

## PHOTOINDUCED ELECTRON TRANSFER QUENCHING OF RHODAMINE B IN POLYMER FILMS

ALAN B. FISCHER<sup>†</sup> and IRENA BRONSTEIN-BONTE<sup>†</sup>

*Polaroid Corporation, 750 Main Street MS-4A, Cambridge, MA 02139 (U.S.A.)*

(Received August 14, 1984; in revised form December 20, 1984)

### Summary

Photoinduced electron transfer reactions of rhodamine B with several redox quenchers in solution-cast films of poly(*N*-vinylpyrrolidone) have been investigated using fluorescence spectroscopy. The quenching of the rhodamine B fluorescence has been used to examine the efficiency of photoinduced electron transfer in a rigid amorphous polymer matrix. The data obtained show that the electron transfer efficiency is a function of the free energy of the transfer and depends on the redox potential of the quencher. The data are analyzed using theories of electron transfer in solid media and are correlated with the redox potentials of the quenchers to derive the distance dependence of the excited state transfer. Photoinduced electron transfer between rhodamine B and both donor and acceptor quenchers in the cast polymer films is observed to occur at distances of up to about 15 Å for this system.

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### 1. Introduction

In recent years electron transfer reactions have been studied both from the standpoint of theory and from its potential applications [1 - 11]. Photoinduced electron transfer has been of particular interest and this has been exploited in many schemes for the conversion of solar energy to electricity or storable fuels [12 - 15]. Electron transfer quenching has also been identified as an efficient mechanism for quenching the reactive excited states of dye chromophores thereby providing an efficient pathway for dye stabilization [16] or image formation [17 - 19].

The problem of energy transfer via electron transfer for systems in solution has received extensive attention in the literature. However, there are only relatively few examples of such investigations performed on solid sam-

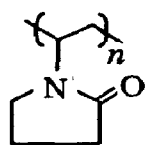
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<sup>†</sup>Current address: Allied Health and Scientific Products, 1 Burt Road, Andover, MA 01810, U.S.A.

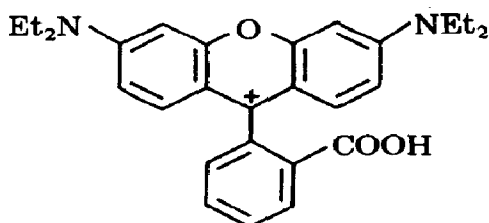
ples [3 - 10]. Most of the studies on solids have been performed on samples in low temperature frozen glasses obtained directly from well-characterized solutions [3 - 10].

Miller and coworkers have examined electron transfer processes for several systems in the solid phase. Using pulse radiolysis to generate biphenyl and perylene molecular ions they observed that electron transfer from *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) occurred over distances of up to 34 Å [4, 5]. More recently Miller examined photoinduced processes and observed transfers that occurred over 25 - 30 Å from long-lived triplet states by phosphorescence quenching of TMPD, *N*-isopropylcarbazole and pyromellitic dianhydride in low temperature frozen glasses [6]. These studies were extended to room temperature and above for an extensive series of acceptors in decalindiol glasses where fluorescence quenching measurements showed that electron transfer occurs at distances up to 15 Å [7]. McLendon [8] has studied the electron transfer quenching emission of the charge transfer excited state of Ru(II)(polypyridine)<sub>3</sub> complexes by varying concentrations of methyl viologen (MV<sup>2+</sup>) in glycerol solutions at temperatures below 250 K. He found a dependence of the electron transfer quenching distance on the redox potential of the ruthenium complex in agreement with the work by Miller and current theory [8]. McLendon recently measured time-resolved emission spectra for one of these complexes and found that the line shape was in agreement with an exponential dependence of the electron transfer rate on the distance of the transfer [9].

