the cyclodextrin inclusion complexes with their excellent single-crystal X-ray structures as models, the molecular conformation of the residues in the helical chains can be predicted. On the basis of these empirical correlations the torsion angles ϕ_2' and ϕ_1 describing the conformation about the glycosidic linkage and the angle χ describing the conformation of the C(6) hydoxyl are predicted. The predicted torsion angles are in general agreement with those previously suggested from X-ray fiber diffraction data and suggest that the helix conformation of the "V" amyloses is different from that of the "A" and "B" starches. The molecular conformation in the noncrystalline regions of starches appears to be similar to that in "V" amylose. The NMR results, previous X-ray fiber diffraction studies, and molecular modeling are consistent with right-handed helices for the "A" and "B" starches and left-handed helices for "V" amylose complexes and starch in noncrystalline regions.

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Registry No. V_h(BuOH), 66461-46-9; V_{DMSO}, 110682-30-9; cyclomaltoheptaose dodecahydrate complex, 20986-19-0.

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Triplet Photophysical Properties of the Alternating Copolymer of 2-Vinylnaphthalene with Methyl Methacrylate

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ABSTRACT: Delayed luminescence spectra of the subject alternating copolymer have been obtained in frozen glassy solutions at 77 K, solid films at 77 K, and fluid solutions at ambient temperature. Delayed fluorescence emission is detected in all three media. In solid films at 77 K and in fluid solutions at ambient temperature the delayed fluorescence emission consists of both monomeric and excimeric components. In frozen glassy solutions both phosphorescence and delayed fluorescence emissions are monomeric in character. Negligible phosphorescence was observed at 77 K from solid films of the copolymer which had been treated by prior heating under vacuum. As a rationale for this unusual behavior it is proposed that triplet exciton trap sites are essentially absent here and so the migratory excursions of these excitons are relatively unhindered. This leads to enhanced rates of triplet–triplet annihilation which are orders of magnitude larger than the rate of phosphorescent decay.

Introduction

In recent years a rather substantial body of evidence has been accumulated attesting to the special photophysical properties of chromophoric groups covalently bonded to the backbone of a polymer chain.^{1} Vinyl aromatic polymers, for example, display some luminescence characteristics similar to their monomeric analogues but other characteristics which serve to remind us of the relatively high local chromophore concentrations and special steric arrangements which are peculiar to the polymeric species.

The excimer fluorescence commonly observed for many polymers, even in dilute solutions, provides a textbook example of this effect.[2] Excimeric phosphorescence frequently reported in solid polymeric films provides another.[3,4]

A modest number of experimental investigations have been carried out to probe the limits of this special influence of the polymeric structure on photophysical behavior. One approach is to insert a flexible short chain segment between the chromophore and the main carbon backbone.[5] This relieves steric crowding and permits greater freedom of motion to the pendant chromophore. As expected, this sort of structure diminishes the relative magnitude of the excimeric fluorescence. Other experiments have indicated that a combination of steric and electronic effects may be used to moderate the magnitude of the excimer fluorescence.[6]

Some of the earliest experiments on polymer luminescence utilized the method of copolymerization to test the effects of varying the local chromophore density.[7] In fact, the currently accepted mechanism of triplet exciton migration received its initial impetus from such experiments. A very systematic way of varying the local chromophore density on a polymer chain is available by the use of either block copolymerization or alternating copolymerization.[8] In the current study an examination of the photophysical properties, primarily of the triplet state, of an alternating copolymer are described. The particular material chosen for study consists of alternating methyl methacrylate and 2-vinylnaphthalene units. The phosphorescence, delayed fluorescence, delayed luminescence decay kinetics, and excimeric luminescence of this polymer are reported. The triplet–triplet absorption spectrum over a limited spectral range has also been examined and the triplet probe method has been used to follow the kinetics of triplet decay.

