Spectral Properties of Rose Bengal Derivatives in Polar and Nonpolar Solvents

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Compounds that absorb strongly in the visible region of the spectrum, in general, do not follow Beer's law at moderate to high concentrations in polar solvents.[1] There are many reasons why this is so. The dyes aggregate and the spectra of the aggregates differ from the spectra of the fully monomeric dyes, the degree of dissociation of ionic dyes changes as a function of the ionic strength of the solution, and the coassociation equilibria with the polar solvents in which the dyes dissolve change as a function of concentration.[2]

As part of our continuing study of Rose Bengal and its derivatives,[3] we have examined the spectral properties of three Rose Bengal derivatives, Rose Bengal, C-2′ benzyl ester, C-6 sodium salt (I), the bis Rose Bengal ester of 1,10-dibromodecane (II), and a low molecular weight

$$\mathrm{RB} + \mathrm{C_6H_5CH_2Cl} \xrightarrow[80\ ^\circ\mathrm{C}]{\mathrm{DMF}} \underset{\mathrm{I}}{\mathrm{RB\text{-}CH_2C_6H_5}}$$

$$2\mathrm{RB} + \mathrm{Br(CH_2)_{10}Br} \rightarrow \underset{\mathrm{II}}{\mathrm{RB\text{-}(CH_2)_{10}\text{-}RB}}$$

polystyrene end-capped with Rose Bengal (III), in solvents of highly different polarity. The goal is to understand the molecular mechanism of dye–dye aggregation in organic solvents and, in so doing, to understand mechanisms of intramolecular energy transfer in linked systems. We have found that in methanol, Rose Bengal, C-2′ benzyl ester, C-6 sodium salt follows Beer's law in the concentration range 10^{-5} to 10^{-7} M and within this concentration range in both methanol and DMF there was no change in either the extinction coefficient of the dye or the position of maximum absorption. In related cases,[4] the equilibrium constant for dimerization is approximately 10^{-3}. Therefore, no intermolecular dimer would be observed in this concentration range. Over the concentration range 10^{-8} to 10^{-5} M, the absorbance of II also shows no deviation from linearity. Thus the dye which can only form intermolecular aggregates in this concentration range (I) remains entirely in the monomeric form and the state of ionization is not changed while the dye which can form both intramolecular and intermolecular aggregates is shown to form neither in dilute solution in the polar solvent.

The ratio of the two Rose Bengal absorptions in I at approximately 560 nm and 525 nm, respectively, decreased as the solvent was changed from polar to nonpolar. In the general sense the spectra are also shifted toward longer wavelengths in more polar solvents, the result of excited state stabilization. These effects can be summarized for the C-2′ ester, C-6 sodium salt. In nonpolar solvents, such as methylene chloride, λ_{max} is found at 563 nm, in hydrogen bonding solvents like methanol at 566 nm, and in nonhydrogen bonding polar solvents (DMF) at 572 nm. The ratio of the two peaks in I as a function of the dielectric constant of the various solvents is shown in Figure 1.

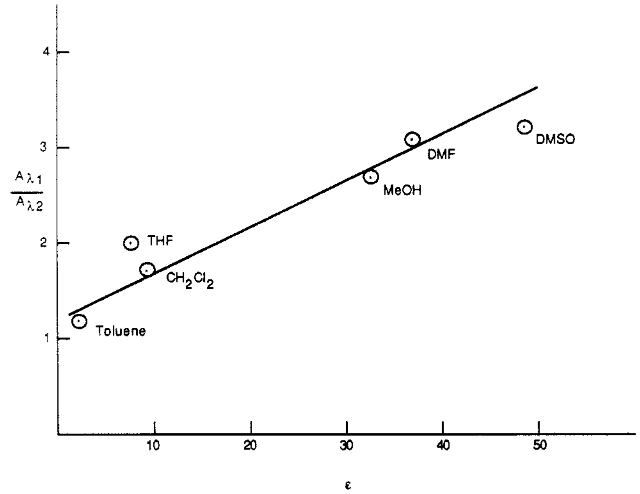

Figure 1. Ratio $A_{560\mathrm{nm}}/A_{525\mathrm{nm}}$ of Rose Bengal, benzyl ester (I) in solvents of differing dielectric constant (ε).