We have been interested for several years in photoinduced electron transfer reactions of dyes in polymeric matrices as a possible method for the stabilization of chromophores. Previous work from our laboratory [20] has helped us to establish that photographic image dyes can and do undergo photoinduced electron transfer and that such a process may be a significant decomposition pathway depending on the matrix and the presence of impurities. However, electron transfer reactions may also be used adventitiously to quench the excited states of dyes and inhibit decomposition reactions via other pathways. An understanding of photoinduced electron transfer processes in polymer matrices with added quenchers will help to define these potential reactions. We have prepared thin films of the polymer poly(*N*-vinylpyrrolidone) (PVP) containing the model dye system rhodamine B (RhB) and various concentrations of redox quenchers and have studied their fluorescence properties.



PVP



RhB

Previously one of us has observed that dyes in polymer films cast from solution exhibited electron transfer products in laser flash photolysis experiments [20]. The work presented below is directed towards understanding these processes for the cast PVP films. The polymer films, produced by solvent evaporation from a coating of RhB, quencher and polymer solution are rigid and amorphous but considerably less homogeneous than the rapidly frozen glasses or cooled glycerol solutions mentioned above. Additionally, RhB can undergo both excited-state oxidation and reduction, permitting study of both donors and acceptors. Samples have been prepared with several different quenchers over a range of quencher concentrations and the results are presented below.

## 2. Experimental details

### 2.1. Chemicals

PVP was obtained from GAF and used as received (K-90 grade; average molecular weight, 700 000).  $\text{RhB}^+\text{Cl}^-$  and  $\text{RhB}^+\text{ClO}_4^-$  were obtained from Eastman Kodak and were purified by recrystallization from ethanol (EtOH).  $\text{RhB}^+\text{Cl}^-$  was also obtained from Exciton Laser Dyes and was used as received, showing little difference from the recrystallized material. Ferrocene was obtained from Aldrich and used after vacuum sublimation and the alkyl ferrocenes were prepared by literature procedures [21].  $\text{MV}^{2+}\text{Cl}_2^-$  was obtained from Aldrich and was recrystallized once before use. TMPD (Aldrich) was sublimed twice under vacuum and stored under nitrogen. The quaternary pyridinium compounds were prepared by refluxing the pyridine compound with the corresponding bromide reagent followed by double recrystallization. 10-methylphenothiazine (Eastman Kodak), ascorbic acid (Aldrich) and ferrocene carboxylic acid (Aldrich) were used as received without further purification.

### 2.2. Coatings

Coatings were made from ethanolic or EtOH-H<sub>2</sub>O solutions of 4% PVP, the appropriate amount of quencher and  $\text{RhB}^+\text{Cl}^-$ . The RhB concentration was the same for all samples and was 0.01 M in the 4% polymer solution before coating. All quencher concentrations listed in the text are the values calculated from the density of the PVP film host and the ratio of the amount of material to the amount of polymer in the coating solution. The solutions were spin coated onto glass slides and dried with forced hot air or N<sub>2</sub> gas. Great care was taken to produce polymer films that were as smooth as possible to avoid surface scattering problems.

### 2.3. Fluorescence

Fluorescence measurements were recorded using a Spex Fluorolog fluorometer operated under computer control with a Tektronix processor. Samples were monitored with front-face detection (45° from the normal to the surface with excitation normal to the surface) on coatings with absorb-

ance values not more than 0.10 absorbance units. Spectra were integrated mathematically in digital form and the integrations were adjusted for any variations in sample absorbance at the excitation wavelength of 530 nm. The fluorescence spectra were corrected for the source intensity but not for the photomultiplier response. Slopes of plots of quenching efficiency *versus* [Q] were calculated using a linear least-squares approximation.

#### 2.4. Electrochemistry

Redox potentials for  $\text{RhB}^+\text{ClO}_4^-$  were determined at a platinum disc microelectrode (Sargeant Welch) in a three-electrode configuration using a platinum gauze counterelectrode and a silver wire quasi-reference electrode, which in turn was referenced either to internal ferrocene or a standard calomel electrode (SCE).  $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$  (TBAP; Bu  $\equiv$  butyl) was used as a supporting electrolyte. The redox potentials for the quenchers are those reported in the literature [21, 22] or determined by cyclic voltammetry as above. A Pine Instruments RDE3 potentiostat was used for all electrochemical measurements.

