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Triplet-State Processes in Doped Films of Poly(*N*-vinylcarbazole)

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ABSTRACT: The delayed emission spectra of poly(*N*-vinylcarbazole) (PVCz) doped with dimethyl terephthalate (DMTP) and pyrene (Py) were studied. The delayed fluorescence observed in undoped PVCz or PVCz–Py is quenched by DMTP. On the basis of the results from ternary mixtures (PVCz–DMTP–Py) it is argued that at room temperature DMTP does not act to completely quench the triplet exciton state of PVCz (T_m), but rather triplet–triplet annihilation between T_m and $^3(Cz^+ \cdot DMTP^-)^*$ does not lead to excited singlet states. It is also concluded that the phosphorescent states in PVCz and PVCz–DMTP are similar, implying a significant charge-transfer character in the former.

Introduction

The photophysical processes that occur in poly(*N*-vinylcarbazole) (PVCz) have been intensely studied both because of the utility of PVCz as a photoconductor and because it seems that PVCz possesses a unique set of properties. Unfortunately the more detailed these studies have been the more PVCz reveals itself as an extremely complex material.

The present study was initiated as a companion study to charge-transfer doped films of poly(2-vinylnaphthalene) (P2VN).[1] For P2VN the S_1–T_1 energy gap is quite large and, since the naphthalene is not a particularly good electron donor, it was proposed (and found) that the charge-transfer singlet state could sensitize the P2VN triplet exciton state. For PVCz the S_1–T_1 energy gap is much smaller and the carbazole moiety is an excellent electron donor such that one does not expect the triplet exciton state to be populated via a charge-transfer absorption. In preliminary studies this seems to be borne out. However, PVCz also has the property of forming exciplex states with weaker electron acceptors such as dimethyl terephthalate (DMTP). The present study was conducted with the aim of elucidating the effect of an exciplex-forming trap on the triplet exciton processes in PVCz. As usual with PVCz, the situation has proved to be complicated. However, some of our results have been unexpected and serve to illustrate some of the phenomena that are present in undoped PVCz. In particular we believe that the present results suggest that the triplet exciton processes in PVCz arise from a combination of deep traps and charge-separated pairs.

Experimental Section

The PVCz was purchased from Aldrich Chemicals (molecular weight $\sim 1.4 \times 10^6$) and purified by multiple precipitations of a benzene solution into methanol. Benzene solutions of PVCz plus dopants were evaporated slowly inside a rotating quartz tube (i.d. ~ 1 cm). The film was outgassed under 10^{-6}-torr vacuum for approximately 12 h, and then the tube was sealed. Films containing up to 2 wt % of pyrene and 5 wt % of DMTP were clear under microscopic examination and presumed to be homogeneous. In addition, if pyrene aggregates, a very prominent pyrex excimer fluorescence is observed. This excimer emission was absent in all samples studied in detail.

The pyrene was purified by reaction with maleic anhydride (to remove traces of anthracene) and recrystallized from benzene followed by vacuum sublimation. The DMTP was purified by vacuum sublimation.

Delayed emission spectra were obtained by using a home-built phosphorimeter described in previous publications.[1] The excitation source is a 200-W high-pressure Hg lamp with a Corning 7-54 UV transmitting filter. The phosphorimeter chopper allows alternate periods of excitation and observation of ~2.3-ms duration. Lifetimes are obtained from asynchronous shutters with an opening/closing period of ~1.5 ms (Vincent Corp.). Excitation dependences were measured by using wire screen neutral density filters. Fluorescence spectra were obtained on a SPEX Fluorolog, modified to hold the quartz tubes supported in a quartz Dewar. All spectra were collected by using an HP-85 microprocessor with a HP-3438A DVM in parallel with a strip chart recorder. This permits simple scaling of spectra for ease of comparison.

Results and Discussion

The experimental results will be divided into four sections: (a) PVCz alone, (b) PVCz + pyrene (Py), (c) PVCz + DMTP, and (d) PVCz + DMTP + Py.

