3^{2+}$ luminescence by Cu^{++} at three different pH values were plotted in Figure 5 according to Equation 2. The quenching data at pH 2 followed the simple Stern-Volmer kinetics(Equation 2), and the K_{SV}'s were calculated as 60 and 80 M^{-1} in PMA and PAA solutions, respectively. These values correspond to k_q value of $1.5\text{-}2\times10^8$ $M^{-1}s^{-1}$ as the life-time of $Ru(bpy_3^{2+}$ is 0.4 μsec in air saturated aqueous solutions.

At pH 5, the quenching data for Cu^{++} in PMA solution show large positive deviation from the Stern-Volmer equation. Such deviation is observed in homogeneous systems[19] as well as in microheterogeneous systems.[16] The negative deviation in Stern-Volmer plot as shown in PMA at pH 6.8 and in PAA at pH 5 and 6.8 is quite common for quenching reactions between charged species having opposite charge to polymers or micelles. This was attributed to the competition between the species for common binding sites in polyions or micelles.[4] Similar Stern-Volmer plots were drawn for MV^{++} and NB in PMA and PAA solutions(data not shown). In these plots, MV^{++} in PMA at pH 5 and 6.8, and NB in PMA at pH 5 showed negative deviation, but with much less degree than the deviation for Cu^{++} in PAA shown in Figure 5.

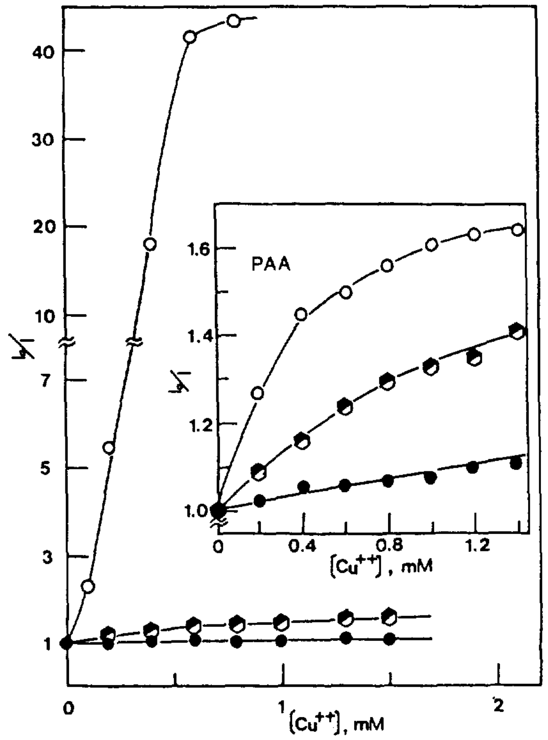

Figure 5. Stern-Volmer plots for quenching of $Ru(bpy)_3^{2+}$ luminescence by Cu^{++} in 8 mM PMA and PAA(inset) solutions at pH 2(●), 5(○), and 6.8(◐).

The apparent quenching constant, K_{SV}'s calculated from Equation 2 by substituting I_0 and I at a given concentration of quencher, 0.5 mM, in 8 mM polymer solutions were plotted as function of pH in Figure 6. This Figure shows remarkably different effects of PMA and PAA on the emission quenching of $Ru(bpy)_3^{2+}$, especially, by Cu^{++} and NB.

When quencher is Cu^{++}, the K_{SV}'s in PMA solutions increased with pH, *i.e.*, with increasing deprotonation of the polymer up to about pH 5.2. The enhancement of K_{SV} at this pH is more than three orders of magnitude larger than the same at pH 2, where the quenching constant is nearly the same as that measured in the absence of the polymer. Above this pH, the K_{SV} decreased sharply with pH reaching slightly higher value than the value at pH 2. The K_{SV} vs pH curve for data taken in PAA solutions was similar to that in PMA solutions. But, the maximum enhancement of K_{SV} was only about 20 times at pH 4.5. The initial increase in K_{SV} with pH can be attributed to the increased local concentration of $Ru(bpy)_3^{2+}$ and Cu^{++} in the polymer domain due to binding(or chelation) as the ionization of the polymer increases.

It is known that PAA is stronger acid than PMA, and the fraction of Cu^{++} bound to PAA is larger than that to PMA at given concentration of H^+.[9] Therefore, the differences in pKa's and Cu^{++} binding affinities between the polymers can not account for the greater enhancement of emission quenching in PMA solutions than in PAA solutions. Rather, the unusually high quenching rate in PMA solutions at pH<5.2 should be attributed to the close proximity of $Ru(bpy)_3^{2+}$ and Cu^{++}, when they binds to PMA in the densely coiled conformation. Lyete *et al.* showed that Cu^{++} forms binuclear complexes with carboxylate groups of PMA when the polymer conforms the densely coiled structure at low degree of neutralization.[21] This dimeric copper complexes dissociate into monomer at high pH. This was explained in terms of greater accessibility of water to the complexes as the result of expansion of the polymer into more extended conformation. The close proximity of $Ru(bpy)_3^{2+}$ and Cu^{++} in PMA at pH<5.2 can be achieved by binding of these cation on the same region of PMA molecules. This can explain the sharply decreasing K_{SV} values

