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# Time Resolved Fluorescence Studies of Poly(*N*-vinylcarbazole), Poly(1-vinylnaphthalene), and 1,3-Bis(*N*-carbazolyl)propane

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Excimer emission from polymers with pendant aromatic groups has recently received considerable attention.[1-12] In nearly every case the excimer emission has been shown to arise from a sandwich type excimer in which the $\pi$ orbitals of the aromatic rings overlap substantially. For example, the excimer fluorescence ($\lambda_{max} \simeq 410$ nm) of poly(1-vinylnaphthalene) (PVN) dominates the relatively weak emission from the naphthyl monomer.[9] However, the excimer emission of poly(naphthyl methacrylate) (PNMA) ($\lambda_{max} \simeq 390$ nm) is approximately equal to the monomer emission ($\lambda_{max} \simeq 340$ nm) in ethyl acetate.[2] In neither case was any type of excimer emission other than that of the low-energy excimer ($\lambda_{max} \simeq 400$ nm) observed.[2,9] In contrast, the emission spectrum of poly(*N*-vinylcarbazole) (PVCz) results from two distinct excimers, a low-energy sandwich type ($\lambda_{max} \simeq 420$ nm) and a high-energy excimer of undefined structure ($\lambda_{max} \simeq 375$ nm).[8] Emission from the high-energy excimer is relatively more intense in a predominately syndiotactic polymer obtained by radical polymerization than in a more isotactic polymer obtained by cationic polymerization.[12] Itaya et al. have proposed that the high-energy excimer has a structure in which only one pair of phenyl rings from the two carbazole chromophores overlaps.[12] The high-energy excimer in PVCz is thought to arise from excimer traps existing prior to the initial absorption of light by the carbazolyl chromophore.[8] The low-energy sandwich excimer can be formed by two possible mechanisms, either directly or by reorientation of the high-energy excimer.

No high-energy excimer occurs from 1,3-bis(*N*-carbazolyl)propane (BCP), the low molecular weight model compound of PVCz.[13] Only monomer emission ($\lambda_{max} \simeq 350, 370$ nm) and low-energy excimer emission ($\lambda_{max} \simeq 420$ nm) can be detected for BCP. The low-energy excimer emission is very weak, suggesting little interaction between the neighboring carbazolyl chromophores. The absence of a high-energy excimer emission suggests that the conformational constraints imposed by the stiff polymer chain in PVCz are not present in BCP.

The formation of two distinct excimers, one of high energy and one of low energy, in PVCz, is, therefore, unique among vinyl aromatic polymers. In order to elucidate further the nature of the excimers formed in polymers and in certain model compounds, we have measured the time resolved spectra of various vinyl aromatic polymers and one model compound, BCP. Time resolved fluorescence spectroscopy has been previously used to study the energy transfer mechanism in a copolymer of naphthyl methacrylate and 9-vinylanthracene and in the poly(naphthyl methacrylate) homopolymer.[14]

## Experimental Section

The PVCz (Monomer–Polymer) was purified by threefold precipitation into methanol followed by chromatography on silica gel. The ultraviolet spectrum, fluorescence emission spectrum, fluorescence decay times, and excitation spectrum all agree with literature data for PVCz. BCP was synthesized by the method of Lewis et al.[15] and purified by preparative thin-layer chromatography. PVN was prepared by spontaneous polymerization and purified by successive precipitation from benzene solution into methanol. Benzene was twice distilled from phosphorus pentoxide retaining the middle fraction each time. Ethyl acetate was distilled and stored in the dark.

Steady state fluorescence spectra were taken on a Hitachi MPF-2A fluorescence spectrometer and corrected for phototube response using quinine sulfate in aqueous sulfuric acid as a standard. The time resolved fluorescence spectra were taken using the single photon counting apparatus in the multichannel scaling mode.[16] A Spex Minimate monochromator (1.25 mm slit width) was installed with a Rapid-Syn-28PS stepping motor attached to rotate the grating. The multichannel analyzer was employed in the multichannel scaling repeat mode with the analog to digital converter serving as a single channel analyzer. The complete wavelength spectrum was scanned over 20 times in each case in order to correct for noise and lamp fluctuation. The steps were made in increments of 0.14 nm with 0.1 s per step. The time window employed was determined by setting the upper and lower voltage (or time) limits for the single channel analyzer. The time limits were calibrated by observing the decay of a lamp profile scattered off a Ludox scattering solution. Since the sample is continually being excited over a finite period defined by the decay of the low-pressure nitrogen lamp intensity profile, it is difficult to assign the exact time values of the time windows for the time resolved spectra.[16b] The time settings are given as the time difference of the upper (or lower) limit, determined by the discriminator settings on the analog to digital converter, from the maximum of the exciting lamp.[17] The time resolved spectra are adjusted to fit on the same time scale. Time resolved fluorescence spectra are uncorrected for photomultiplier tube response. All samples were degassed with five freeze–pump–thaw cycles before sealing in quartz test tubes.