III	λ_{max1}	λ_{max2}	$\varepsilon_{\lambda 1}$	$\varepsilon_{\lambda 2}$	$\varepsilon_{\lambda 1}/\varepsilon_{\lambda 2}$
– – – DMF	572	529	1.628	0.470	3.46
–·–· CH_2Cl_2	562	523	1.167	0.587	1.99
····· Toluene	562	534	0.935	0.780	1.20
—— cyclohexane	562	534	0.932	0.870	1.07

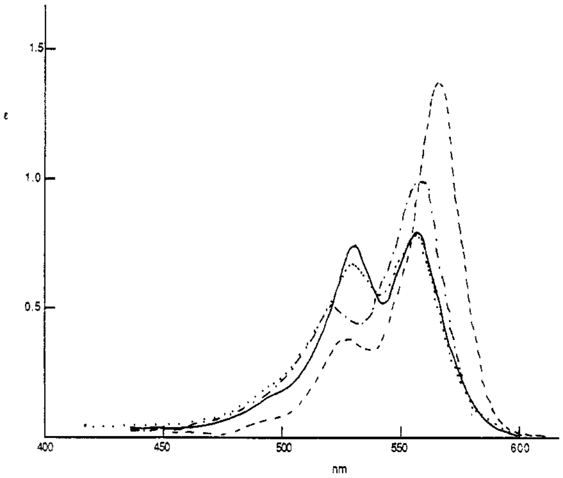

Figure 2. Solvent dependence of absorption spectrum $RBCH_2CH_2$-polystyrene-CH_2CH_2RB (II).

Low molecular weight polymeric Rose Bengals in which a nonpolar polymer backbone provides complete solubility in nonpolar solvents such as toluene and cyclohexane allow one to examine spectral parameters for very polar dyes in solvents which they are not routinely soluble. Polystyrene was anionically polymerized and the living polymer terminated with 1,2-dibromoethane. Displacement of bromide from the terminae of the polymer with Rose Bengal, disodium salt, in DMF gave polystyrene end-capped with Rose Bengal.

$$\mathrm{styrene} + \mathrm{Na^+,Naph^-} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} \text{living polymer}$$

$$\mathrm{C_6H_5CHCH_2(C_6H_5CHCH_2)_{\mathit{n}}CH_2(C_6H_6)\bar{C}H} \xrightarrow[\text{excess}]{\mathrm{BrCH_2CH_2Br}}$$

$$\mathrm{BrCH_2CH_2\text{-}polystyrene\text{-}CH_2CH_2Br} \xrightarrow[\text{dry DMF}]{\mathrm{RB}}$$

$$\mathrm{RBCH_2CH_2\text{-}polystyrene\text{-}CH_2CH_2RB}$$

In the example chosen for spectral study (M_w = 4700) the two terminal Rose Bengals are separated by, on the average, 27 styrene monomer units. The spectrum of this polymer is dramatically solvent-dependent, Figure 2. In

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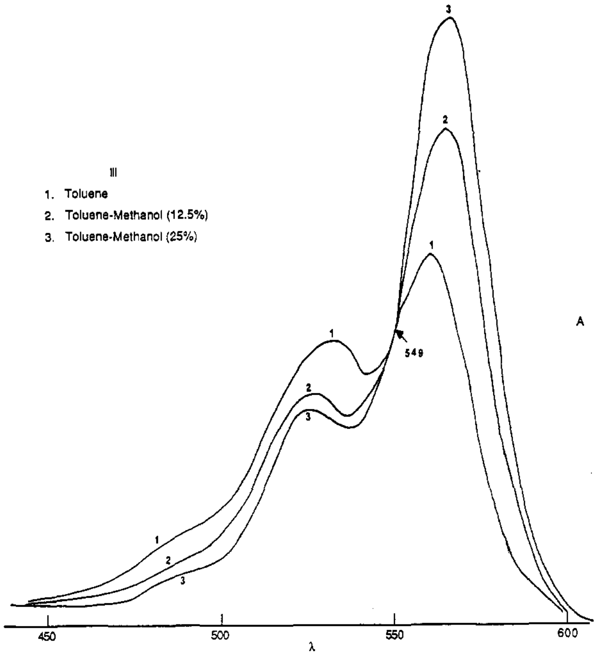