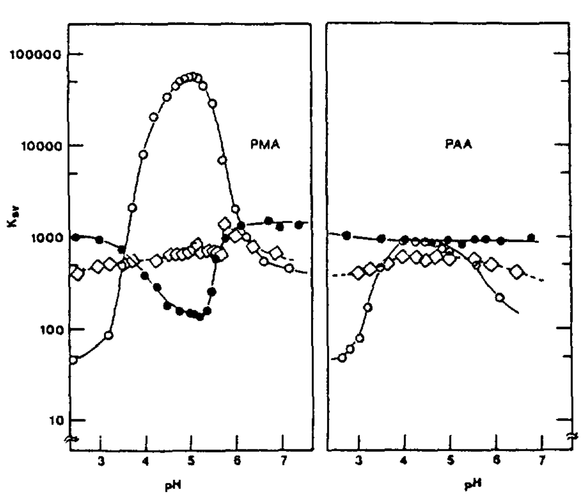

Figure 6. The pH dependences of K_{SV}'s for quenching reactions of $Ru(bpy)_3^{2+}$ with Cu^{++}(○), nitrobenzene (●) and MV^{++} (◇) in 8 mM PMA(left) and PAA(right) solutions. Quencher concentration was fixed at 0.5 mM.

as pH of solutions increased through the value where PMA changes its conformation to more extended one.

PAA does not undergo the sharp, cooperative conformational transition with pH as PMA does. Rather, this polymer expands gradually as more carboxylate groups are ionized. Such expansion of the polymer may result in less efficient emission quenching provided that both $Ru(bpy)_3^{2+}$ and Cu^{++} are bound on the polymer. Thus, raising pH of PAA solutions exerts two opposite effects on the quenching rate: one is the enhancing effect due to localization of the reacting pair in the polymer domain, and the other is reducing effect by expansion of the polymer. The former effect would be predominant factor in deciding the pH dependence of K_{SV}, when degree of neutralization is low(at low pH), while the latter effect would be large when most of $Ru(bpy)_3^{2+}$ and Cu^{++} are bound to the polymer at high pH. The observation of maximum in K_{SV} vs pH curve supports this view.

The pH dependence of quenching constant of $Ru(bpy)_3^{2+}$ by NB in PMA solutions showed nearly opposite trend to the same by Cu^{++}. This implies that NB is not accessible to $Ru(bpy)_3^{2+}$ bound to PMA in the densely coiled conformation. Since NB is not charged and fairly soluble in water, most of NB molecules are expected to be dissolved in bulk aqueous water phase.[22] The inaccessibility of NB to $Ru(bpy)_3^{2+}$ at pH<5.5 matches well with the inaccessibility of water to Cu^{++} complexes with the polymer at the same pH range. This also supports our conclusion given in previous paragraph that $Ru(bpy)_3^{2+}$ and Cu^{++} bind to the same region of PMA molecule in densely coiled structure. The virtual pH independence of K_{SV} of NB in PAA solutions reaffirms us that the dependence in PMA is indeed arised from the conformational transition of the polymer.

In case of MV^{++}, the pH dependence of K_{SV}'s was composite of those for Cu^{++} and NB. In PMA solutions, the K_{SV} increased with pH, but with much less degree than that for Cu^{++} up to pH 5.5. At this pH, K_{SV} increased abruptly as observed in case of NB, and then decreased gradually with pH. The MV^{++} can interact with the ionized polymer by electrostatic force. However, the binding affinity of this cation to PMA is smaller by several orders of magnitude than the same of Cu^{++} to the polymer.[16] Thus, most of MV^{++} stay in bulk aqueous phase and can not interact with $Ru(bpy)_3^{2+}$ bound to PMA in its densely coiled conformation, *i.e.*, at pH<5.5. Only small fraction of MV^{++} is concentrated in the domain of PMA, and the fraction increases with pH due to increased neutralization of the polymer. This appears as slight enhancement of K_{SV} with pH at pH<5.5. As PMA changes its conformation to more extended structure, the free MV^{++} becomes accessible to PMA bound $Ru(bpy)_3^{2+}$ resulting in abrupt enhancement of K_{SV}. The K_{SV} vs pH curve for MV^{++} in PAA solution resembled to that for Cu^{++} in the same polymer solution, but the dependence of K_{SV} on pH was much weaker in MV^{++}. This suggests that the binding affinity of MV^{++} to PAA is also much smaller than that of Cu^{++}.