(a) Undoped PVCz. PVCz has been studied many times and we carried out studies on the undoped film in order to establish that our material did not exhibit suspect behavior. We observed that the prompt and delayed fluorescences at 77 K are not identical, as previously pointed out by Klöpffer.[2] This has been interpreted in terms of heterogeneous annihilation between a mobile triplet exciton (T_m) and a deep trap (T_d) yielding S_d fluorescence (energetically a mobile singlet exciton (S_m) can also be formed, with a finite probability of escaping the deep trap). These processes can be summarized as

$$T_m + T_d \rightarrow S_d\ (+S_m) \rightarrow S_d \text{ fluorescence} \qquad (1)$$

Klöpffer et al.[2] have pointed out that the deep trap must not be identical with the normal singlet excimer forming site (sefs) since there is no saturation of the prompt fluorescence at excitation intensities sufficient to saturate the phosphorescence and delayed fluorescence. Klöpffer has also argued that most trapped triplets do not phosphoresce, under the assumption that $S \rightsquigarrow G$ (internal conversion) is inefficient for all singlet species. We will come back to this point.

The PVCz delayed fluorescence at room temperature is weaker relative to the phosphorescence, consistent with the results of Burkhart et al.[3] The delayed fluorescence and the prompt fluorescence are fairly similar to each other, and both are red shifted relative to the 77 K spectra. The room-temperature phosphorescence is also strongly red shifted. These features will be illustrated in the discussion of PVCz–DMTP (part c of this section).

As is usual with polymer systems the decay of the delayed fluorescence is highly nonexponential. The relationship often obtained for small molecules in the fluid phase (under low excitation intensities), $\tau_{DF} \sim {}^1/_2\tau_{Ph}$, is *not* obeyed. Instead it is found that $\tau_{DF} < {}^1/_2\tau_{Ph}$, and both are temperature dependent. These lifetimes, as well as others relevant to this study, are presented in Table I. In general, the decay of both delayed fluorescence and

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Table I
Emission Lifetimes of Various Features in PVCz-DMTP-Py

	77 K			room temp		
λ_{obsd}, nm	$\tau_{1/e}$,[a] ms	τ_{∞},[b] ms	assignment	$\tau_{1/e}$,[a] ms	τ_{∞},[b] ms	assignment
Sample: PVCz						
380	22	290	$T_m + T_d \rightarrow S_d$	c	c	$T_m \rightarrow S_d$
420	35	300	$T_m + T_d \rightarrow S_d$	c	c	$T_m \rightarrow S_d$
500	650	1000	T_d phos	c	c	
530	c	c		50	200	T_d phos
560	c	c		80	370	T_d phos
Sample: PVCz + 1 wt % Py						
380	20	200	$T_m + {}^3Py^* \rightarrow {}^1Py^*, S_d$	c	c	$T_m + {}^3Py^* \rightarrow S_d$
400	40	220	$T_m + {}^3Py^* \rightarrow {}^1Py^*, S_d$	40	140	$T_m + {}^3Py^* \rightarrow S_d$
430	c	c		43	120	$T_m + {}^3Py^* \rightarrow S_d$
595	540	600	${}^3Py^*$ phos	400	410	${}^3Py^*$ phos
Sample: PVCz + 10 wt % DMTP						
470	70	490	${}^3(Cz^+DMTP^-)^*$ phos			
500	77	490	${}^3(Cz^+DMTP^-)^*$ phos	13	140	${}^3(Cz^+DMTP^-)^*$ phos (multiple species)
530	90	500	${}^3(Cz^+DMTP^-)^*$ phos	28	195	(see above)
560	c	c		46	245	(see above)
Sample: PVCz + 10 wt % DMTP + 2 wt % Py						
460			${}^3(Cz^+DMTP^-)^*$ phos	50	140	$T_m + {}^3Py^* \rightarrow {}^1(Cz^+DMTP^-)^*$
480			${}^3(Cz^+DMTP^-)^*$ phos	50	140	(see above)
500	78	390	${}^3(Cz^+DMTP^-)^*$ phos	50	140	(see above)
530	77	390	${}^3(Cz^+DMTP^-)^*$ phos	51	145	(see above)
595	520	590	${}^3Py^*$ phos	350	400	${}^3Py^*$ phos

[a] $1/e$ time for initial portion of decay curve. [b] Inverse of decay rate for times greater than τ_e. [c] Intensity too low for reliable delay measurement.

phosphorescence is slightly dependent on the intensity of excitation (I_{ex}), especially the former.