Figure 3. Equilibrium between intramolecular aggregate in II and free monomeric form.

toluene and cyclohexane where the nonpolar polystyrene backbone is responsible for solubility, the individual dye molecules appear to be highly aggregated. This is shown by the relatively small ratio of the absorbances at 562 and 534 nm, respectively, and the lack of absorption at 405 nm. The latter absorption is due to the nonionized or molecular form of the dye (III). In DMF, where the dye associates with the solvent preferentially, not only is the ratio of the two peaks at 572 nm and 529 nm large but the longer wavelength absorbance is red-shifted and the peak at 500—due to an aggregated form—reduced in size. In mixed toluene–methanol, the spectra of the aggregated and nonaggregated form exist in equilibrium and the spectra pass through an isobestic point at 549 nm, Figure 3. The decrease in $A_{\lambda 1}/A_{\lambda 2}$ is shown to be entirely in a decrease in the longer wavelength absorption, Figure 4a. This same thing is true for the benzyl ester in mixed solvents, Figure 4b.

Finally, as the data in Figure 5 show, the absorption maximum at longer wavelengths of the polymeric sample dissolved in toluene passes through a maximum at about 20% polar solvent with both DMF and methanol as the cosolvents. Then the absorption maximum drops again toward the blue. In pure methanol or pure DMF, the absorption maximum is red-shifted relative to toluene, but by only 11 nm and 9 nm, respectively, not by the maximum of 15 nm which is obtained in the 20% mixed solvent. This suggests that as polar solvent is added to toluene, aggregates are first broken up and the spectrum of the dissociated monomeric form is obtained. That the changes are due to aggregation effects rather than changes in dye ionization is indicated by the lack of change in absorption at 405 nm. In the nonionized form of the dye, this absorption is approximately three times the absorption at 490 nm. If the 490 peak were due to ionization effects rather than aggregation, a peak would appear at 410 nm for the nonionized form. It does not. As additional polar solvent is added, it coassociates with the ground state relative to the excited state, stabilizing the ground state and causing a shift toward the blue.