Conclusion

$Ru(bpy)_3^{2+}$ bound to PMA in its densely coiled conformation at pH<5.5 exhibits enhanced luminescence which accompanied the blue shift of emission maxima. This is due to the restricted rotational mobility of ligand of the PMA bound cation around the metal. The emission intensity decreases sharply, as pH of the solution increases further. This reflects the conformational transition of the polymer to more extended structure, in which the bound $Ru(bpy)_3^{2+}$ regains its rotational mobility of the ligand. The pH dependence of emission spectra of the cation in the presence of PAA is minimized indicating the absence of the sharp, cooperative conformational transition in PAA. The binding of $Ru(bpy)_3^{2+}$ to PMA is by electrostatic interaction in origin. The binding constant of the cation to pair of carboxylate groups of PMA was $2x10^5$ M^{-1} in 0.1 M NaCl solution at pH 5.2. The emission quenching of $Ru(bpy)_3^{2+}$ by Cu^{++} in PMA solution increased with pH up to pH 5. Beyond the pH, the quenchng rate decreased sharply with pH. The maximum enhancement of quenching rate was more than three orders of magnitude in 8 mM PMA solution than the rate in the absence of the polymer, whereas the enhancement in PAA solution was only about 20 times. This suggests that both $Ru(bpy)_3^{2+}$ and Cu^{++} bind to same region of PMA, and thus in close proximity in the densely coiled PMA at pH<5.5. The quenching rate with the water soluble neutral quencher, nitrobenzene, showed opposite pH dependence, compared to that for Cu^{++}. This implies that the PMA-bound $Ru(bpy)_3^{2+}$ in coiled conformation is not accessible by the NB in bulk aqueous phase. The pH dependence of quenching rate with MV^{++} was composite of those with Cu^{++} and NB. The binding affinity of MV^{++} to the ionized PMA is much smaller than that of Cu^{++}. Therefore, only small fraction of MV^{++} is bound to PMA at a given pH and behaves like Cu^{++} in quenching process, whereas most of MV^{++} is free and does not contribute to quenching at pH<5.5 as NB does.

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22. Because of partial hydrophobic character of nitrobenzene, some of NB molecules might be dissolved in the hydrophobic region of PMA. However, the large K value at pH 2, at which Ru(bpy)$_3^{2+}$ does not bind to PMA suggests that most of NB molecules are in aqueous bulk water phase.

Vinylation of β-Acetoxyvinyl Mercurials with Olefins by Palladium (II) Salt

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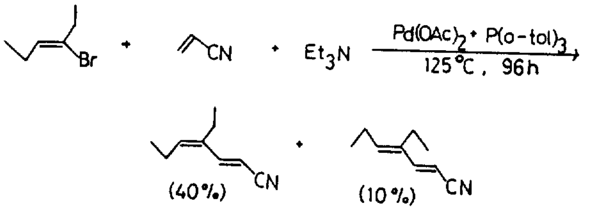
Vinylation of highly hindered β-acetoxyvinyl mercurials with olefins in acetonitrile at room temperature in the presence of cupric chloride, as a reoxidant for the palladium, and a catalytic amount of $LiPdCl_3$ gave the corresponding conjugated dienes in moderate to good yields. The (E) or (Z) geometry in vinyl mercurials was retained in the vinylated products. The reaction was tolerant of a wide variety of functional groups (CO_2R, CN, OR, OAc) on either the vinyl mercurial or olefin compounds.

Introduction

The stereo- and regiospecific synthesis of conjugated dienes are of considerable importance in organic chemistry.[1] The palladium catalyzed vinylation of vinylic bromides or iodides with olefins in the presence of an amine, usually triethylamine or piperidine, has been shown to be a useful method for the synthesis of conjugated dienes.[2-5] While the reactions are successful in most instances, they have some limitations. One of the limitations is that the reaction of (Z) isomers of sterically hindered vinylic bromides, such as (Z)-3-bromo-3-hexene, with acrylic acid derivatives proceeds very slowly even at 125°C and gives a mixture of (E,Z)- and (E,E)-conjugated dienes (eq. 1).[5]



(eq. 1)

The vinylic palladium halide intermediates in the above reaction may also be prepared by another method, the exchange reaction of palladium (II) salts with vinylic derivatives of the main group elements. A number of other methods utilizing organometallic compounds for the preparation of conjugated dienes have been developed.[6] However, there are only a few reports as to the vinylation of organometallic compounds with olefins by the exchange reaction of palladium (II) salts. For example, reaction of vinyl silanes with palladium (II) salts,[7,8] allylation of alkenylpentafluorosilicates[9] and arylation of olefins with arylmercuric salts[10-12] have been reported. Larock *et al.*[13] have reported that the reaction of vinylmercuric chlorides with $LiPdCl_3$ and olefins gives high yields of the corresponding π-allylpalladium compounds.

We recently reported that the reaction of (E)-1-alkenylboronic acids with $LiPdCl_3$ and olefins in the presence of triethylamine gives good yields of (E,E)-conjugated dienes.[14] The reaction also proceeded well catalytically with aid of a reoxidant for the palladium.

In this paper, we wish to report the vinylation of highly hindered (E)- or (Z)-β-acetoxyvinyl mercurials, prepared by acetoxymercuration of internal alkynes,[15,16] with several olefins in the presence of cupric chloride, as a reoxidant for the palladium, and a catalytic amount of $LiPdCl_3$.

Results and Discussion

Vinylation of highly hindered (E)- or (Z)-β-acetoxyvinyl mercurials with olefins such as ethyl acrylate, acrylonitrile, methyl crotonate, and 1-hexene in acetonitrile at room