In the following work a special emphasis has been placed upon those photophysical processes which depend upon interchromophore interactions. Examples of such processes include delayed fluorescence, exciton migration, and excimer formation. The alternating copolymer contains a naphthalene chromophore on every fifth backbone carbon atom and it might be suspected that most of these interchromophore processes would be diminished in importance compared with a vinylnaphthalene homopolymer. This investigation is intended to address that particular point.

Experimental Section

Preparation and Purification of Chemicals. The alternating copolyer is the same material described in earlier work.[8] The 2-methyltetrahydrofuran (MTHF) was treated by passing it through an alumina column followed by distillation from lithium aluminum hydride. Benzene was refluxed over concentrated H_2SO_4 for 24 h and was then shaken with dilute base and distilled water. After drying over anhydrous sodium sulfate it was then distilled.

Sample Preparations. Three different types of samples were used in this work. Neat polymer films were cast from benzene solution onto quartz plates and were allowed to dry in a solvent-saturated atmosphere. They were then heated at 100 °C in a vacuum oven overnight. Solutions were prepared in either 1- or 10-mm cylindrical quartz cells. The 1'mm cells are used in the cryotip apparatus and these samples were all examined at 77 K. This apparatus does not presently accommodate cells of longer path length and so the samples in 10-mm cells were all examined at room temperature. The samples in 1'mm cells were sealed off with a hand torch after two freeze–pump–thaw cycles on the vacuum system. The samples in 10-mm cells were also sealed off under vacuum but were more thoroughly degassed, usually with six or seven freeze–pump–thaw cycles at 1.3×10^{-3} Pa.

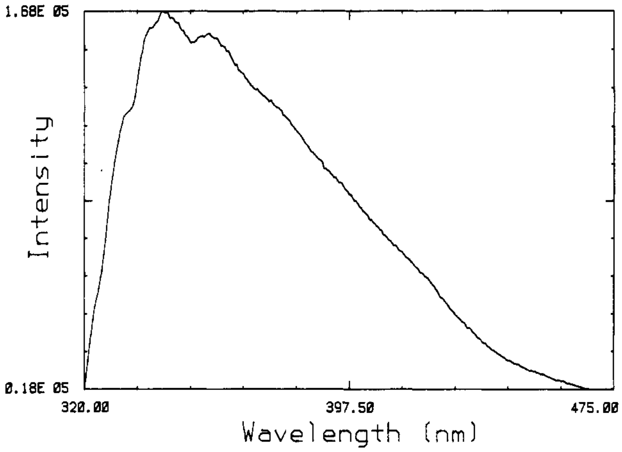

Figure 1. Fluorescence spectrum of a degassed solution, 1.4×10^{-3} M in monomer units, of the alternating copolymer in MTHF.

Apparatus for Photophysical Studies. A Spex Model III Fluorolog spectrometer was used to obtain fluorescence spectra. Delayed emission spectra and lifetimes used either a conventional phosphorimeter built in the laboratory or a second custom-built system utilizing excimer laser excitation. The conventional system has been described before.[9] Its essential features consist of a Hg–Xe excitation source and separate excitation and emission choppers driven by synchronous motors. The emission beam is directed to a monochromator (Spex Model 1670) and is detected by an EMI 9789 photomultiplier. The emission signal is recorded by using a Nicolet Model 1072 signal averager. The data may then be relayed to other computer facilities for analysis. The laser system has also been recently described.[10] In this case the excitation source is a Tachisto Model 401XR XeCl excimer laser. The system may be used both for luminescence spectroscopy and kinetics for pump–probe experiments involving triplet–triplet absorption. The probe beam is a tungsten lamp. In either type of experiment the optical signal is passed through a Spex Model 1690B monochromator, detected by an EMI 9789 photomultiplier, and recorded by using a Nicolet 12/70 signal averager.