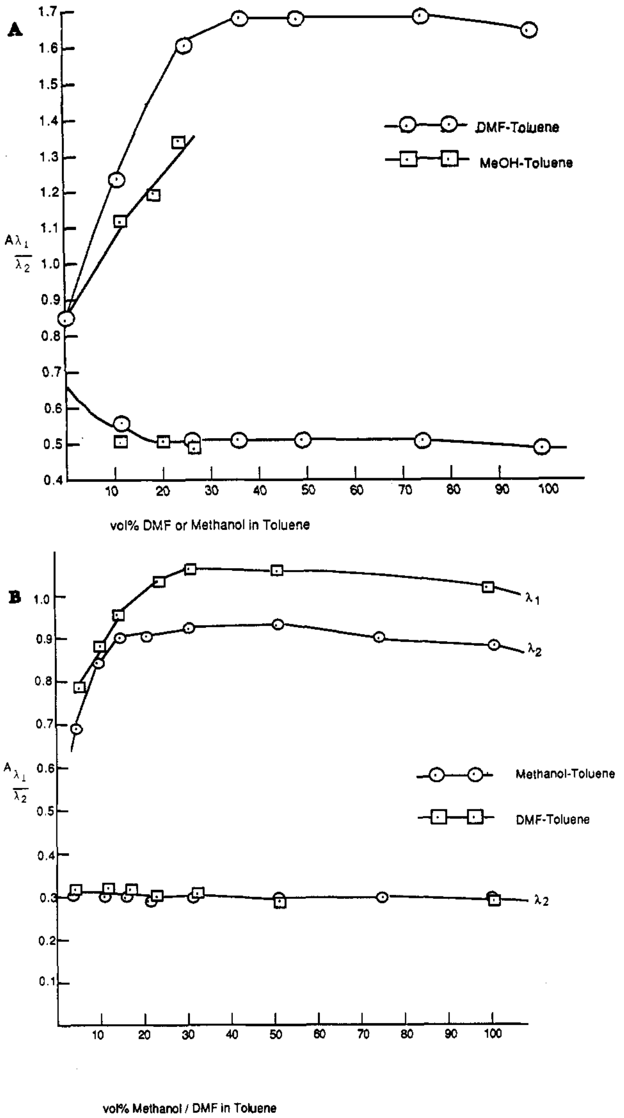

Figure 4. (a) Absorbance ($A_{\lambda 1}$ and $A_{\lambda 2}$) in mixed solvents I. (b) Absorbance ($A_{\lambda 1}$ and $A_{\lambda 2}$) in mixed solvents III.

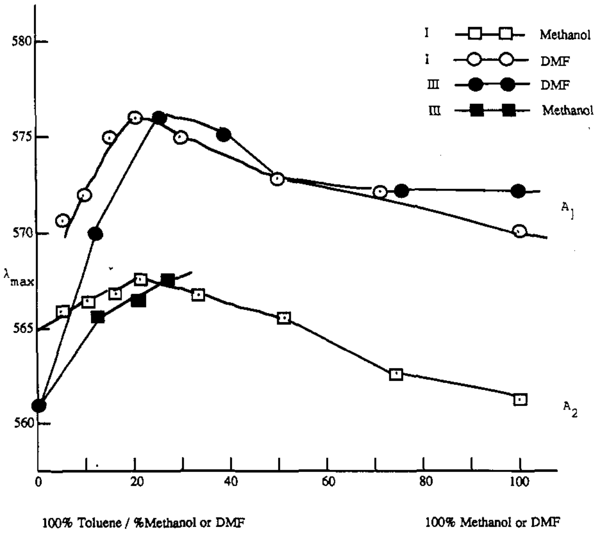

Figure 5. λ_{max}(I) and λ_{max}(III) in mixtures of DMF or MeOH and toluene.

Current results indicate that association can be brought about between the two end-capped dye molecules when low molecular weight "Rose Bengal" end-capped polystyrenes are irradiated in toluene. This work will be the subject of a future paper.

Experimental Section

Rose Bengal (DyeTel) was converted to its benzyl ester as previously described.[3] It was purified by flash chromatography on a silica gel column with dimethoxyethane (DME) as the eluent. Solvents were spectroscopic grade (Aldrich). Absorption spectra were obtained on a Varian Cary 219 instrument.

Preparation of 1,10-Decanediylbis(Rose Bengal) (II). Rose Bengal, 4.07 g (4 mmol), and 1,10-dibromodecane, 0.3 g (1 mmol) were added to 100 mL of DMF and heated for 48 h at 70 °C. The DMF is removed in vacuo and the solid red product washed several times with water and several times with ether. The product after drying is passed through a flash column and eluted with a mixture of methylene chloride/methanol (8:1). There are four distinguishable colored fractions, the first fraction being the monoester and the third fraction the dimer. The dimer ($\delta_{CH_2O(O)CR}$ = 4.11 ppm) is distinguished from the monosubstituted ester (δ_{CH_2Br} = 3.38 ppm) by proton NMR.

Preparation of Polystyrene Containing Rose Bengal as the End Groups (III). In 100 mL of dry, freshly distilled THF, recrystallized naphthalene, 2.56 g (20 mmol), was dissolved under argon. To this solution was added sodium, 0.46 g (20 mmol), in small pieces. The mixture was stirred magnetically until all of the sodium dissolved, giving a deep green solution. This solution was filtered through sintered glass and stirred under argon as the stock initiator whose concentration was determined by titration with a standard acid. For polymerization an appropriate amount of the initiator was transferred into a 100-mL, three-necked flash fitted with a gas inlet and let out system and a septum through which extra THF was injected to make the solution volume about 50 mL. The filled flask was then cooled in an isopropyl alcohol-dry ice bath to about -78 °C and 6 mL of dry, distilled inhibitor-free styrene was injected. The solution turned red immediately and the polymerization was continued for 1 h. The living polymer chains (indicated because the color remained deep red) were then quenched with a large excess of dry, distilled 1,2-bromoethane until the solution became colorless. The polymer was subsequently precipitated with methanol and purified by repeated precipitation from benzene solution with methanol. The purified polymer was dried in vacuo at 45 °C.

