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Oxidation Potential of Intramolecular Exciplex on a Vinyl Copolymer as Estimated by Electron-transfer Quenching Reactions

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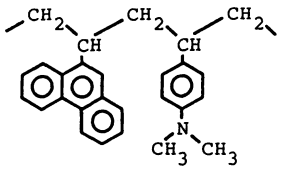
In the electron-transfer reaction from the fluorescent intramolecular exciplexes of a copolymer containing phenanthrene and *N,N*-dimethylaniline moieties, and of a model compound to electron acceptors, the reactivity of the exciplexes was studied kinetically in polar and nonpolar media. The copolymer was poly(9-vinylphenanthrene-co-*p*-dimethylaminostyrene) and the model compound was *N,N*-dimethyl-4-[3-(9-phenanthryl)propyl]aniline. The oxidation potential of the exciplex was evaluated by the relation of the exciplex-quenching rate constants to the reduction potentials of electron-accepting quenchers according to the equations of Rehm and Weller. It was found that the electron-donating ability of these intramolecular exciplexes resembled with each other and was larger than that of excited phenanthrene. In polar media the donating ability was very close to that of the phenanthrene anion radical.

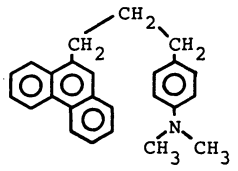
Much attention has been given to exciplexes as reaction intermediates in photoinduced electron-transfer and photochemical reactions. In the field of polymer chemistry, several papers have been published dealing with exciplex-forming polymers in recent years.[1-4] In a previous paper[2] we reported the intramolecular exciplex formation in 9-vinylphenanthrene–*p*-dimethylaminostyrene copolymers, P(VPh–co-DMAS), and photoinduced electron transfer from the copolymer to *p*-dicyanobenzene. The *p*-dicyanobenzene anion radical was concluded to be generated by both the electron-transfer process *via* exciplex and the direct electron-transfer process from the excited phenanthrene unit in the copolymer.

We now want to estimate the reactivity of the exciplex in the electron-transfer reaction between an exciplex and other molecules. The electron-donating ability of an exciplex can be estimated from the relation between exciplex-quenching rate constants by electron acceptors and reduction potentials of the acceptors applying the equations of Rehm and Weller.[5,6] Such a reaction between an exciplex and other molecules has been studied recently and a few papers on exciplex-quenching reactions have appeared in the field of low-molecular-weight compound.[7-11]

In this paper the reactivity of the fluorescent exciplex formed on P(VPh–co-DMAS) is estimated kinetically in polar and nonpolar media, and compared with that of the model compound *N,N*-dimethyl-4-[3-(9-phenanthryl)propyl]aniline, Ph$\{CH_2\}_3$DMA.



P(VPh-co-DMAS)