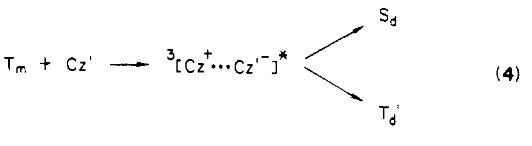
Under the conditions of our experiment the delayed fluorescence is supralinear and phosphorescence is sublinear in I_{ex}, as is expected when T–T annihilation processes such as represented in eq 1 are important to the overall triplet-state concentration.[2] From log–log plots of I_{DF} or I_{Ph} as a function of I_{ex} one can determine the exponential dependence expressed in eq 2. The log–log plots tend to

$$I_{DF} \propto (I_{ex})^{n_{DF}}$$
$$I_{Ph} \propto (I_{ex})^{n_{Ph}} \qquad (2)$$

be slightly curved, such that n_{DF} and n_{Ph} are larger for lower values of I_{ex}. This behavior is expected in the "intermediate region" of excitation intensities (e.g., ideally for low I_{ex}, $n_{DF} = 2$, $n_{Ph} = 1$; for high I_{ex}, $n_{DF} = 1$, $n_{Ph} = 0.5$). If the delayed fluorescence results from a "biphotonic" process (see eq 1), one always expects $n_{DF} > n_{Ph}$. However, for E-type delayed fluorescence

$$T_m \rightsquigarrow S_d \rightarrow S_d \text{ fluorescence} \qquad (3)$$

one would expect $n_{DF} \simeq n_{Ph}$. This latter point is raised because at 77 K $n_{DF} \sim 1.2$–1.5 and $n_{Ph} \sim 0.7$–0.8 but at room temperature $n_{DF} \simeq 1.1$–1.2 and $n_{Ph} \sim 0.9$. We note that the isolated carbazole phosphorescence 0,0 peak is ~410 nm, near the maximum of the delayed fluorescence; consequently a contribution from E-type delayed fluorescence as described in eq 3 is not out of the question. For later reference we note that photoionization followed by radiative recombination is equivalent to eq 3, i.e.



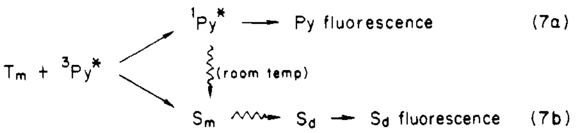
where Cz′ is a "trap" carbazole (e.g., a special arrangement of nearest neighboring carbazoles or possibly a carbazole perturbed by an impurity) suitable for stabilizing the negative charge. This species could also be an intrinsic or extrinsic impurity with a higher electron affinity than normal carbazole. The trapped triplet, T_d' may not be equivalent to T_d in eq 1. Klöpffer has discounted this mechanism for the delayed fluorescence at 77 K, but has pointed out that the phosphorescent triplet excimer state has a large degree of charge-transfer character.[2b] Our experimental results on pure PVCz do not differentiate between the monophotonic results of eq 3 or 4.

(b) PVCz–Py. The singlet state of Py is essentially isoenergetic with the fluorescent excimer state(s) of PVCz such that the prompt fluorescence of PVCz–Py at room temperature or 77 K is largely dominated by the carbazole excimers. Hence, light directly absorbed by Py serves to sensitize the carbazole singlet state. However, pyrene is a deep trap for triplet excitons (0,0 band of phosphorescence for ${}^3Py^* \cong 595$ nm) and the introduction of pyrene into the PVCz dramatically changes the delayed emission spectra.

At 77 K the carbazole phosphorescence is much weaker than for pure PVCz, and the ${}^3Py^*$ phosphorescence is quite prominent (see Figure 1A). This is what one would expect from the simple addition of another trapping site to the system, i.e.

$$T_m + G_d \rightarrow T_d \qquad (5)$$
$$T_m + Py \rightarrow {}^3Py^* \qquad (6)$$

where G_d is the ground state of the phosphorescent deep trap in PVCz. The delayed fluorescence has an obvious component of ${}^1Py^*$, such that the following heterogeneous annihilation scheme must be postulated in addition to that in eq 1:



We note that the delayed fluorescence is supralinear in I_{ex} ($n_{DF} \simeq 1.3$) while the ${}^3Py^*$ phosphorescence is slightly

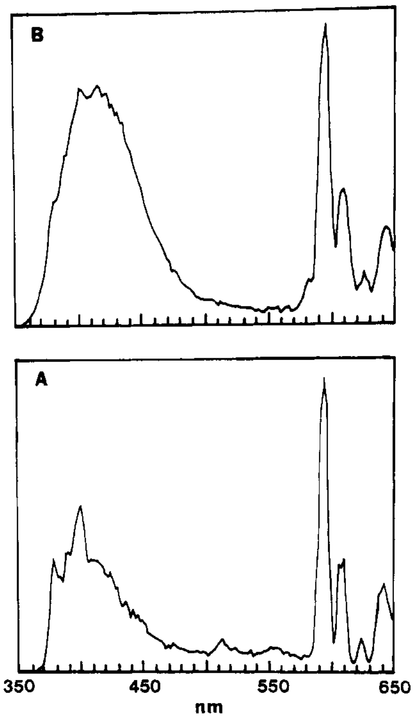


Figure 1. (A) 77 K and (B) room-temperature delayed emission spectra for PVCz-pyrene (2% pyrene by weight).