Experimental Results

In Figure 1 a fluorescence spectrum is presented of the copolymer in solution at ambient temperature. The long tail of the emission signal extending to lower energies and the lack of any emergent structural features for the degassed sample suggest that an excimeric component is present here. By contrast the air-saturated solution possesses little indication of excimeric emission. Analogous results were observed previously by using CCl_4 quenching.[8] Thus, it appears that even though neighboring chromophore groups are separated by a five-carbon segment there is sufficient local flexibility in the polymer coil to bring at least some groups together in an arrangement properly oriented for excimer formation.

Phosphorescence spectra of this copolymer were recorded by using a variety of experimental conditions. The spectrum of a dilute solution of the polymer in MTHF at 77 K is presented in Figure 2. The emission shown here was recorded at 50 ms after the excitation pulse so the fluorescence emission is definitely delayed fluorescence.

The dependence of the phosphorescence intensity (I_{em}) upon the excitation intensity (I_{ex}) was determined by a systematic attenuation of the excitation beam by using neutral density filters. The average value of n in the equation $I_{1,em}/I_{2,em} = [I_{1,ex}/I_{2,ex}]^n$ was 1.1 for four separate determinations. A similar set of experiments was carried out for the delayed fluorescence and a value of n equal to 1.8 was found.

The lifetimes of both delayed fluorescence and phosphorescence emissions were also determined for this dilute solution at 77 K. They are 2.4 s and 0.6 s for phos-

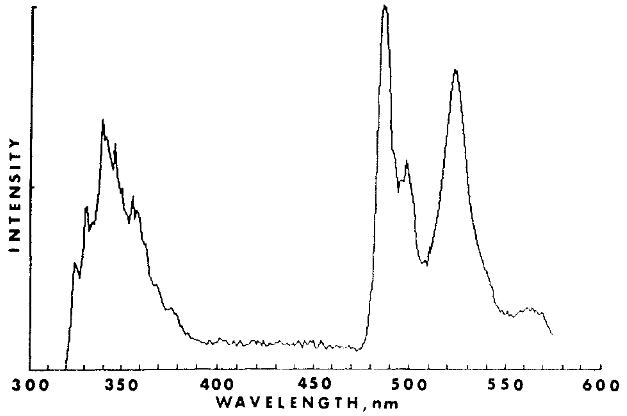

Figure 2. Delayed luminescence spectrum of the alternating copolymer 2.97×10^{-3} M in monomer units in MTHF at 77 K. Delay time after excitation is 50 ms.

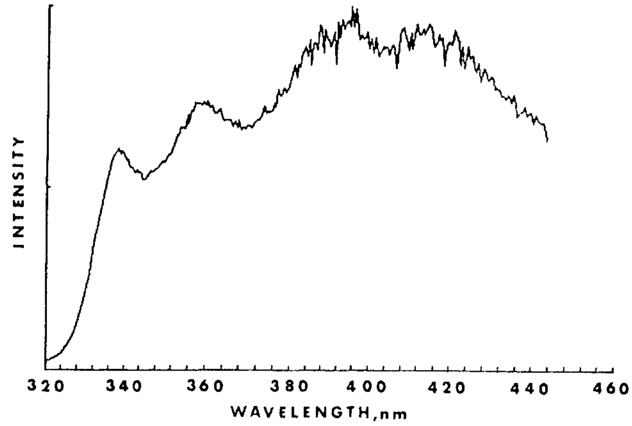

Figure 3. Delayed luminescence spectrum of the alternating copolymer 1.4×10^{-3} M in monomer units in MTHF at ambient temperature. Delay time after excitation is 50 μs.

phorescence and delayed fluorescence, respectively. In both cases there was found a reasonably good fit to a single exponential decay at long times after the excitation pulse.