Ph$\{CH_2\}_3$DMA

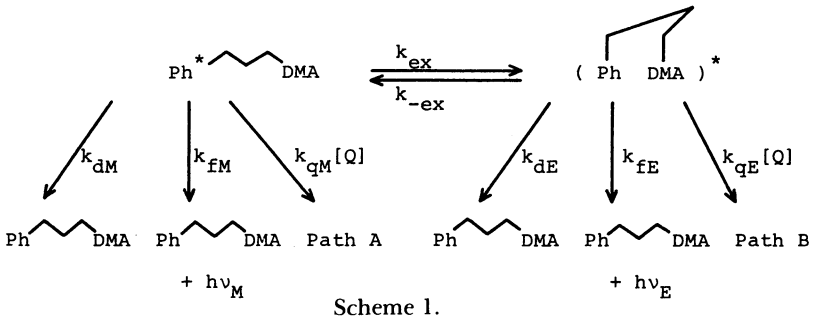
Experimental

Materials. P(VPh–co-DMAS), which has 59 mol% of the VPh unit, was described in the literature.[2] Ph$\{CH_2\}_3$DMA[12] was synthesized according to the method of Thomas and coworkers who prepared *N,N*-dimethyl-4-[3-(1-pyrenyl)-propyl]aniline.[13] Phenanthrene used for measurements was zone-refined reagent (Tokyo Chemical Ind. Co.). *N,N*-dimethylformamide (DMF) was obtained by removing water as benzene azeotrope, followed by fractional distillation after drying over CaH_2. CH_3CN was Dotite Spectrosol Grade and was used without further purification. 1,4-Dioxane was refluxed over sodium and then distilled through a Vigreux column. *p*-Dicyanobenzene was sublimed under reduced pressure and recrystallized from acetone. Benzonitrile was purified by fractional distillation after drying over P_2O_5. Pyridine, acrylonitrile, and cinnamonitrile were purified by fractional distillation. Biphenyl and naphthalene were recrystallized from methanol and tetrahydrofuran, respectively. Fumaronitrile (Tokyo Chemical Ind. Co.) was used without purification. Another electron-accepting quenchers (Guaranteed Reagent, Nakarai Chemicals, LTD) were used without further purification.

Measurements. Fluorescence spectra were recorded by a Shimadzu RF-502A spectrofluorometer at 25 °C. Solution samples were made free from oxygen by freeze-pump-thaw cycles on a vacuum line. Fluorescence lifetime was measured by the pulse method with a small Blumlein-type nitrogen gas laser as described in the literature.[2] A sample solution was sealed in a 3 mm Pyrex glass capillary tube after degassed by four freeze-pump-thaw cycles on a vacuum line. Fluorescence was detected through appropriate cutoff filters and a monochrometer (Union FS-401) by a photomultiplier (Hamamatsu TV 1P28) and an oscilloscope (Tektronix 485). The exciplex fluorescence was monitored at 440 nm in dioxane and at 460 nm in CH_3CN and in DMF. Phenanthrene fluorescence was monitored at 370 nm both in dioxane and CH_3CN.

Results and Discussion

In Fig. 1 are shown the fluorescence spectra of P(VPh–co-DMAS) containing 59 mol % of the VPh unit and Ph$\{CH_2\}_3$DMA in dioxane. They are found to exhibit an intense and broad intramolecular exciplex fluorescence at *ca.* 440 nm. These exciplex fluorescence are observed in a longer wavelength region in a polar solvent DMF also as shown in Fig. 1. We have determined the quenching rate constants of these two kinds of (Ph–DMA) intramolecular exciplexes with a number of electron acceptors. In general, a fluorescence-quenching rate constant can be determined by either a fluorescence intensity measurement or a fluorescence



Scheme 1.

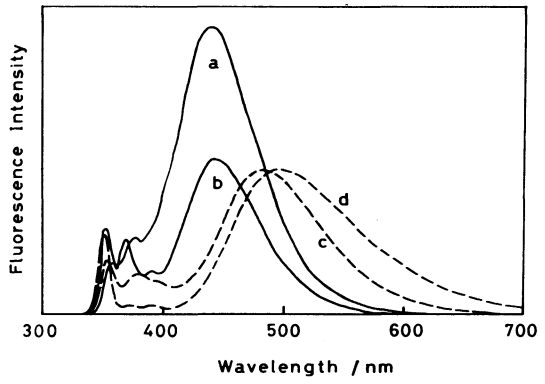


Fig. 1. Fluorescence spectra of P(VPh-co-DMAS) and Ph{CH_2}$_3$DMA: P(VPh-co-DMAS) in (a) dioxane and in (c) DMF, [VPh unit]=3×10^{-4} mol dm^{-3}, excitation at 352 nm; Ph{CH_2}$_3$DMA in (b) dioxane and in (d) DMF, [Ph{CH_2}$_3$DMA]=2×10^{-4} mol dm^{-3}, excitation at 350 nm. Fluorescence intensities were normalized at Ph monomer fluorescence part [(a) and (b)] or at exciplex fluorescence part [(c) and (d)].

lifetime measurement. In this paper the exciplex-quenching rate constant, k_{qE}, was obtained from exciplex fluorescence lifetime data but not from exciplex fluorescence intensity quenching data by the following reasons. As shown in Scheme 1 some electron acceptors, Q, can quench an excited phenanthrene portion, Ph*, (Path A) as well as the exciplex (Path B). In such a case, the quantum yields of the exciplex and Ph* monomer fluorescence under stationary conditions are presented by the following equations 1—4.