sublinear ($n_{\mathrm{Ph}}(^3\mathrm{Py}^*) \simeq 0.85$). The carbazole phosphorescence is clearly sublinear ($n_{\mathrm{Ph}}(^3\mathrm{Cz}^*) \simeq 0.67$). Thus, the biphotonic steps in eq 1 and 7 are implicated. The phosphorescence decay of $^3\mathrm{Py}^*$ at 77 K and room temperature is fairly exponential (see Table I) with no obvious dependence on I_{ex}, at least at times longer than ~5 ms.

At room temperature the $^3\mathrm{Py}^*$ phosphorescence is still quite prominent (with slighly shortened lifetime) but now the delayed fluorescence is dominated by the PVCz excimer (with some higher energy structure that undoubtedly represents a contribution from $^1\mathrm{Py}^*$) (see Figure 1B). The delayed fluorescence is supralinear ($n_{\mathrm{DF}} \simeq 1.25$) and the $^3\mathrm{Py}^*$ phosphorescence is slightly sublinear ($n_{\mathrm{Ph}}(^3\mathrm{Py}^*) \simeq 0.89$) (the carbazole phosphorescence is too weak for a reliable measurement of the power dependence).

Thus, it seems that the heterogeneous annihilation scheme in eq 7 is still applicable, but the sensitization route (eq 7b) now dominates. As noted in the previous section, the prompt fluorescence spectrum of pure PVCz is temperature dependent. This implies that the density of excimer energy acceptor states depends on temperature. We note that for PVCz-Py the rate of delayed fluorescence decay at room temperature is lower than for undoped PVCz. We ascribe this to the longer lifetime of the $^3\mathrm{Py}^*$ deep trap compared to T_d, which in turn implies that the lifetime of T_m is similar in PVCz and PVCz-Py. Since additional traps would be expected to shorten the lifetime of T_m (see eq 5 and 6), one is forced to postulate that T_m is in equilibrium with a shallow trap

$$T_s \rightleftarrows T_m \tag{8}$$

in which the rate of detrapping is the rate-determining step in the decay of T_s. Shallow triplet traps in PVCz have been postulated by Klöpffer et al.[2] and Burkhart et al.[3]

While PVCz-Py presents an interesting case of heterogeneous T-T annihilation in polymer films, the primary utility of these results is to elucidate the triplet exciton processes that occur in PVCz in the presence of a well-understood deep triplet trap. Previous analyses of PVCz have the difficulty that there are multiple triplet traps in PVCz that depend on the history of the sample, including the method of polymerization. What we have found is that heterogeneous T-T annihilation between T_m and $^3\mathrm{Py}^*$ at 77 K and room temperature appears to be P-type, with the complication that there are multiple depopulation processes available to T_m. We will use these findings to aid the analysis of PVCz-DMTP-Py films in part d of this section.

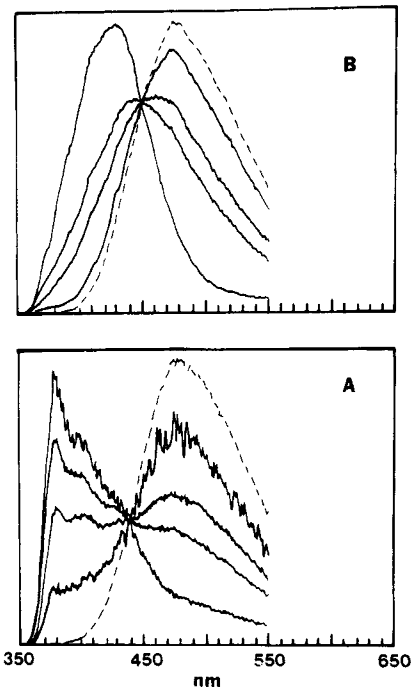
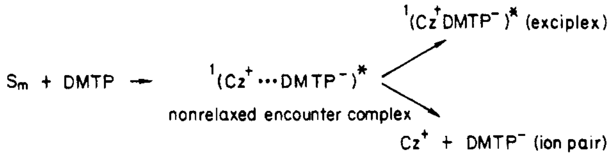


Figure 2. Composite prompt fluorescence spectra of PVCz-DMTP at (A) 77 K and (B) room temperature. The carbazole component (360-440 nm) steadily decreases as the weight percent of DMTP increases. Spectra for 0, 0.5, 1, 2, and 10 wt % DMTP, (the 10 wt % spectra shown with dashed line for clarity).