The delayed luminescence emission was also investigated in a fluid solution of MTHF at ambient temperature. Figures 3 and 4 represent a summary of these experiments. In Figure 3 it can be seen that at a delay time of 50 μs after excitation the luminescence in the delayed fluorescence region consists of a mixture of monomeric and excimeric components. In Figure 4 it will be noted that at longer delay times of 200 μs and 2 ms the monomeric component of the delayed fluorescence has nearly disappeared leaving a prominent excimeric type of delayed fluorescence. At the longest delay time of 2 ms after excitation the luminescence signal has become very weak and a poorly resolved long-wavelength emission becomes the dominant component. The wavelength range of this emission corresponds to that of ordinary phosphorescence of the naphthalene chromophore.

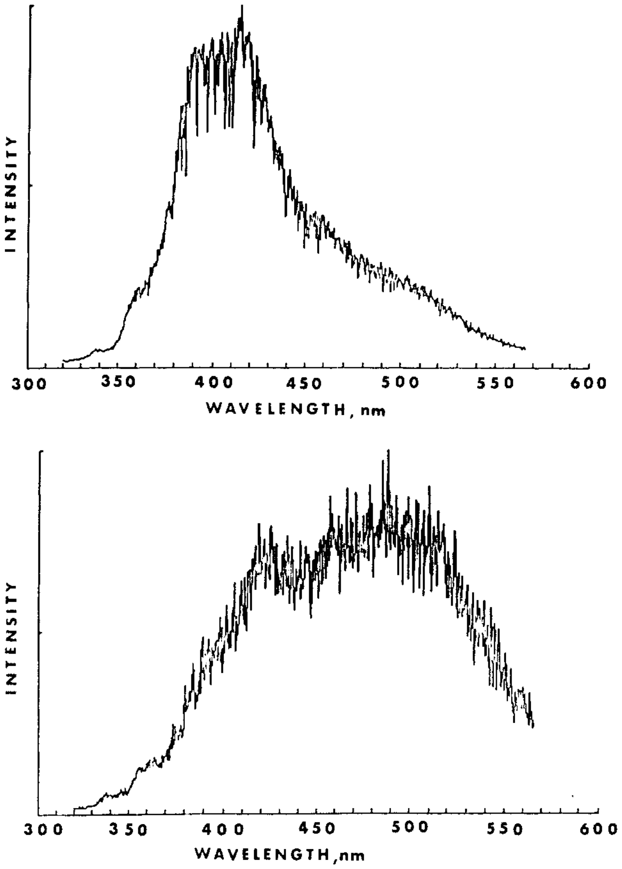

Figure 4. Delayed luminescence spectra of the alternating copolymer 1.4×10^{-3} M in monomer units in MTHF at ambient temperature. (Top) Delay time after excitation is 200 μs. (Bottom) Delay time after excitation is 2 ms.

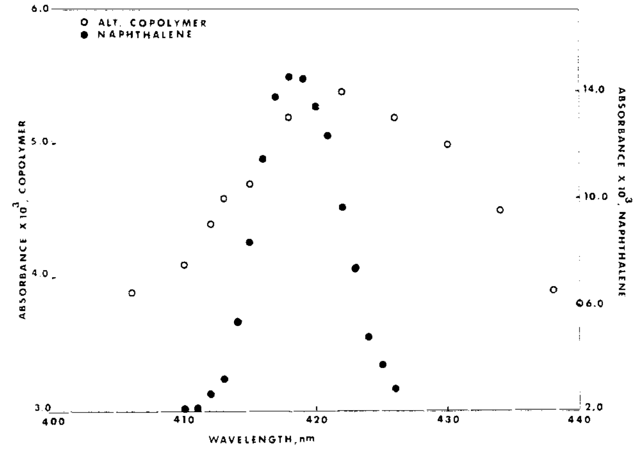

Figure 5. Triplet–triplet absorption spectra for naphthalene (●) and for the alternating copolymer (○) at ambient temperature in fluid solution.