Rose Bengal was attached to the polymer chains as follows: the polystyrene prepared above (2 g) was dissolved in dry DMF (50 mL) and Rose Bengal, 4 g (0.004 mol), added. The solution was magnetically stirred and heated for 24 h under nitrogen in the dark at 70 °C. The polymer was precipitated from the cooled solution with methanol and the Rose Bengal red polymer recrystallized by continual precipitation with methanol from a benzene solution.

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Absolute Rate Constants for the Reaction of Triethylsilyl Radicals with Ring-Substituted Benzyl Chlorides[1]

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We have recently measured the absolute rate constants, k_1, for a large number of halogen atom abstraction reactions by the triethylsilyl radical.[3] Our results led us to propose that charge transfer in the transition state, as indicated in 1, was extensive for abstraction from alkyl

$$Et_3Si^\bullet + XR \rightarrow \underset{1}{[Et_3Si^+ \ {}^\bullet X \ :\bar{R}]} \rightarrow Et_3SiX + R^\bullet \quad (1)$$

iodides and bromides and from carbon tetrachloride. Although charge transfer appeared to be relatively unimportant in chlorine atom abstractions from simple alkyl chlorides,[3] it certainly would be expected to manifest itself if rate constants were measured for the reactions of the $Et_3Si^\bullet$ radical with a series of ring-substituted benzyl chlorides. The direction of charge separation shown above implies that electron-withdrawing substituents would increase the reaction rate. That is, a Hammett plot of log (k_2/M^{-1} s^{-1}) vs. substituent constant would be expected to have a positive slope, i.e., a positive ρ value.[4]

$$Et_3Si^\bullet + XC_6H_4CH_2Cl \rightarrow Et_3SiCl + XC_6H_4CH_2^\bullet \quad (2)$$

A search of the literature uncovered only one, very limited, study of the relative reactivities of ring-substituted benzyl chlorides toward a silicon-centered radical.[5,6] The radical in question was $Me_3Si\dot{S}iMe_2$ and its relative reactivity at 60 °C toward benzyl chloride and the 4-CH_3, 3-CH_3, and 3-CF_3 substituted benzyl chlorides was measured[5] and apparently[13] gave a ρ value of +0.29. We therefore decided to measure absolute rate constants for

Table I. Kinetic Data for Chlorine Atom Abstraction from Substituted Benzyl Chlorides by the Triethylsilyl Radical

substituent(s)	$\Sigma\sigma$[a]	$10^{-7}k_2$ (M^{-1} s^{-1})[b]	k_2^{subst}/k_2^{H}[c]
3,5-$(CF_3)_2$	0.92	11.5 ± 1.6	7.54
3,5-Cl_2	0.72	9.3 ± 0.8	7.35
4-CN	0.70	8.3 ± 0.5	
3,4-Cl_2	0.61	4.8 ± 0.3	
3-CF_3	0.46	4.5 ± 0.1	3.57
3-F	0.34	4.2 ± 0.2	
3-Cl	0.37	3.7 ± 0.2	3.61
4-F	0.15	3.3 ± 0.2	
3-CH_3	−0.06	3.3 ± 0.2	
3-OCH_3	0.10	3.1 ± 0.2	
4-$C(CH_3)_3$	−0.15	2.4 ± 0.2	
4-CH_3	−0.14	2.2 ± 0.2	
none	0	1.9 ± 0.6[d]	(1.0)

[a] From ref 18. [b] Absolute rate constants measured at 24 ± 2 °C in EtSiH:$Me_3COOCMe_3$ solvent by using benzil as probe. Errors correspond to 95% confidence limits but include only random error. [c] Relative rate constants measured at 40 °C in Et_3SiH solvent. [d] Calculated at 24 °C from the Arrhenius parameters given in the supplementary material of ref 3.

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