Photophysics of the Poly(*N*-vinylcarbazole)–Dimethyl Terephthalate Interaction

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ABSTRACT: Studies have been made of the fluorescence emission spectra and decay rates for solutions of poly(*N*-vinylcarbazole) (PVCz) containing dimethyl terephthalate (DMTP) using a photon counting technique. The kinetics of the emission decay and its variation with the wavelength of observation are consistent with the formation of both a singlet exciplex and an "exterplex" consisting of two carbazolyl groups and one molecule of DMPT. The lifetime of the exciplex is found to be 71 ± 2 ns.

Polymers with pendant aromatic groups are known to show intramolecular excimer fluorescence in dilute solution[1–7] or films.[8,9] The excimer emission of poly(*N*-vinylcarbazole) (PVCz), first noted by Klöpffer[9] in both film and solution, has received considerable attention.[6,7,10–13] Klöpffer[9] assigned the long-wavelength emission of PVCz (shown in Figure 1) above 400 nm ($\lambda_{\max}$ 420) to that of an intramolecular excimer formed between an excited and a ground state carbazole chromophore both pendant to the polymer chain. From fluorescence studies of 1:1 alternating copolymers of *N*-vinylcarbazole with dimethyl fumarate or fumaronitrile, Yokoyama et al.[11] found that excimer formation in PVCz is between nearest neighbors rather than between two separated carbazole chromophores close to each other as a result of chain folding.

David et al.[6] explained the temperature dependence of the PVCz emission in solution by postulating the existence of two different excimers. From comparison of the fluorescence decay curves and emission spectra of PVCz with several similar carbazole polymers, as well as 1,3-bis(*N*-carbazolyl)propane, Johnson[7] assigned the fluorescence maximum of PVCz at 370 nm to that of a high-energy excimer whose conformation exists prior to the initial excitation. The long-wavelength emission above 400 nm ($\lambda_{\max}$ 420 nm), which was identical to the red-shifted fluorescence tail from 1,3-bis(*N*-carbazolyl)propane, was attributed to a sandwich type excimer in which the two interacting chromophores are eclipsed

The fluorescence of PVCz is readily quenched in the presence of a variety of small ground state molecules.[13–16] In at least one case[14] the quenching process is nonuniform as a function of emission wavelength. In several instances,[13,15,16] the fluorescence quenching is accompanied by the appearance of a new structureless red-shifted emission. Yamamoto et al.[16] first reported the appearance of such a long-wavelength emission upon quenching the fluorescence of PVCz by dimethyl terephthalate (DMTP) in solution. Okamoto et al.[15] obtained similar results in PVCz films doped with DMTP. The new emission was assigned to an exciplex formed between a single excited carbazole (Cz) chromophore and DMTP. Recently, Itaya et al.[13] reported a detailed study of the fluorescence quenching of aerated PVCz by DMTP in solution. The nonuniform quenching of PVCz by DMTP was attributed to a difference in the quenching process for the excimer responsible for the 370-nm emission and the excimer responsible for the emission with maximum at 420 nm.

The present communication compares the fluorescence decay curves and emission spectra of the PVCz–DMTP system and the model ethylcarbazole (EtCz)–DMTP exciplex system. A scheme is proposed to account for the differences in these two systems.

Experimental Section

Poly(*N*-vinylcarbazole) in benzene solution (Monomer–Polymer) was reprecipitated several times into methanol and was found to have a viscosity average molecular weight of 1.2×10^6. The results obtained in this paper did not depend upon the PVCz sample used. The PVCz from Monomer–Polymer, PVCz made directly from carefully purified *N*-vinylcarbazole, and highly purified samples of PVCz supplied by A. North at the University of Strathclyde and A. Ledwith at the University of Liverpool all gave equivalent results. All polymers were radically polymerized. No *N*-vinylcarbazole was present in any of the PVCz samples. EtCz (Eastman) was recrystallized several times in ethanol and benzene. No traces of anthracene could be detected in either PVCz or EtCz. Dimethyl terephthalate was recrystallized several times in benzene and vacuum sublimed. Spectroanalyzed benzene was refluxed twice over P_2O_5 for 24 h and distilled each time, keeping only the middle third. Fluorescence spectra were measured on a Hitachi MPF-2A spectrometer corrected using a quinine sulfate standard in 1 N H_2SO_4. The single photon counting apparatus has been described by Lewis et al.[18] All samples were degassed with five freeze–thaw cycles before sealing in quartz tubes.