(c) PVCz-DMTP. DMTP has been recognized as a weak electron acceptor that is capable of forming an exciplex with excited carbazole moieties (in fact in fluid solution an "exterplex" was suggested by Hoyle and Guillet[4] based on time-dependent fluorescence spectra. The structure of the exterplex is represented by $(^1(\overline{\mathrm{CzCz}^+})(\mathrm{DMTP})^-)^*)$. Addition of DMTP to PVCz only slightly perturbs the absorption spectrum (i.e., no ground-state charge-transfer complex is formed) but the fluorescence spectrum is dramatically altered with the growing in of the exciplex fluorescence at 77 K (Figure 2A) or at room temperature (Figure 2B). These results agree with previous papers. We note that the mechanism of exciplex formation in films is not absolutely established. In a series of papers Yokoyama et al.[5] have shown that the room-temperature exciplex fluorescence is partially quenched by application of electric fields on the order of 10^5 V cm^{-1}, while the excimer fluorescence is unaffected. This has been interpreted in terms of the following mechanism:



(9)

As Yokoyama et al.[5] point out, experimentally accessible electric fields are too weak to dissociate the exciplex at molecular separations, but the dissociation of the encounter complex to an ion pair can be assisted by the external field if the initial charge separation is sufficiently

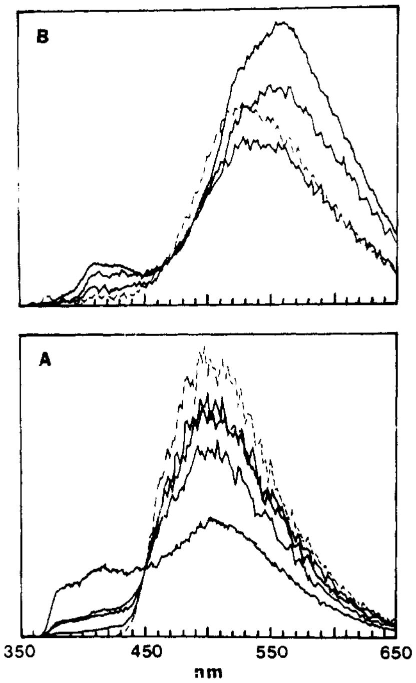


Figure 3. Delayed emission spectra of PVCz–DMTP at (A) 77 K and (B) room temperature, as a function of weight percent DMTP (same weight percent values as Figure 2). (The 10 wt % DMTP spectrum is shown with a dashed line.) Addition of DMTP steadily quenches the delayed fluorescence (360–440-nm region).

large. In fact, a reasonably good fit to Onsager theory is found with an initial charge separation of ca. 25 Å. In eq 9 singlet excited states are denoted. Similar processes could occur from the triplet state, although so far as we know a triplet exciplex state for carbazole–DMTP has not been identified. Williams et al.[6] have shown $^1(Cz^+DMTP^-)^*$ to dissociate to form the Cz triplet state in solution only if the carbazole moieties are isolated from each other (i.e., PVCz does not dissociate to $^3Cz^*$). Thus, one might speculate that doping the PVCz films with DMTP will simply serve to quench all triplet processes. This might be expected to be particularly important at sufficiently high DMTP concentrations that the carbazole singlet state is totally quenched by the exciplex.

We do observe that the addition of DMTP strongly quenches the delayed fluorescence, at both 77 K and room temperature (see Figure 3). At 77 K the phosphorescence is very similar to undoped PVCz although the initial rate of the nonexponential decay is much faster than undoped PVCz (see Table I). The phosphorescence decay is independent of wavelength from 470 to 530 nm. If we assume that the observed phosphorescence is composed of overlapping T_d and $^3(Cz^+DMTP^-)^*$ emissions, then these two species are very similar.

At room temperature all emissions are red shifted with respect to the 77 K spectra, but less so for larger DMTP concentrations. The nonexponential decay is faster than at 77 K and, as was the case for undoped PVCz, the decay rate is wavelength dependent (generally faster decay at the shorter wavelengths over the range 500–560 nm). Thus, there must be a group of phosphorescent states in this energy range, which is not surprising considering the many different local conformations that could coexist and thermally interconvert.