## Results and Discussion

The steady state fluorescence spectra of PVCz ($5 \times 10^{-4}$ M) and BCP ($2 \times 10^{-4}$ M) in benzene are shown in Figure 1. The low-energy excimer emission (above 420 nm) is seen for both PVCz and BCP. The time resolved emission spectra for PVCz are shown in Figure 2 at several time intervals. (In curve a, the points from the multichannel analyzer are actually plotted.) The spectrum in curve a was taken at an upper "time setting" of 0.23 ns from the peak maximum of the exciting lamp intensity. From a consideration of the intensity of exciting light as a function of time, it follows that >96% of the

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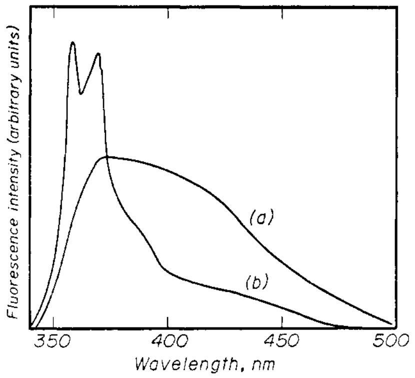

**Figure 1.** Fluorescence spectra of (a) PVCz ($5 \times 10^{-4}$ M) and (b) BCP ($2 \times 10^{-4}$ M), both in degassed benzene at 23 °C: excitation wavelength, 330 nm; corrected for phototube response. Note that the spectra are not on the same absolute scale and are adjusted to fit on the same intensity scale.

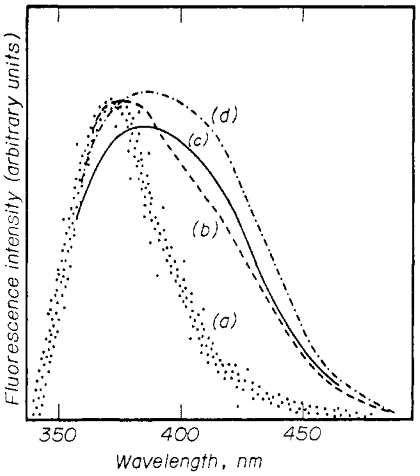

**Figure 2.** Time resolved fluorescence spectra of PVCz ($5 \times 10^{-4}$ M) in degassed benzene at 23 °C: excitation wavelength, 313 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 0.23 ns from lamp maximum; (b) lower limit 8 ns and upper limit 9.4 ns from lamp maximum; (c) lower limit 19 ns and upper limit 35 ns from lamp maximum; (d) lower limit 182 ns and upper limit 323 ns from lamp maximum. Note that the spectra are adjusted to fit on the same intensity scale.

fluorescence intensity of the emission spectrum in curve a is derived from fluorescence emitted within 2 ns after the initial absorption of light. This spectrum shows only the fluorescence of the high-energy excimer ($\lambda_{max} \simeq 375$ nm). The emission from the low-energy sandwich excimer is virtually absent or else is very weak on this short time scale. It is obvious that the high-energy excimer is formed almost immediately upon excitation. This is consistent with the formation of the high-energy excimer from traps preformed in the polymer chain.[8] The low-energy sandwich excimer, as previously discussed, is probably formed from either a reorientation of the high-energy excimer or a direct interaction of an excited carbazolyl and a ground state carbazolyl chromophore. In Figure 2, curve b, taken at time settings between 8 and 9.4 ns from the peak of the lamp maximum, relatively weak emission from the low-energy excimer appears above 400 nm, but the emission from the high-energy excimer ($\lambda_{max} \simeq 375$ nm) still dominates. The spectrum in Figure 2, curve c, taken at even longer time settings, shows a strong emission from the low-energy excimer comparable to the emission from the high-energy excimer. The spectrum shown in Figure 2, curve d, was taken at very long times. The intensity of the low-energy excimer relative to the high-energy excimer has not changed appreciably from Figure 2, curve c. Thus once the low-energy excimer is formed, its emission intensity (and therefore concentration) relative to that of the high-energy excimer does not change.