Results and Discussion

The fluorescence of PVCz (5×10^{-4} M) and EtCz (5×10^{-4} M) in the presence of DMTP (0.07 M) is shown in Figure 2 in thoroughly degassed benzene solutions. Identical spectra were obtained when concentrations of EtCz or PVCz from 10^{-3} to 10^{-5} M were employed in 0.07 M solutions of DMTP in benzene. Excitation at several wavelengths from 300 to 355 nm did not change the shape of the emission spectra. In the concentrated solution of EtCz, the fluorescence peak at 350 nm was not observed due to reabsorption by EtCz itself.[11] In all cases the emission of PVCz and EtCz is quenched greater than 90% by the DMTP concentrations used. The emission maximum of the long-wavelength emission from the PVCz–DMTP solution is 520 ± 10 nm (Figure 2, curve a) and is broadened in the region about 460 nm. The maximum of the long-wavelength emission of the EtCz–DMTP solution is at 460 ± 10 nm (Figure 2, curve b). The excitation spectrum for the broad, red-shifted (above 420 nm) wavelength emission of the PVCz–DMTP solution corresponds to that of PVCz. Similarly, the excitation spectrum for the red-shifted emission (above 420 nm) of the EtCz–DMTP solution is identical to that of EtCz. Furthermore, the absorption spectrum of EtCz or PVCz is not changed in the presence of DMTP, eliminating the possibility of a ground-state charge-transfer complex. Thus, both of the red-shifted emissions result from initial absorption by a carbazole chromophore.

Emission decay curves were obtained using the single photon counting method.[18] The fluorescent decay curves for PVCz and EtCz in the presence of DMTP are shown in Figure 3. The decay curves for the broad red-shifted spectra were observed through a 3.69 Corning filter and a K-470 Schott filter, thus eliminating emission below 520 nm. The fluorescence decay curve for the EtCz–DMTP solution in the region from 370 to 400 nm was measured through a 0.52 Corning filter and a 7-54 Corning filter. The decay curves did not vary with excitation wavelength or concentration of EtCz or PVCz employed (10^{-2} to 10^{-4} M). Equivalent decay curves were also

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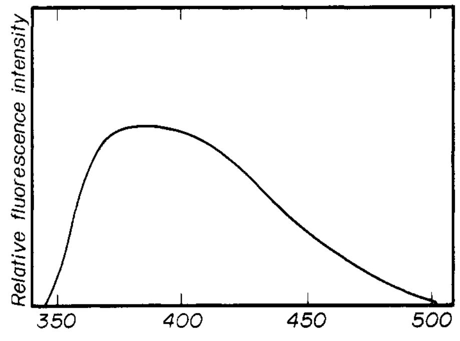

Figure 1. Fluorescence spectrum of PVCz (5×10^{-4} M) in degassed benzene at 23 °C, λ_{ex} 330 nm.

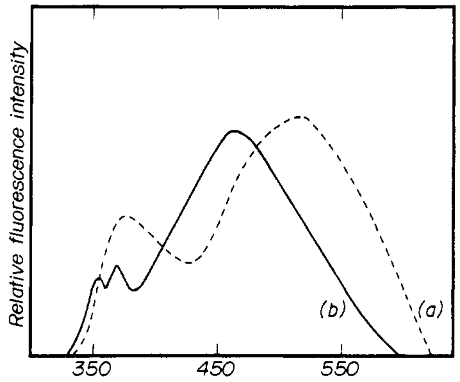

Figure 2. Fluorescence spectra of (a) PVCz (5×10^{-4} M)-DMTP (0.07 M) and (b) EtCz (5×10^{-4} M)-DMTP (0.07 M) in degassed benzene at 23 °C, λ_{ex} 330 nm. (Spectra are not on the same absolute scale.)

measured using a Spex Minimate monochromator to observe the sample fluorescence. Negligible fluorescence from PVCz (5×10^{-4} M) could be detected by the photon counter through the K-470 Schott and 3-69 Corning filters used to observe the decay curves of the broad red-shifted emissions.