All emission features at 77 K or room temperature from 480 to 550 nm are linear or slightly sublinear in I_{ex} for DMTP concentrations greater than 2 wt %. Presumably the exciplex delayed fluorescence would be similar to the exciplex prompt fluorescence, which is to the blue of the phosphorescence. We do not observe such a shoulder in the delayed emission spectra (cf. Figures 2 and 3). Thus, there is no evidence for significant T–T annihilation in this system and we conclude that the following process does *not* occur:

$$T_m + {}^3(Cz^+DMTP^-)^* \not\rightarrow S_m, S_d, {}^1(Cz^+DMTP^-)^* \quad (10)$$

This could be the case because the DMTP sites are so efficient in quenching the precursor state S_m via exciplex formation of the triplet such that the T_m concentration is quickly depleted. Alternatively, the annihilation process in eq 10 may occur but no excited singlets result. We will argue in favor of the second possibility (at room temperature) in the next section.

Is there any rationale for the prohibition of singlet-state formation in eq 10? There is only one that we can suggest. If the charge pairs in the triplet exciplex are treated as ground-state, weakly coupled doublets ($S = {}^1/_2$), then the annihilation process in eq 10 can be thought of as the coupling of an $S = 1$ state to an $S = {}^1/_2$ state with resultant $S = {}^3/_2, {}^1/_2$ states. If the doublet is in a ground state, then the T_m state could undergo an isoenergetic transition to either the ground-state singlet (plus many phonons) or the S_d state.[7,8] Thus, one can imagine an exciplex "catalyzed" E-type delayed fluorescence (which would be energetically possible only at room temperature). We postulate that if a process like that in eq 10 does occur, the dominant process is the quenching of T_m to form ground-state carbazoles. This is consistent with the observation that the phosphorescence is slightly sublinear in excitation intensity and the usual delayed fluorescence is strongly quenched.

As noted above, the phosphoresence of PVCz–DMTP is quite similar to that of PVCz alone, unlike the prompt fluorescence which is strongly perturbed. This suggests that the T_d state in PVCz is similar to the $^3(Cz^+DMTP^-)^*$ state. We also note that the phosphorescence spectrum for both PVCz and PVCz–DMTP undergoes a strong red shift in going from 77 K to room temperature. The DMTP enhances the phosphorescence intensity at 77 K and diminishes it at room temperature, relative to undoped PVCz. Since it seems reasonable that DMTP stabilizes any ion pair state, which presumably would be nonphosphorescent, we speculate that formation of these states is thermally assisted (for example, via an "exterplex" type state,[4] $(\overline{CzCz}^+)(DMTP^-)$). As mentioned in part a of this section, the triplet state of PVCz has been shown to have a significant fraction of charge-transfer character,[2] which presumably may be represented by a configuration like $^3(Cz^+Cz^-)^*$. Viewed in this way, the overall similarity of the phosphorescence characteristics of PVCz and PVCz–DMTP is not so surprising. Two comments follow from the suggestion that the T_d state is formed via a mechanism analogous to that proposed by Yokoyama et al.[5] (see eq 9, in which T_m replaces S_m and the triplet spin state is invoked): (1) the nonphosphorescent triplet state proposed by Klöpffer[2] could be a separated ion pair such that geminant ion pair recombination is required before phosphorescence is possible; (2) by analogy to E-field perturbed exciplex fluorescence the phosphorescence of an exciplex should be modulated by external electric fields.

(d) PVCz–DMTP–Py. For relatively small dopings of DMTP (holding the pyrene concentration constant at 2 wt %) the delayed emission spectrum is similar to PVCz–Py. For 10 wt % DMTP the prompt fluorescence spectrum is dominated by the exciplex emission. In all cases the delayed emission spectrum exhibits a strong $^3Py^*$ component (see Figure 4), but for 10 wt % DMTP at room temperature there is a "delayed fluorescence" component

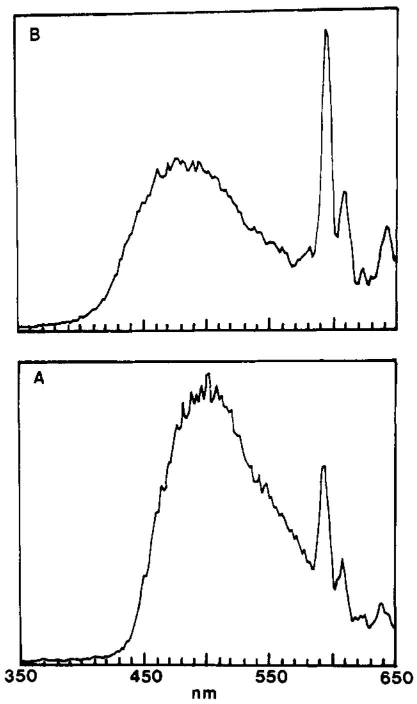
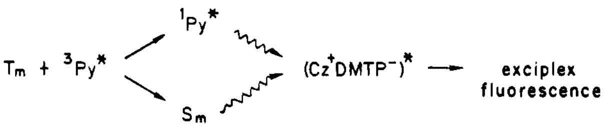


Figure 4. Delayed emission of PVCz–DMTP (10 wt %)–Py (2 wt %) at (A) 77 K and (B) room temperature.