$$\Phi_E^\circ = \frac{k_{ex}k_{fE}}{(k_{fM}+k_{dM}+k_{ex})(k_{fE}+k_{dE}+k_{-ex})-k_{ex}k_{-ex}}, \quad (1)$$

$$\Phi_E = \frac{k_{ex}k_{fE}}{(k_{fM}+k_{dM}+k_{ex}+k_{qM}[Q])(k_{fE}+k_{dE}+k_{-ex}+k_{qE}[Q])-k_{ex}k_{-ex}}, \quad (2)$$

$$\Phi_M^\circ = \frac{k_{fM}(k_{fE}+k_{dE}+k_{-ex})}{(k_{fM}+k_{dM}+k_{ex})(k_{fE}+k_{dE}+k_{-ex})-k_{ex}k_{-ex}}, \quad (3)$$

$$\Phi_M = \frac{k_{fM}(k_{fE}+k_{dE}+k_{-ex}+k_{qE}[Q])}{(k_{fM}+k_{dM}+k_{ex}+k_{qM}[Q])(k_{fE}+k_{dE}+k_{-ex}+k_{qE}[Q])-k_{ex}k_{-ex}}, \quad (4)$$

where Φ_E° and Φ_E are the exciplex fluorescence quantum yields in the absence and presence of Q, Φ_M° and Φ_M are the Ph* monomer fluorescence quantum yields in the absence and presence of Q, respectively, k_{ex} and k_{-ex} are the rate constants of the exciplex formation and dissociation processes, respectively, k_{dM}, k_{fM}, and k_{qM} are the rate constants of radiationless deactivation, fluorescence and quenching of the excited phenanthrene part, respectively, and k_{dE}, k_{fE}, and k_{qE}, are the corresponding rate constants of the exciplex. The value of I_E°/I_E ratio can be expressed by Eq. 5,

$$I_E^\circ/I_E = \Phi_E^\circ/\Phi_E = \frac{\Phi_M^\circ}{\Phi_M}\times\left(\frac{k_{qE}[Q]}{k_{fE}+k_{dE}+k_{-ex}}+1\right) = \frac{I_M^\circ}{I_M}\times(1+k_{qE}\tau_E^\circ[Q]), \quad (5)$$

where I_E° and I_E are the exciplex fluorescence intensity in the absence and presence of Q, I_M° and I_M are the Ph* monomer fluorescence intensity in the absence and presence of Q, and τ_E° is lifetime of the exciplex fluorescence in the absence of Q, respectively. Therefore k_{qE} cannot be determined from the measurement of exciplex fluorescence intensity only. On the other hand, as the exciplex fluorescence lifetime depends only on its decay processes, the value of τ_E°/τ_E can be expressed by Stern-Volmer equation 6. Typical examples of exciplex

$$\tau_E^\circ/\tau_E = 1 + k_{qE}\tau_E^\circ[Q], \quad (6)$$

fluorescence lifetime measurements for P(VPh-co-DMAS) - and Ph{CH_2}$_3$DMA - acceptor systems are shown in Figs. 2 and 3, respectively. It has been reported that in such intramolecular excited complex systems, especially in polymer systems, the accurate fluorescence decay seemed to be multicomponent decay.[14] However, the observed exciplex fluorescence decay curves could be analyzed by a single exponential kinetics as shown in Figs. 2 and 3.

The phenanthrene fluorescence-quenching rate constant, k_{qPh}, for phenanthrene-acceptor systems and k_{qE} for (Ph-DMA) intramolecular exciplexes-acceptor systems by Eq. 6 are listed in Table 1 together with the reduction half-wave potentials[15] of electron-accepting quenchers, $E_{1/2}$. Phenanthrene has a unique redox potential in the sense that the electron-donating ability of the phenanthrene anion radical [$E_{1/2}(Ph/Ph^-)=-2.5$ V[16]] is larger than that of excited phenanthrene [$E_{1/2}(Ph^+/Ph^*)=-2.1$ V[15]] (Scheme 2). In this respect the quenchers are classified into three groups in Table 1. As shown in Scheme 2, Q_c is a strong electron acceptor which can accept an electron from both the phenanthrene anion radical and excited phenanthrene, Q_b is a moderate one which can accept only from the phenanthrene anion radical, and Q_a is a weak one which cannot accept from either.