The decay curves of the EtCz-DMTP system can be described by application of exciplex kinetics (Scheme I after Birks)[17] and will be discussed first. [EtCz-DMTP]* represents the exciplex formed from excited EtCz* and ground-state DMTP. The rate constants k_{FM} and k_{FE} are those for radiative decay of free EtCz* and the exciplex, respectively. The rate constants k_{IM} and k_{IE} are those for nonradiative decay of EtCz* and [EtCz-DMTP]*. The rate constant for exciplex formation is k_{EM} and the rate constant for the feedback step to give EtCz* and DMTP is k_{ME}. From Scheme I, eq 1 can be derived for $I_m(t)$, the emission intensity of uncomplexed EtCz* at time t. Similarly, eq 2 is derived for the exciplex emissions intensity $I_e(t)$, as a function of time.[17]

$$I_m(t) = k_{FM}\left(\frac{X - B_1}{B_2 - B_1}\right) e^{-B_2 t} + \left(\frac{B_2 - X}{X - B_1}\right) e^{-B_1 t} \qquad (1)$$

$$I_e(t) = \left(\frac{k_{FE}(k_{EM})}{B_2 - B_1}\right)(e^{-B_1 t} - e^{-B_2 t}) \qquad (2)$$

where

$$B_{1,2} = \tfrac{1}{2}\{(X + Y) \mp [(X - Y)^2 + 4k_{ME}k_{EM}[\mathrm{DMTP}]]^{1/2}\}$$

and

$$X = k_{FM} + k_{IM} + k_{EM}[\mathrm{DMTP}]$$
$$Y = k_{FE} + k_{IE} + k_{ME}$$

Therefore, uncomplexed EtCz should decay according to the sum of two exponentials (eq 1), while the exciplex emission should decay as the difference of two exponentials (eq 2). Such behavior is qualitatively seen in Figure 3. A unique value for $(B_1)^{-1}$ of 71 ± 2 ns is obtained from either the negative gradient of the exciplex decay (Figure 3a) or the long lived portion of the uncomplexed EtCz decay (Figure 3, curve c). The reciprocal of the long-lived component (B^{-1}) is often referred to as the exciplex lifetime, although this nomenclature is not strictly correct since the exciplex is reversibly formed.

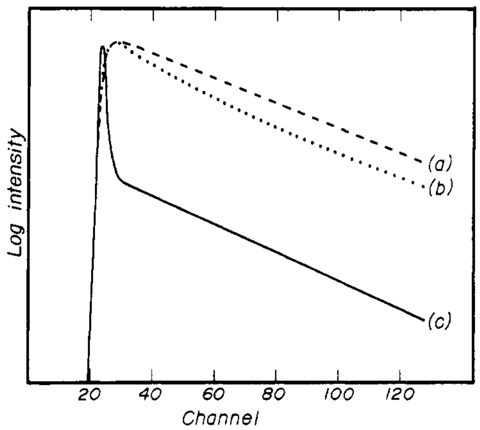

Figure 3. Fluorescence decay curves of (a) EtCz (5×10^{-4} M)-DMTP (0.07 M) and (b) PVCz (5×10^{-4} M)-DMTP (0.07 M) in degassed benzene at 23 °C observed through a 3-69 Corning filter and a K-470 Schott filter, λ_{ex} 330 nm, and (c) EtCz (5×10^{-4} M)-DMTP (0.07 M) in benzene solution through a 0-52 Corning filter and 7-54 Corning filter, λ_{ex} 330 nm. Time scale, 2.94 ns per channel.

Scheme I

$$\begin{tikzcd}
& \mathrm{EtCz^* + DMTP} \arrow[dl, "k_{FM}"'] \arrow[dr, "k_{IM}"] \arrow[rrrr, shift left, "k_{EM}"] & & & & \mathrm{[EtCz\text{-}DMTP]^*} \arrow[llll, shift left, "k_{EM}"] \arrow[dl, "k_{FE}"'] \arrow[dr, "k_{IE}"] & \\
\mathrm{EtCz} + h\nu & & \mathrm{EtCz} & & \mathrm{EtCz + DMTP} + h\nu' & & \mathrm{EtCz + DMTP}
\end{tikzcd}$$

Since EtCz forms an exciplex with DMTP, it should be possible to estimate the dipole moment of the exciplex from the shift in the emission maximum in solvents of increasing polarity.[19] The [EtCz-DMTP]* exciplex emission decreases and its maximum shifts to the red in nitrogen-purged pure solvents of increasing polarity or in mixed solvents of benzene and acetonitrile (λ_{max} 490 ± 10 nm in solvent of dielectric constant 5.3). This emission is completely extinguished in solvents of dielectric constant greater than 20. A dipole moment greater than 12 D can be inferred from the magnitude of the exciplex shift as a function of solvent polarity.[19]