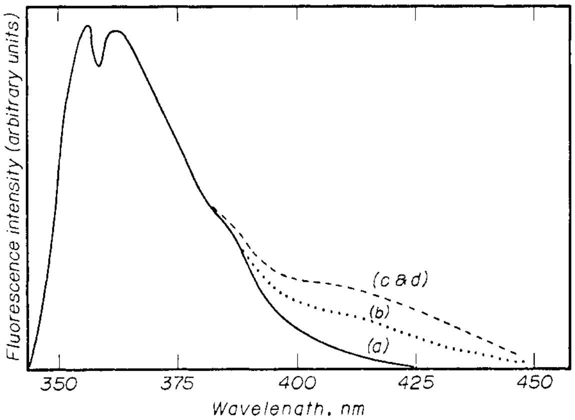

**Figure 3.** Time resolved fluorescence spectra of BCP ($2 \times 10^{-4}$ M) in degassed benzene at 23 °C: excitation wavelength, 313 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 0.23 ns from lamp maximum; (b) lower limit 8 ns and upper limit 9.4 ns from lamp maximum; (c) lower limit 19 ns and upper limit 24 ns from lamp maximum; (d) lower limit 139 ns and upper limit 290 ns from lamp maximum. Curves (c) and (d) are both shown the same since there is no appreciable difference in the structure of the two spectra. Note that the spectra are adjusted to fit on the same intensity scale.

The time resolved emission from BCP is shown in Figure 3 for several time settings. The spectrum of Figure 3, curve a (taken at the same time settings as Figure 2, curve a), shows emission from only the monomer ($\lambda_{max} \simeq 360$ nm) of a single carbazolyl chromophore. Almost no emission can be observed at wavelengths above 400 nm. Thus, as in the case of PVCz, no appreciable emission from the carbazolyl excimer emission at wavelengths corresponding to the sandwich excimer ($\lambda_{max} \simeq 420$ nm) is observed. In Figure 3, curves b and c (taken at longer time intervals), the excimer emission is present, but it has a weak intensity compared to the monomer emission with a maximum at 360 nm. The spectrum in Figure 3, curve d, taken at the longest time setting, is identical to the spectrum in curve c of the same figure, taken at a shorter time interval. Thus, as with PVCz, once the low-energy excimer is formed, its intensity relative to that of the monomer (high-energy excimer in the case of PVCz) does not change appreciably. These results suggest that there is a reversible path between the monomer and the low-energy excimer for BCP and a reversible path between the high-energy excimer and the low-energy excimer for PVCz. Johnson has previously proposed reversible pathways on the basis of the variation of the steady state emission spectra with temperature.[8]

In order to understand better the time resolved spectra of PVCz and BCP, the time resolved spectra of PVN, which show only naphthyl monomer emission and the low-energy excimer, were taken for comparison. The steady state fluorescence spectrum of PVN ($4 \times 10^{-3}$ M) is shown in Figure 4. There is emission from the naphthyl monomer chromophore around 340 nm and excimer near 400 nm. The ratio of excimer to naphthyl monomer emission is very high for PVN.

The time resolved spectra of PVN shown in Figure 5 are for several time intervals. At the shortest time (curve a, Figure 5), the excimer emission ($\lambda_{max} \simeq 400$ nm for PVN) and the monomer emission from the naphthyl chromophore ($\lambda_{max} \simeq 340$ nm) are both present, At longer times (curve b, Figure 5), the excimer emission increases relative to the monomer emission. Curves c and d (Figure 5) show an appreciable emission from the naphthyl monomer as well as the strong

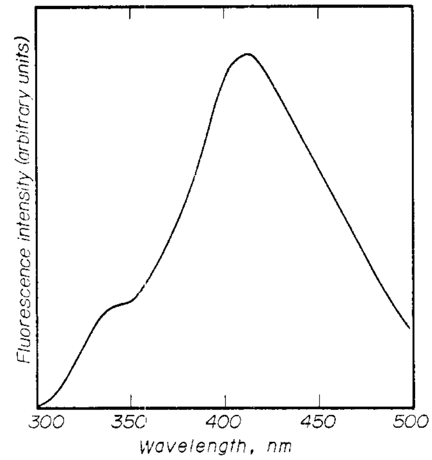

**Figure 4.** Fluorescence spectrum of PVN ($4 \times 10^{-3}$ M) in degassed benzene at 23 °C; excitation wavelength, 320 nm.