TABLE 1. EXCIPLEX AND PHENANTHRENE FLUORESCENCE QUENCHING RATE CONSTANTS MEASURED IN POLAR SOLVENTS

Quencher	$E_{1/2}$[b]/V		k_q[a]/mol^{-1} dm^3 s^{-1}		
			Phenanthrene	Ph{CH_2}$_3$DMA	P(VPh-co-DMAS)
Biphenyl	−2.70[e]				9.8×10^6
Naphthalene	−2.63[d]	Q_a		1.5×10^8	3.0×10^7
Pyridine	−2.62[d]		*6.8×10^5		
Benzonitrile	−2.44[c]		*1.2×10^6	5.0×10^9	2.0×10^9
Methyl benzoate	−2.32[c]			4.2×10^9	2.3×10^9
Acrylonitrile	−2.17[c]	Q_b		3.8×10^9	2.0×10^9
Ethyl benzoate	−2.14[e]			4.8×10^9	1.8×10^9
Cinnamonitrile	−1.99[c]		*3.0×10^9	6.3×10^9	4.2×10^9
p-Dicyanobenzene	−1.67[c]		*9.3×10^9	7.3×10^9	4.7×10^9
Fumaronitrile	−1.36[c]	Q_c	*1.2×10^{10}	7.1×10^9	5.7×10^9
Maleic anhydride	−0.85[d]		*1.6×10^{10}	7.3×10^9	5.6×10^9

a) Fluorescence-quenching rate constants k_q were determined in DMF and CH_3CN(*). b) $E_{1/2}$ (V *vs.* SCE). c) In DMF. d) In CH_3CN. e) In 75% aqueous dioxane.

In simple fluorescer-quencher systems, fluorescence-quenching rate constants k_q are correlated to the free energy change for the reaction ΔG and the free energy change of activation ΔG^* by Eq. 7,[5,6]

$$k_q = \frac{2.0 \times 10^{10}}{1 + 0.25\left[\exp\left(\frac{\Delta G^*}{RT}\right) + \exp\left(\frac{\Delta G}{RT}\right)\right]}, \quad (7)$$

$$\Delta G = 23.06\,[E_{1/2}(D^+/D) - E_{1/2}(A/A^-) - e_0^2/\varepsilon a] - \Delta E_{0,0},$$

$$\Delta G^* = \left[\left(\frac{\Delta G}{2}\right)^2 + (\Delta G^*(0))^2\right]^{1/2} + \frac{\Delta G}{2},$$

where $\Delta G^*(0)$ is ΔG^* at $\Delta G=0$, and is assumed to be 2.4 kcal mol^{-1},[6] $\Delta E_{0,0}$ is the 0-0 excitation energy of fluorophore, and the term $e_0^2/\varepsilon a$ is the Coulomb attraction energy and is *ca.* 0.06 V in CH_3CN solution (calculated with the values of dielectric constant ε=37.5

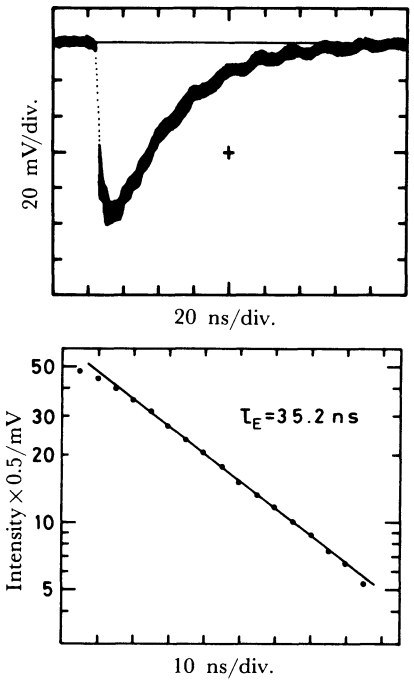


Fig. 2. Typical exciplex fluorescence decay curve and its semilogarithmic plot of P(VPh-co-DMAS)-maleic anhydride system in dioxane: [VPh unit]= 1.4×10^{-3} mol dm^{-3}, [maleic anhydride]=2.23×10^{-3} mol dm^{-3}. Monitored at 440 nm.