To be certain that the emission observed from these room temperature solutions was actually arising from naphthalene triplets, a triplet–triplet absorption spectrum was recorded. A wavelength range was selected which included the prominent T–T absorption band for naphthalene at 418 nm. The resulting spectrum for the copolymer along with a similar one for naphthalene itself is presented in Figure 5. The copolymer band is seen to be shifted by about 4 nm to the red and is broader by about a factor of 3 than the monomer band. Assuming the copolymer phosphorescence originates from triplet states having a range of energies typified by this absorption envelope, the lack of structure in the phosphorescence band is certainly understandable.

In Figure 6 is presented a delayed luminescence spectrum found by excitation of a solid film of the copolymer at 77 K. The spectrum is actually very different from those found for solid films of the vinylnaphthalene homopolymers. It is quite surprising to find no emission signal in the wavelength range normally expected for either monomeric or excimer phosphorescence of the naphthalene chromophore. Instead the entire emission envelope is centered in the region corresponding to monomeric and excimeric delayed fluorescence. It is worth noting that these spectra were obtained by using the laser system with

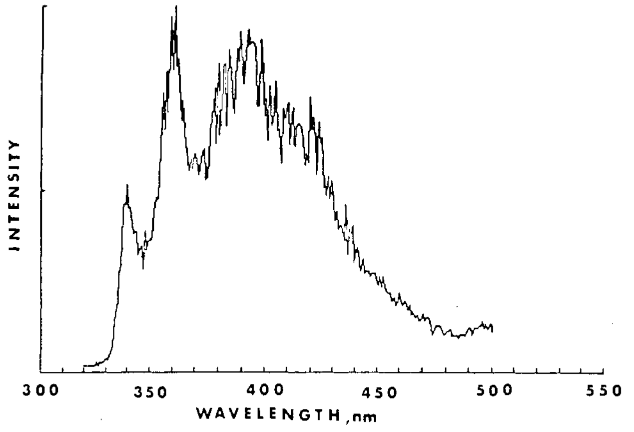

Figure 6. Delayed luminescence spectrum of a solid film of the alternating copolymer at 77 K.

a delay time of 5 ms between excitation and signal measurement. It should also be noted that only film samples heated under vacuum display negligible phosphorescence signals. Other solid films prepared by air drying or by evacuation at ambient temperature emit small but measureable phosphorescence emission bands.

Another unusual aspect of the solid film delayed emission is its very rapid decay. A lifetime of 3 ms was found for the emission signal monitored at 385 nm. It often happens in polymeric systems that a rapid initial decay is followed by a much longer lived component. A search for such a long-lived component was made here but nothing of the sort was found. Since the origin of the delayed fluorescence emission is undoubtedly by way of triplet–triplet annihilation, it seemed worthwhile to attempt to observe triplets in this system by triplet–triplet absorption. It was decided to probe in the neighborhood of the T–T absorption band for naphthalene at 418 nm. In fact an absorption signal is found in this spectral range which has a λ_{max} at 425 nm. The resulting spectrum is presented in Figure 7.

If the rate of triplet decay in the polymer film is exclusively by second-order triplet–triplet annihilation then the intermediate concentration of triplets should depend upon the square root of the excitation light intensity and the rate of delayed fluorescence production should vary linearly with excitation intensity. This dependence was tested by measuring ratios of delayed fluorescence intensities in the presence and in the absence of a neutral density filter to attenuate the excitation beam. The ratios were measured at various times after the excitation pulse in order to evaluate n in the equation $n = (\log I^0_{DF}/I_{DF})/(\log I^0_{ex}/\log I_{ex})$ where superscript 0 indicates nonattenuated and nonsuperscript indicates attenuated excitation. Values of n during the first 3 ms after the excitation pulse were 1.0 ± 0.05. However, a gradual increase in the n values was noted rising to 1.3 ± 0.1 at times as long as 10 ms after excitation. At longer times the emission signals are too weak to measure with reliability. When this dependence was tested with films which had not been subjected to heat treatment under vacuum, larger n values of 1.4 were obtained.