### 3. Results and discussion

The electrochemistry of RhB shows both a reversible oxidation and an irreversible reduction under dry,  $\text{N}_2$ -purged conditions. Figure 1 is a cyclic voltammogram of  $\text{RhB}^+\text{ClO}_4^-$  in EtOH showing the reversible one-electron oxidation at +1.2 V *versus* SCE and the reversible one-electron reduction at -0.8 V *versus* SCE. As a ground-state species RhB can function as both a donor or an acceptor and the same holds true for the excited state. The estimated excited-state oxidation and reduction potentials are calculated by adding the excited-state energy to the ground-state redox potentials<sup>†</sup> and are -0.94 V and +1.34 V *versus* SCE respectively. RhB in the excited state is clearly both a powerful donor and acceptor. The matrix chosen for these studies, PVP, is electrochemically inert over this potential range and is not observed to interact significantly. Thus, donors with oxidation potentials less than +1.34 V *versus* SCE and acceptors with reduction potentials less than -0.94 V *versus* SCE will be able to serve as electron transfer quenchers for excited RhB. The donors and acceptors chosen for these studies all have lowest excited-state energies that are much higher than the fluorescent RhB excited state and thus can quench the emission only by electron transfer and not by simple energy transfer.

The RhB-PVP films were all characterized by an analysis of their absorption and emission properties. The absorption spectra indicated that

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<sup>†</sup>The excited state energy is chosen as the photon energy corresponding to the intersection of excitation and emission spectra for  $\text{RhB}^+\text{Cl}^-$  in a PVP film. The value obtained is 2.15 eV. The redox levels of ground state RhB in the polymer film cannot be determined and the solution values are thus an approximation of the conditions in the solid samples.

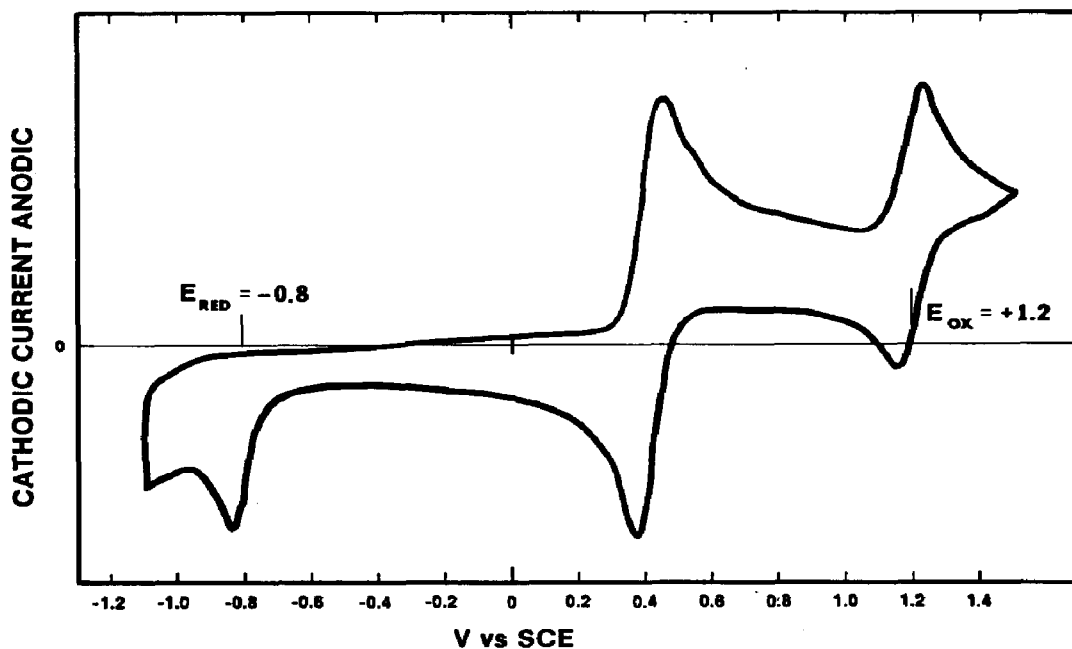


Fig. 1. Cyclic voltammogram of  $\text{RhB}^+\text{ClO}_4^-$  in degassed EtOH solution containing  $(n\text{-Bu})_4\text{N}^+\text{BF}_4^-$ .