($n_{DF} \simeq 1.3$–1.4 from 475 to 550 nm) that resembles the exciplex fluorescence more than the PVCz delayed fluorescence or phosphorescence or the PVCz–DMTP phosphorescence (Figure 4A). Thus, we propose that the following heterogeneous annihilation process occurs at room temperature:



(11)

Thus, at room temperature the 10 wt % DMTP does not totally quench the T_m state (which was one of the possible conclusions from the PVCz–DMTP results), or we would not observe a superlinear dependence on I_{ex}. It is for this reason that we favor the (non) mechanism in eq 10, i.e., no T_m, $^3(Cz^+DMTP^-)^*$ annihilation leading to singlet states.

The 77 K delayed emission spectrum is essentially identical with the corresponding spectrum for PVCz–DMTP (10%) (cf. Figure 3A and 4A) (except for the contribution from $^3Py^*$) and all components are linear in I_{ex}. Thus, unlike PVCz or PVCz–Py there does not seem to be significant T–T annihilation. The most obvious interpretation of this observation is that the efficiency of trapping T_m by the DMTP is temperature dependent. Thus, a scheme like eq 9 might be applicable, except for the addition of the thermally assisted back-reaction

$$T_m + \mathrm{DMTP} \overset{\Delta}{\rightleftarrows} \underset{\substack{\text{nonrelaxed}\\ \text{encounter}\\ \text{complex}}}{{}^3(Cz^+\cdots DMTP^-)^*} \rightarrow \underset{\substack{\text{triplet}\\ \text{exciplex}}}{{}^3(Cz^+DMTP^-)^*} \qquad (12)$$

(ion pair separation of the nonrelaxed encounter complex could occur, but there is no experimental evidence for this in films to our knowledge). Thus, at 77 K the concentration of T_m is reduced by irreversible formation of $^3(Cz^+DMTP^-)^*$, in addition to $^3Py^*$, and annihilation processes are eliminated. Note that for PVCz–DMTP the phosphorescence assigned to $^3(Cz^+DMTP^-)^*$ is strongly red shifted in going from 77 K to room temperature, which we have attributed to a further relaxation of the triplet exciplex state (see part c of this section).

Summary and Conclusions

All spectroscopic studies of polymer films tend to yield complex results and imply multiple excited-state species. The present study is no exception and is further complicated by the deliberate addition of pyrene as a trap for triplet excitons or DMTP as an exiplex-forming partner with carbazole. The present study represents the only example of "exciplex phosphorescence" in polymer films we are aware of. We may summarize our observations and our conclusions as follows:

(1) The PVCz–Py mixed film represents a clear-cut example of a deep trap (Py) which can participate in triplet–triplet annihilation. This is consistent with previous studies[2,3] that suggest a heterogeneous annihilation process between triplet excitons (T_m) and trapped triplets (T_d) (see eq 1).

(2) The phosphorescence of PVCz–DMTP is rather similar to undoped PVCz, but with a shortened lifetime (all phosphorescence decays are highly nonexponential). We speculate that the phosphorescent species is exciplex-like (represented by $^3(Cz^+DMTP^-)^*$). Because of the similarity to undoped PVCz phosphorescence we further speculate that the phosphorescent species in PVCz may have strong charge-transfer character. Perhaps separated ion pairs are the "nonphosphorescent triplet states" postulated by Klöpffer.[2]

(3) Delayed fluorescence is not observed in PVCz–DMTP, yet from the ternary mixture PVCz–DMTP–Py it would seem that the triplet exciton state (T_m) is not completely quenched by DMTP at room temperature. Hence, we conclude that the triplet exciplex discussed in conclusion 2 does not participate in triplet–triplet annihilation leading to a fluorescent singlet state. We have postulated that the reaction of T_m with $^3(Cz^+DMTP^-)^*$ is analogous to a triplet–doublet quenching process.