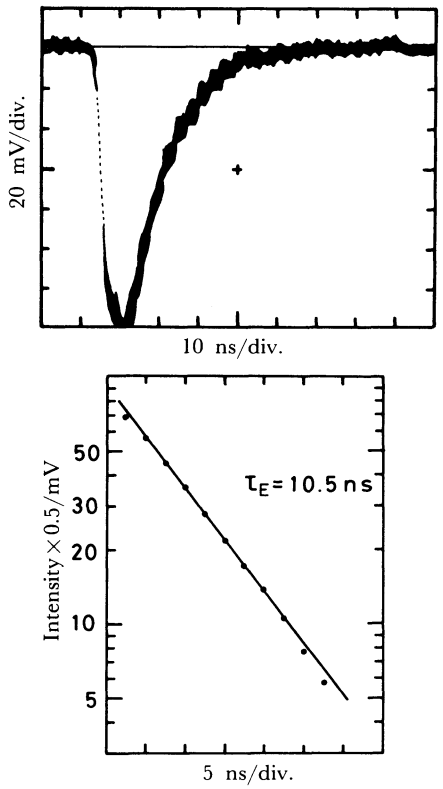
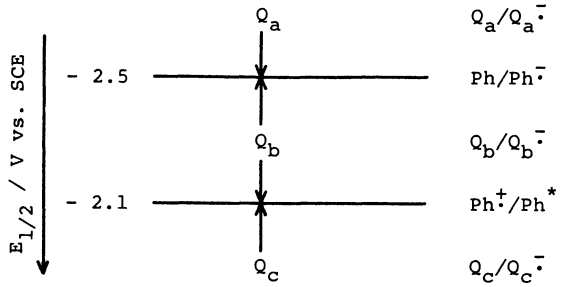


Fig. 3. Typical exciplex fluorescence decay curve and its semilogarithmic plot of Ph{CH_2}$_3$DMA-maleic anhydride system in CH_3CN:[Ph{CH_2}$_3$DMA]= 1.4×10^{-3} mol dm^{-3}, [maleic anhydride]=3.34×10^{-3} mol dm^{-3}. Monitored at 460 nm.



Scheme 2. Redox potential diagram.

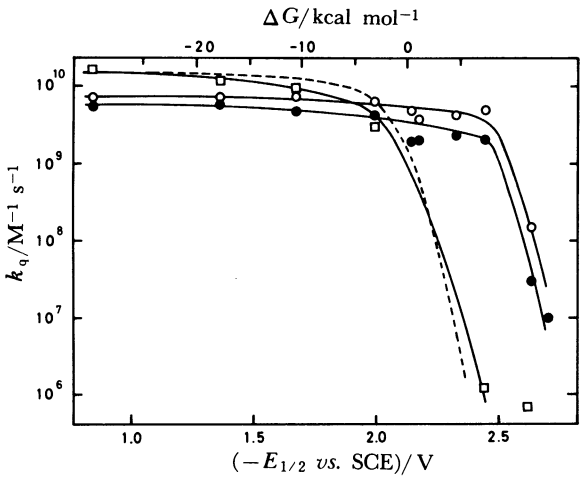


Fig. 4. Quenching of (Ph-DMA) intramolecular exciplexes by electron acceptors in polar solvents. Plots of log k_q *vs.* $E_{1/2}$ of the quenchers: (●) P(VPh-co-DMAS) in DMF, (○) Ph{CH_2}$_3$DMA in DMF, (□) phenanthrene in CH_3CN, the dotted line was calculated from the Eq. 7 for the phenanthrene-acceptor system.

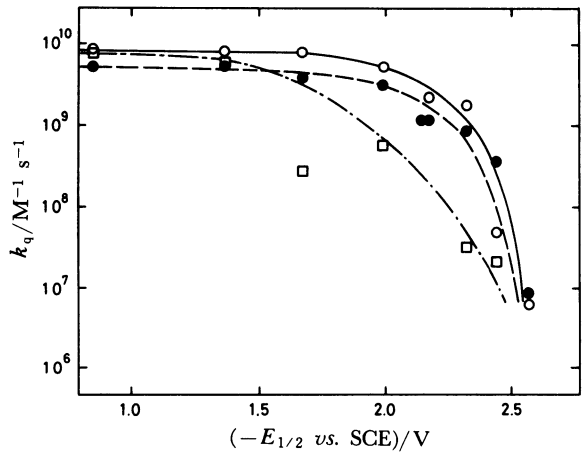


Fig. 5. Quenching of (Ph-DMA) intramolecular exciplexes by electron acceptors in nonpolar solvent(dioxane). Plots of log k_q *vs.* $E_{1/2}$ of the quenchers: (●) P(VPh-co-DMAS), (○) Ph{CH_2}$_3$DMA, (□) phenanthrene.