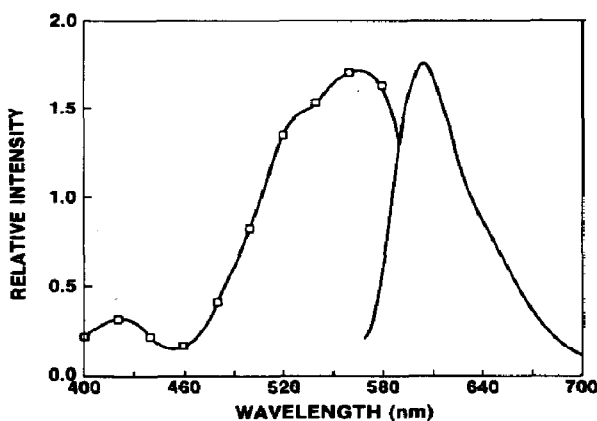


Fig. 2. Fluorescence excitation and emission spectra of RhB at 0.01 M concentration in a PVP thin film ( $-\square-$ , excitation;  $—$ , emission).

the spectral characteristics of the dye remained unchanged with the addition of the quenchers to the films. Figure 2 shows the excitation and emission spectra for a  $\text{RhB}^+\text{Cl}^-$ -PVP film sample with no added quencher. The curves are similar to those obtained for the dye in a solution of *N*-methylpyrrolidone and do not suggest that there is extensive aggregation. Aggregation can not be totally ruled out, however.

Similar spectra were obtained for films that also contained redox quenchers and very little change was observed in either the absorbance or excitation spectra. There are some changes in the absorbance spectra owing

to the decreased emission but these can be explained by the characteristics of the measuring instrument. The lack of significant changes in the absorbance and excitation spectra suggest that no ground-state complexes have been formed between the  $\text{RhB}^+\text{Cl}^-$  and the quenchers in the polymer matrix during film fabrication and drying. The extent of fluorescence quenching in the polymer films is measured by integration of the corrected emission curves. Absorption spectra were measured for all of the samples to ensure that the changes in the emission intensity were due only to quenching and not to any change in the excitation spectra. Samples were prepared with a range of concentrations of quencher and a family of fluorescence curves were obtained for each one. Figure 3 shows such a family of curves for the quencher 1,1'-ethylene-2,2'-bipyridinium chloride at various concentrations in PVP films containing a constant concentration of  $\text{RhB}^+\text{Cl}^-$ . The integrated fluorescence intensity is clearly decreased by increasing the amounts of quencher. The shape of each of the curves in Fig. 3 does not change appreciably as the amount of quencher is increased, supporting the claim that the decrease in fluorescence intensity is due to quenching and not to dye aggregation or complexation of the dye and the quencher. The theory describing electron transfer in solid matrices has been very well outlined [3 - 10] and will not be repeated here. However, a brief derivation of the few equations used to analyze these data is important and is included below.

A simple but effective model that can be used to understand energy transfer parameters in the solid state was developed by Perrin [23] to describe static quenching in cases where the donor and the acceptor are not free