In the above we have attempted to interpret the emission properties of doped PVCz in terms of various exciplex species. The actual degree of charge transfer in the excited state, the possible existence of nonemitting excited states, and even the number of excited-state species present in these doped films are not directly evaluated in the present study. Future work in these (and similar) systems should include time-resolved emission/absorption spectroscopy if at all possible. In addition electric field modulation of these spectroscopic features could help elucidate the extent of excited charge separations.[5]

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Registry No. PVCz (homopolymer), 25067-59-8; DMTP, 120-61-6; Py, 129-00-0.

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Isothermal Growth of Low Molecular Weight Polyethylene Single Crystals from Solution. 1. Variation of Equilibrium Dissolution Temperature with Molecular Weight and Lamellar Thickness with Crystallization Temperature

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ABSTRACT: The relation between the equilibrium melting/dissolution temperature ($T_m°/T_d°$), the molecular weight, the lamellar thickness, and the crystallization temperature has been investigated for linear polyethylene fractions, with molecular weights ranging from 1000 to 11600, crystallized from dilute xylene solution. The values of $T_m°$ and $T_d°$ increase sharply with molecular weight and approach an asymptotic value above a molecular weight of about 5000. The measured values of $T_m°$ are found to be in excellent accord with the values calculated from the Flory–Vrij equation. On the other hand, the observed values of $T_d°$ are always somewhat higher than estimates from either the Pennings equation or the Sanchez–DiMarzio equation. It is found that the lamellar thickness increases continuously with crystallization temperature. This is in contrast to the behavior of low molecular weight poly(ethylene oxide) fractions which show a stepwise variation with crystallization temperature. Analysis of the observed temperature variation of the lamellar thickness, using the kinetic theory of polymer crystal growth, yields values of the interfacial free energy σ_e ranging from 20 to 60 erg/cm^2. These observed values of σ_e are low by comparison with the value of about 90 erg/cm^2 expected for high molecular weight samples. The difference may be attributed to the effects of chain ends in the interfacial regions of the crystals.

Introduction

Flexible stereoregular polymers generally crystallize from solution as lamellar structures in which the chain molecules are folded.[1,2] Although this phenomenon has been widely studied, it is still not completely understood. In the present series of papers, we propose to address the question of the origin of chain folding by studying the kinetics of crystal growth from solution, using low molecular weight fractions of polyethylene for which the transition from extended- to folded-chain growth should be observable. In this connection it is important to have accurate data on the variation of the lamellar thickness of the crystals with the temperature of crystallization and of the equilibrium dissolution temperature with molecular weight. This is the essential purpose of the present paper. Comparison of the lamellar thickness with the overall chain length provides information on the structure of the crystals by indicating whether the chains are extended or folded in the crystal lattice and the number of folds per molecule. As will be seen later, these questions are important in attempting to analyze and interpret the results of the growth rate experiments.

The lamellar thickness of single crystals of linear crystalline polymers, notably polyethylene, is generally known to increase monotonically with the temperature of crystallization (T_c).[3–6] However, in the case of low molecular weight hydroxy-terminated poly(ethylene oxide) (PEO) crystallized from the melt, the lamellar thickness increases in a stepwise manner with T_c.[7] The question arises whether a similar effect can be demonstrated in polyethylene by careful measurements on low molecular weight samples.

Previous studies of the temperature variation of the lamellar thickness of solution-grown polyethylene crystals have been mainly concerned with samples of high molecular weight. Few attempts have been made so far to systematically explore these effects for well-defined low molecular weight material.[8] In the present work we have measured the lamellar thickness of solution-grown polyethylene crystals over a wide range of crystallization temperatures for fractions ranging from 1000 to 11600 in molecular weight. The data have been analyzed in terms of the kinetic theory of polymer crystal growth in order to derive values of the basal surface free energy.

In analysis of the experimental data a knowledge of the supercooling ($\Delta T = T_d° - T_c$) or the equilibrium dissolution temperature ($T_d°$) (where T_c is the crystallization temperature) is critically important. $T_d°$ is defined as the temperature at which dilute polymer solution is in equilibrium with the equilibrium (i.e., extended-chain) crystal and is dependent on the molecular weight of the polymer.[10,11] A widely used procedure to determine $T_d°$ is to measure the dissolution temperature of crystals of various lamellar thicknesses and extrapolate the data to infinite lamellar thickness by using the Gibbs–Thompson equation.[9] This procedure will be discussed in part 2. For polyethylene, an alternative approach is used to estimate $T_d°$ using semiempirical equations derived by Pennings[11]

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