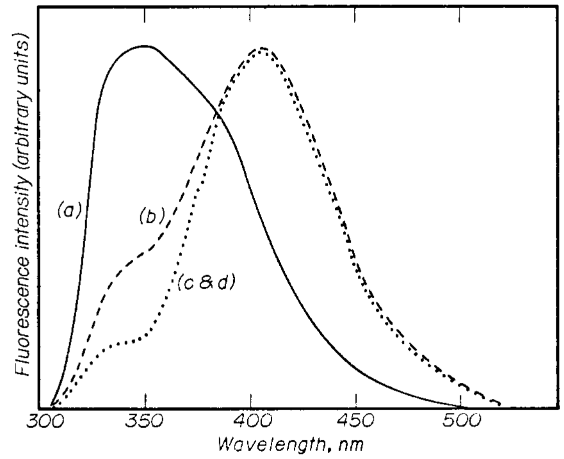

**Figure 5.** Time resolved fluorescence spectra of PVN ($4 \times 10^{-3}$ M) in degassed benzene at 23 °C: excitation wavelength, 313 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 0.23 ns from lamp maximum; (b) lower limit 8 ns and upper limit 9.4 ns from lamp maximum; (c) lower limit 19 ns and upper limit 35 ns from lamp maximum; (d) lower limit 110 ns and upper limit 290 ns from lamp maximum. Curves (c) and (d) are both drawn the same since there is no appreciable difference in the structure of the two. Note, spectra are adjusted to fit on the same intensity scale.

excimer fluorescence of PVN. As in the cases of PVCz and BCP, the excimer is formed reversibly and partially dissociates to an excited monomer and ground state monomer after being formed, and even on the longest time scale, the monomer emission does not disappear.

The PVN low-energy excimer is formed rapidly, being present at the shortest time scale employed. For PVN, the orientation required for excimer formation must be accomplished on a time scale less than 2 ns. Evidently, in the case of PVN, it is possible for a significant number of the naphthyl groups to rotate into position for excimer emission at times less than 2 ns. This is feasible only if the rotation relaxation time of the naphthyl groups in PVN is <10 ns or if there are a number of sites of suitable geometry formed before the initial excitation. The excimers in PVN may be formed as a result of a combination of these two processes.

The high-energy excimer of PVCz is also formed rapidly, being observable at the shortest time scale (Figure 2, curve a), while the low-energy excimer, like that of BCP and in contrast to PVN, does not. It should be noted that within the limits of our instrumentation it might be difficult to detect a small intensity of emission. Despite this, only a very weak, negligible emission from the PVCz or BCP low-energy excimer could possibly be present on the shortest time scale employed. A reasonable interpretation for the lack of appreciable emission from the low-energy excimer at short time scales is offered by a consideration of the dynamic properties of the two interacting chromophores in the excimer. PVCz has a dielectric segmental rotational relaxation time[18] for chains $M_w > 4 \times 10^4$ of about 180 ns, indicative of a very stiff chain. Thus it probably requires a certain time for the low-energy excimer to form. This would explain why a significant emission from the low-energy sandwich excimer is not seen on the short time scales but is evident at later times (Figure 2, curves b, c, and d). This is in contrast to the results observed for the low-energy excimer for a more flexible carbazolyl methacrylate polymer.[19] The high-energy excimer of PVCz is formed rapidly. This evidence suggests that in PVCz the high-energy excimer is located at preformed sites (or traps) which are available because of the restricted rotations imposed on the carbazole chromophores by the stiff PVCz chain.

In conclusion, the use of time resolved fluorescence spectroscopy yields a great deal of information about the formation of excimers of PVCz, BCP, and PVN. The results suggest that the low-energy excimers in all three systems are formed reversibly. However, only the low-energy excimer of PVN and the high-energy excimer of PVCz are formed appreciably on the shortest time scales used. It may be that the rapidity with which sandwich type, low-energy excimers of polymers are formed can be correlated with the rotational relaxation times of the interacting groups. However, the formation of excimers in polymers certainly depends also on other factors such as the stiffness of the polymer backbone and the steric restraints imposed by bulky side groups which may cause preformed excimer sites. This new technique should resolve many problems in polymer photophysics and should prove to be a powerful method for elucidating the mechanisms of energy transfer and trapping in polymer systems.

**Acknowledgments.** The authors wish to acknowledge the generous financial support of the National Research Council of Canada and helpful discussions with Dr. J. R. MacCallum.

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