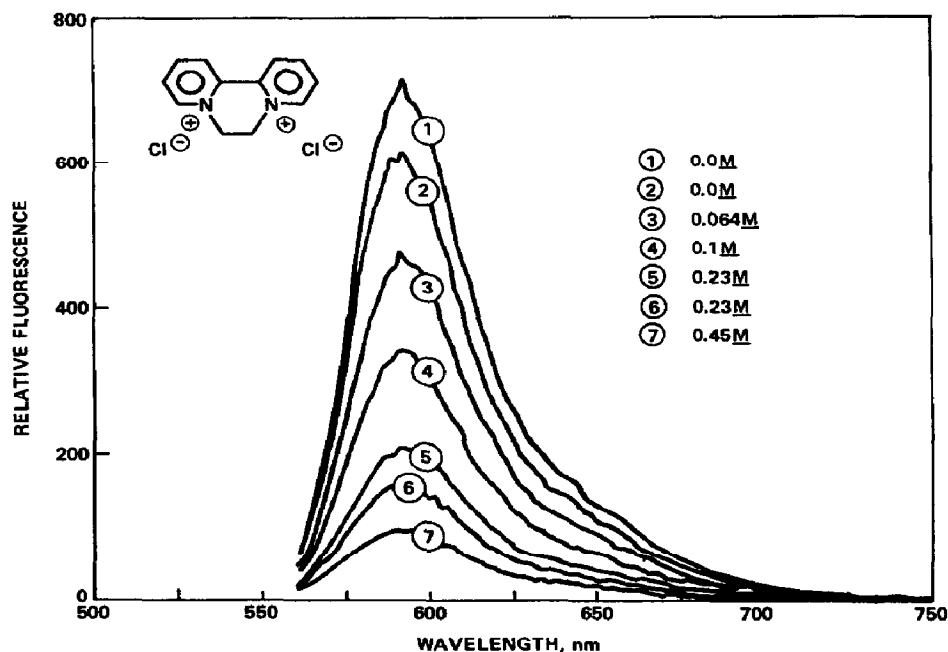


Fig. 3. Fluorescence spectra of RhB in PVP thin films with varying concentrations of the acceptor quencher 1,1'-ethylene-2,2'-bipyridinium chloride, as indicated.

to undergo spatial movement during the lifetime of the excited state. Perrin's model is based on the construct of an "active sphere", which is a volume of interaction around an excited fluorescent molecule. If a quencher lies within the active sphere then the fluorescence of the molecule will be quenched. If, however, no quencher lies within the active sphere then the excited state will not be quenched. In this model the formation of a bound complex between fluorescing molecules and the quenchers is not required, although it may occur.

The results of the analysis of the data of Fig. 3 are exhibited in Fig. 4, which shows a plot of the natural logarithm of the normalized fluorescence *versus* the quencher concentration, as derived from the Perrin model. The natural logarithm of the normalized fluorescence quenching efficiency shows an almost linear dependence on the quencher concentration as predicted by the model. The close agreement of the data with the Perrin model is surprising in view of the model's simplicity. The straight line in Fig. 4 was obtained by a linear least-squares analysis of the data in Fig. 3. Similar curves have been obtained for the other quenchers although not all quenchers yielded such linear dependencies. The slope of the least-squares fit to the data is used to obtain the effective quenching radius  $R_Q$  and the values obtained are listed together with other data on the quenchers in Table 1.

There is a variability in the results owing to the difficulty in making identical cast polymer films from each of the film-forming solutions. The variability is exhibited in the data in Fig. 3 where emission spectra for different samples with the same composition are displayed. Slight differences in the surface roughness of the polymer films have a significant effect on the

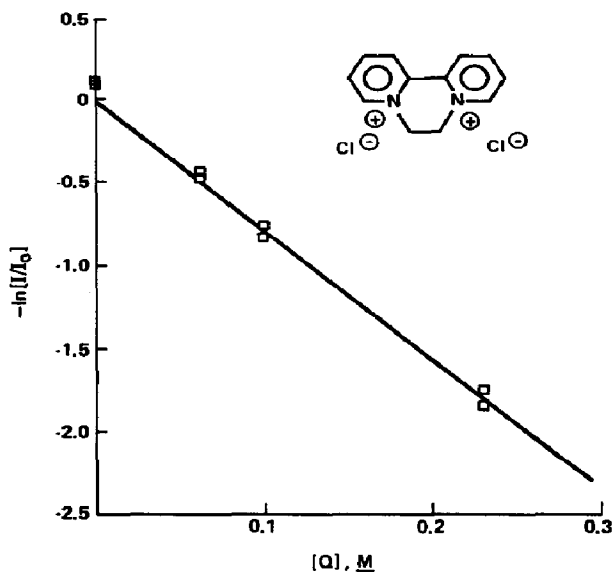


Fig. 4. Plot of  $-\ln(\Phi/\Phi_0)$  (data from Fig. 3) *vs.* the concentration of the acceptor quencher 1,1'-ethylene-2,2'-bipyridinium chloride.