and distance between ion radicals a=7 Å). Figure 4 illustrates the plots of log k_{qPh} *vs.* ΔG for the excited phenanthrene-acceptor system in CH_3CN. The experimental values of k_{qPh} are in fair agreement with the calculated dotted line by equation 7. Similar relation can be expected for two (Ph-DMA) intramolecular exciplexes-acceptor systems in DMF. The determined k_{qE} values are plotted for $E_{1/2}$ values also in Fig. 4. The tendency of k_{qE} for two intramolecular exciplex systems is similar to each other. In the phenanthrene system, k_{qPh} has diffusion-controlled values only for strong quenchers Q_c and decreases with decreasing reduction potentials of quenchers, whereas in these intramolecular exciplex systems the quenching reactions for Q_c and moderate quenchers Q_b are found to proceed at nearly diffusion-controlled rates and for weak quenchers Q_a smaller values of k_{qE} are obtained. Therefore the electron-donating ability of these intramolecular exciplexes resembles with each other and can be larger than that of excited phenanthrene. That is, the oxidation potentials of the exciplexes can be located in between the two observed points —2.44 V of benzonitrile and —2.63 V of naphthalene, where a large decrease in the quenching rate constant k_{qE} was observed. Although the experimental data points at low $E_{1/2}$ region were not sufficient, we estimated the oxidation potentials of the exciplexes. From Eq. 7 it can be seen that a plot of log k_q *vs.* ΔG (or $E_{1/2}$) should approach a constant limiting value at large negative ΔG (or higher $E_{1/2}$), be linear at large positive ΔG (or low $E_{1/2}$) with a slope of $-(1/2.303\,RT)$, and have an intermediate region (centered at $\Delta G=0$[17]). For very small values of $\Delta G^*(0)$ the intermediate region is very small and the connection between the limiting value and the limiting slope takes place in a very narrow ΔG range. These two lines intersect at *ca.* $\Delta G=0$[18] ultimately. The constant limiting value at higher $E_{1/2}$ and the limiting slope at low $E_{1/2}$ intersect at the oxidation potentials of exciplexes, yielding $E_{1/2}$ values of *ca.* —2.5 V[19] for two kinds of intramolecular exciplexes. This value —2.5 V happens to be very close to the reduction potential of phenanthrene.

One can conclude from the results in polar media that the electron-donating ability of the intramolecular exciplex on P(VPh-co-DMAS) is similar to that of Ph{CH_2}$_3$DMA, is larger than that of excited phenanthrene, and is very close to that of the phenanthrene anion radical.

In nonpolar solvent dioxane k_{qE} and k_{qPh} are also similarly determined and plotted for $E_{1/2}$ in Fig. 5. The estimation of electron-donating ability of (Ph-DMA) intramolcular exciplexes was not feasible because $E_{1/2}$ measured in polar media was used instead of one in dioxane. It can be seen, nevertheless, that the behavior of k_{qE} of two exciplex systems was similar to each other and the exciplexes were better donors than excited phenanthrene.

As a photosensitizer excited phenanthrene cannot donate an electron to moderate electron acceptors, Q_b, but the (Ph-DMA) intramolecular exciplexes can. P(VPh-co-DMAS) may act as a photosensitizer in the case of the electron-transfer reactions to moderate electron acceptors because in this copolymer the efficient energy migration can take place from an excited phenanthrene unit to an exciplex-forming site on the polymer chain.[2]

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18) For phenanthrene–acceptor system the intersection of these two lines was calculated to be at ΔG=0.6 kcal mol^{-1} (0.026 V) from the equations of Rehm and Weller and their experimental data.
19) In DMF solution the Coulomb attraction energy is *ca.* 0.06 V (ε=36.7 and a=7 Å) and is negligible for the estimation of the oxidation potential.