Upon qualitative inspection of the steady state emission spectra and fluorescence decay curves of the broad red-shifted emission of the EtCz-DMTP and PVCz-DMTP solutions, two observations can be readily made. The fluorescence maximum of the long-wavelength emission in the PVCz*-DMTP solution is red shifted by 60 nm from the [EtCz-DMTP]* exciplex emission. The decay curve for the [EtCz-DMTP]* exciplex is clearly exponential after the initial portion of the decay, and the complete curve is described by eq 2 where a difference of exponentials accounts for the shift of the decay curve maximum (Figure 3, curve a) to longer times (compared with the decay curve of EtCz-DMTP observed from 370-400 nm in Figure 3, curve c). However, the decay curve for the red-shifted emission of the PVCz-DMTP solution is a sum of exponentials (after the initial portion of the decay) and fails to satisfy eq 2. Therefore, the complex(es) responsible for the long-wavelength emission of the PVCz-DMTP system is not described solely by the small molecular analogue [EtCz–DMTP]* exciplex. It is suggested that an additional complex, an excited triplex, formed from an interaction between a [Cz–DMTP]* exciplex and a pendant carbazole chromophore (Cz) accounts for both the observed multiexponential (sum) decay curves and the 60-nm red shift of the long-wavelength emission maximum. Emission from both the exciplex [Cz–DMTP]* and the excited triplex, with maxima at 460 and 520 nm, respectively, would result in a double exponential (sum) decay curve (Figure 3, curve b).[2] The initial shift in the decay curve maximum in Figure 3, curve b, is the same as in Figure 3, curve a. Furthermore, the decay constant obtained for the negative gradient of Figure 3, curve b, after channel 90 is 74 ± 3 ns, within the experimental error of the decay constant of 71 ± 2 ns for $(B_1)^{-1}$ obtained for the [EtCz–DMTP]* exciplex in Figure 3, curve a.

Recent work by Caldwell et al.[21] suggests that an exciplex formed between an excited aromatic donor and a ground-state acceptor readily forms an excited triplex or "exterplex" with an appropriate third molecule. From a consideration of orbital interactions and electronic effects, they found that the geometry for the exterplex formation always resulted from the interaction of an identical aromatic donor (or other donor) with the excited electron-deficient donor partner of the exciplex. Furthermore, an exterplex was previously identified for the 1,3-bis(dinaphthylpropane)dicyanobenzene system using time-resolved fluorescence spectra.[22] The exterplex was formed from interaction of the second ground-state naphthalene (Na) with the [Na–DBNB]* exciplex rather than interaction of DCNB with the [Na–Na]* excimer. Thus the proposed exterplex formed between PVCz and DMTP most likely results from the attack by a neighboring Cz chromophore on the Cz partner of the [Cz–DMTP]* exciplex.

Interactions between ground-state carbazole groups in PVCz have been postulated to account for the red shift in the PVCz absorption spectrum compared to EtCz.[23] Furthermore, a shift in the absorption spectra maxima of charge-transfer complexes formed between ground-state PVCz and strong ground-state acceptors such as tetrocyanoethylene (as opposed to absorption maxima of charge-transfer complexes between ground-state EtCz and the same electron acceptors) has previously been attributed to an electronic interaction between neighboring Cz groups on the same polymer chain.[24] An interaction between the $[\mathrm{Cz}^+\text{–DMTP}^-]$ exciplex and a neighboring carbazole chromophore (Cz) would be even more favorable than the PVCz–electron acceptor ground-state interaction, due to the degree of charge transfer in the exciplex (dipole moment is >12 D). Thus, a neighboring electron-rich Cz group strongly interacts with the electron-deficient partner (Cz^+ group) of a $[\mathrm{Cz}^+\text{–DMTP}^-]^*$ exciplex to give a new excited ternary complex or exterplex.

$$\mathrm{Cz} + \underset{\text{exciplex}}{[\mathrm{Cz}^+\text{-DMTP}^-]^*} \longrightarrow \underset{\text{exterplex}}{[\overbrace{\mathrm{Cz\text{-}Cz}}^{+}\text{-DMPT}^-]^*}$$

The positive charge is now delocalized over two Cz groups, thus enhancing the electron-transfer process while leading to charge separation. The complexation of two carbazole chromophores with a single electron acceptor is similar to the two-chlorophyll molecule interaction with a quinone in the primary process in photosynthesis.[25] Such a polymer model may provide useful information regarding the migration and transfer of energy in highly aggregated systems.

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