Discussion

Let us turn first to experiments carried out on dilute solutions of the copolymer in MTHF both at 77 K and at ambient temperature. At 77 K there are essentially no aspects of the spectral or lifetime data which are different from those of the vinylnaphthalene homopolymer. The phosphorescence and delayed fluorescence are essentially monomeric in nature and the delayed fluorescence evidently arises by a process of triplet–triplet annihilation.

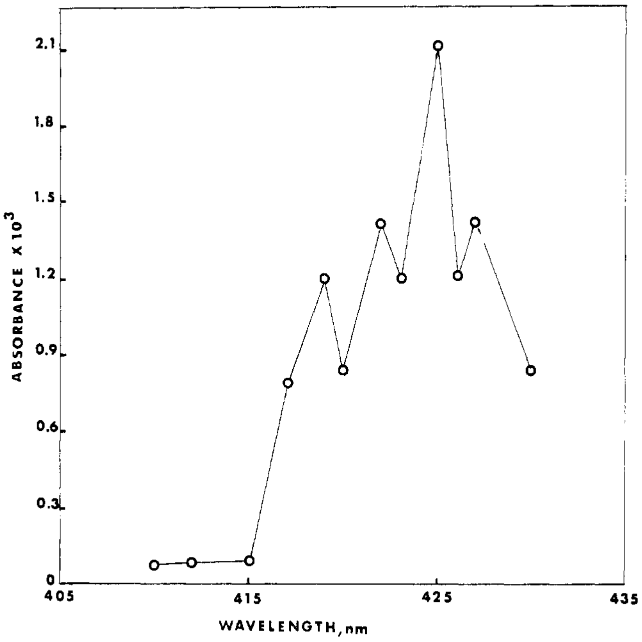

Figure 7. Triplet–triplet absorption spectrum of a solid film of the alternating copolymer at 77 K.

At ambient temperature in degassed solutions the copolymer emits a very prominent delayed excimer fluorescence. The monomeric delayed fluorescence is also present but to an extent which decreases relative to the excimer signal with increasing delay time following excitation. While an unambiguous identification of the rate-controlling step in this process is impossible some potentially important rate processes would include the following:

$$T_m + T_m \rightarrow {}^1S^* + {}^1S^\circ \qquad (1)$$

$$^1S^* + {}^1E^\circ \rightarrow {}^1S^\circ + {}^1E^* \qquad (2)$$

$$T_m + {}^1D^\circ \rightarrow {}^1S^\circ + T_d \qquad (3)$$

$$T_m + T_d \rightarrow {}^1S^\circ + {}^1E^* \qquad (4)$$

where T_m represents a mobile triplet exciton, $^1S^\circ$ is an isolated ground state chromophore, $^1S^*$ is an isolated chromophore in the excited singlet state, $^1E^\circ$ is a pair site suitable for singlet excimer formation, $^1E^*$ is a singlet excimer, $^1D^\circ$ is a trap site for triplets, and T_d is a trapped triplet. All four of these bimolecular processes could occur by exciton migration, by segmental motion of the polymer chain, or by some combination of the two.

Both $^1S^*$ and $^1E^*$ are expected to have lifetimes which are orders of magnitude shorter than the time domains used in this work. That is, their decay to the ground state would be instantaneous on the time scale used here. Therefore, the spectral shift observed between delay times of 50 and 200 μs must be due to differing lifetimes of precursors to these excited-state species. For this reason it is possible to conclude that step 4 is a much more likely mechanism for $^1E^*$ formation than is the tandem set of processes including steps 1 and 2.