TABLE 1

Donor and acceptor quenchers: redox potentials in solution, slopes from  $-\ln(\Phi/\Phi_0)$  versus  $[Q]$  plots, and calculated  $R_Q$  values

Quencher	$E_{OX}$ (V versus SCE)	Slope of quenching data	$R_Q$ (Å)
<i>Donors</i>			
RhB <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	+1.25	—	—
10-Methylphenothiazine	+0.83	0.34	5.1
Ferrocene	+0.35	10.4	16
TMPD	+0.24	9.2	15.4
1,1,1,1,1-Pentamethylferrocene	+0.15	9.5	15.6
Ascorbic acid (pH 7.2)	0.02	1.3	8.02
Ferrocene carboxylic acid	+0.53	5.1	12.6
<i>Acceptors</i>			
RhB <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	-1.0	—	—
<i>N</i> -ethyl-4-amidopyridinium tetrafluoroborate	-1.06	0	0
<i>N</i> -ethyl-4-cyanopyridinium tetrafluoroborate	-0.79	0.9	7.1
<i>N</i> -methyl-4-carbomethoxypyridinium tetrafluoroborate	-0.93	0.04	2.5
<i>N,N'</i> -dimethyl-4',4'-bipyridinium tetrafluoroborate	-0.45	3.7	11.4
<i>N,N'</i> -dibenzyl-4',4'-bipyridinium tetrafluoroborate	-0.36	7.2	14.2
1,1'-ethylene-2,2'-bipyridinium chloride	-0.36	7.9	14.6

front surface emission properties and several samples were required to average out some of these variations.

The rate of the electron transfer and hence the factor determining the distance over which the process will occur is determined by the free energy of the reaction. The thermodynamics of electron transfer processes have been very thoroughly covered by several workers [24, 25] and can be described simply by

$$-\Delta G_{et}^{\circ} = E(S_1) - E(D^+/D) + E(A/A^-) + \frac{e^2}{\epsilon R} \quad (1)$$

where  $E(S_1)$  is the excited-state energy of RhB<sup>+</sup> in this case and  $E(D^+/D)$  is the oxidation potential of the donor and  $E(A/A^-)$  is the reduction potential of the acceptor. The last term accounts for the Coulomb energy associated with the separation of charges in the electron transfer products. This factor has been ignored in this work. RhB<sup>+</sup> is cationically charged and the quenchers used are both cations and anions but the data in Table 1 and Fig. 5 do not have enough resolution to show any systematic variation attributable to this factor. Thus, the scatter in the data precludes any strong statement about



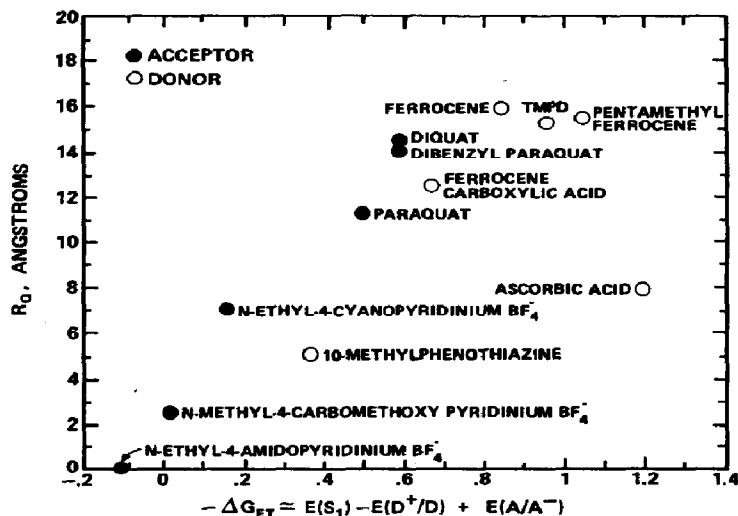


Fig. 5. Plot of  $R_Q$  (in angstroms) vs. the free energy for electron transfer for RhB plus either acceptor or donor quenchers, as indicated. (The Coulomb term of Weller's equation is neglected.)