Although the existence of T_d and $^1D^\circ$ is postulated here to account for the observed time-resolved delayed luminescence spectra from fluid solutions of the copolymer, there is, in addition, independent evidence for the existence of these species. However, T_d is not being proposed as an excimeric species. There is no evidence for triplet excimeric emission in any of the solution spectra recorded for this copolymer. Instead, it is noted that the long time phosphorescence spectrum from the degassed fluid solution is lacking in structure and that the triplet–triplet absorption band near 418 nm is significantly broadened for the copolymer compared with naphthalene itself. These results indicate that naphthalene chromophores in the copolymer are definitely in a nonhomogeneous environment. One could imagine an extreme example of this inhomogeneity involving a chromophore pair which is oriented properly to form an excimer if one of the partners were in an excited singlet state. If instead, one of the partners is in the lowest triplet state, the resulting environment would be a low-energy sink for the triplet species. A $^1D°$ species would be defined as a chromophore pair having this same configuration but in which neither partner is electronically excited.

Certainly the most provocative results of this investigation involve the solid copolymer film at 77 K. The emission spectrum observed is quite unlike that of the vinylnaphthalene homopolymer[11] in several respects. First of all, there is no indication of any phosphorescence whereas, in the homopolymer, an excimeric type of phosphorescence is observed. Second, the delayed fluorescence emission of the copolymer contains both monomeric and excimeric components whereas, for the homopolymer, the monomeric component is not obvious and may be entirely absent.

We are aware of no other example of a solid polymer film for which delayed fluorescence but essentially no phosphorescence is observed. Certainly this is not the case for P2VN.[11] Since we know that isolated naphthalene chromophore groups do, in fact, emit phosphorescence, the only viable conclusion seems to be that the rate of the annihilative process is so large that the first-order radiative relaxation cannot compete.[12] Several lines of evidence support this conclusion.

In the first place one notes the rapid decay of the delayed fluorescence such that its detection is very difficult at times greater than 10 ms after the excitation pulse. By comparison, the phosphorescence lifetime for glassy MTHF solutions of the copolymer is 2.4 s. Thus, it appears that the rate of the annihilative process in a solid film is approximately 3 orders of magnitude faster than that of the first-order relaxation to the ground state of an individual chromophore. In addition, it is found that the delayed fluorescence intensity depends upon the first power of the excitation intensity in the early 1–3 ms of the triplet decay. This is a very direct indication of the dominance of the second-order annihilative process.

The procedure of heating these films under vacuum evidently produces an environment which is favorable for enhanced triplet exciton migration. The temperatures used are well-below glass transitions for either of the related homopolymers (i.e., P2VN or PMMA) and it is probable, therefore, that trace solvent removal, as opposed to effects of annealing, is responsible for the observations. It is not clear at this time how solvent molecules might interfere with triplet exciton migration, but it is clear that in the limit of large ratios of solvent to polymer, that is in dilute solutions, triplet decay kinetics indicate a much reduced rate of triplet exciton migration.

One further observation is of interest in connection with triplet exciton properties. The origin of the delayed fluorescence band for the copolymer in MTHF at 77 K is found at 322 nm. In all other delayed fluorescence spectra obtained in this work, a delayed excimer component is found to coexist with the monomeric emission and, in each case, the origin of the DF band occurs at a wavelength greater than 322 nm. In solid films and in liquid solutions at room temperature the origin is at 340 nm. Evidently delayed fluorescence bands of Figure 3 and Figure 6 are associated with chromophores which are interacting with neighboring groups and are not isolated in a spectroscopic sense. In solid films such interactions are, no doubt, enforced by steric crowding, but in fluid solutions the interaction mechanism probably involves transient encounters brought about by internal chain rotations. Of course these rotations would be frozen out in glassy solvents at 77 K.

Finally, it may be noted that there is a curious paradox here associated with rates of triplet exciton migration and evidence for excimeric delayed fluorescence. Thus, exciton migration appears to be more rapid in those systems (fluid solutions and solid films) for which excimeric delayed fluorescence is observed. That is, triplet exciton migration rates seem to be enhanced by steric crowding of chromophores or by transient chromophore encounters. In neither case do we see significant emission from triplet excimer. Thus, it appears that in this particular polymer a favorable balance has been achieved of interchromophore distances which are just large enough to eliminate triplet excimeric traps but still small enough to favor interchromophore energy transfer.

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