the validity of dropping the coulombic correction. The data in Table 1 are grouped into donor and acceptor quenchers. The quenchers have a range of ionic charges and cover a wide range of redox potentials. The redox potentials are from solution measurements and may not be truly representative of the redox potentials of the quenchers in the PVP films. In cases where the solubility and stability permitted, the redox potentials were determined by cyclic voltammetry in *N*-methylpyrrolidone and the results obtained did not differ substantially from the values obtained in acetonitrile or EtOH.

The dependence of the quenching efficiency as a function of the free energy for the electron transfer quenching process is illustrated by the plot in Fig. 5. This is a plot of the  $R_Q$  value obtained for each of the quenchers from plots of  $\ln(\Phi/\Phi_0)$  versus  $[Q]$ , such as Fig. 4, as a function of  $E(S_1) - E(D^+/D) + E(A/A^-)$ . Coulombic corrections have been neglected and should be small for these systems where the dye and the quencher are immobilized in a rigid matrix. The data in the figure clearly show that electron transfer quenching can take place over very long distances. For the samples where the free energy for the electron transfer event was very large the distance over which the electron could be transferred approached 15 Å for RhB in the PVP matrix.

The analysis of the data shows that a close adherence of these fluorescence quenching data to the Perrin model for quenching in a rigid matrix exists despite the model's simplicity. While it is not proof, the agreement lends support to several of the underlying assumptions in this work. There do not appear to be any large effects due to aggregation of the RhB. One might expect significant deviations due to exciton migration between the chromophores as has been observed previously [26 - 28], but this does not appear to be the case in these experiments. Our data do not rule out the

possibility that aggregation leads to non-fluorescent RhB that is not probed by our experiments and would therefore not be a factor in the quenching data. Additionally, the close agreement of the data with the model adds strength to our contention that ground state complexes between the RhB and the quenchers are not a major complication. Quite high concentrations of quencher are required for these experiments and interactions probably occur even at the lowest concentrations of quenchers used. Neither the absorbance nor the fluorescence excitation spectra suggest the presence of ground state complexes.

The data in Fig. 5 appear to level off at the higher values of the free energy for the electron transfer. Clearly the levelling would be more convincing if quenchers with larger free energy differences were used; however, even with the scatter in our data, there appears to be a limiting distance over which the electron transfer event will occur. These results are very close to those obtained by previous workers [6, 8] for entirely different systems and demonstrate that the polymer matrix does not exert any unusual effects. The solvent-cast polymer films containing RhB and quenchers yield results at room temperature that parallel those obtained by others with low temperature glasses. The absence of effects attributable to aggregation further indicates that the film-forming process used results in homogeneous dispersions within the amorphous polymer matrix. These results show that electron transfer quenching occurs over distances up to 15 Å in solvent-cast polymer films. The agreement between these findings and those obtained by previous workers for reagents in frozen glasses is a very positive result. Solvent-cast polymer films containing dyes and other materials are very easily fabricated and are common to many technologies. These results demonstrate that photoinduced electron transfer processes occur efficiently in such films and suggest that electron transfer may be of general use for quenching excited chromophores or initiating further chemical reactions. In this case, we looked into the possibility of using photoinduced electron transfer as a mode of dye stabilization in polymeric film matrices. However, novel imaging schemes could also be investigated which are based on using unusually long-lived [20] and matrix-stabilized radical ions as initiators. These reactive species could also serve as catalysts for solid state reactions.

## Acknowledgment

This work was supported in part by the National Science Foundation Grant DMR-8116629 under the Industry-University Co-op Program.

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