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"Second Excimer" Luminescence from Polymers with Sterically Hindered Naphthalene Chromophores

Since Johnson's finding in poly(*N*-vinylcarbazole) (PVCz)[1] of a high-energy trap, which he referred to as a second excimer, considerable interest has been aroused in the nature of the high-energy trap and its relationship to the normal low-energy excimer.[2-4] Despite the obvious implication that bulky pendant chromophores, in general, may cause second-excimer-like trap formation, no work along this line has been reported to our knowledge. This might be partially due to the finding of Johnson[1] and Keyanpour-Rad et al.[5] that other carbazole-containing polymers do not afford second excimer emission. This implies that among various vinyl aromatic polymers, only PVCz fulfills the strict geometric requirements for formation of the high-energy trap and subsequent emission.

In the present communication we present evidence that polymers having sterically hindered naphthalene chromophores do, in fact, form second-excimer-like high-energy traps in a film and to a lesser extent in fluid solution.

The monomer 2-*tert*-butyl-6-vinylnaphthalene (tBVN), its homopolymer (PtBVN, $\bar{M}_n = 79000$), and its copolymer with styrene (P(tBVN-*co*-St), 8 mol % in tBVN content, $\bar{M}_n = 40000$) were prepared as described previously.[6] Films ca. 15 μm thick were prepared by solvent casting from benzene (ca. 5 wt % in polymer concentration) on a quartz plate and dried in vacuo at room temperature. The emission spectra of the films, mounted at an angle of 30° to the exciting light, were measured at right angles to the exciting light using front-side illumination. The spectra were uncorrected.

When excited at 308 nm, PtBVN film emits fluorescence in the wavelength region intermediate between the normal monomer and excimer emissions, with peaks at 345, 362, and 381 nm, while in good solvents such as tetrahydrofuran normal monomer and excimer emissions are observed at 320–400 and 350–450 nm, respectively, with the former dominating (Figure 1).[6] Poly(2-vinylnaphthalene) (PVN) film, on the other hand, gives emission dominated by excimer emission.[7] The absorption spectrum of PtBVN film, as well as the excitation spectrum monitored at $\lambda_{em} = 362$ nm, shows an additional absorption at $\lambda_{max} = 340$ nm, while the corresponding absorption is not found with PVN film. Direct excitation of this band gives emission in the wavelength region ≥350 nm nearly identical with that shown in Figure 1, suggesting the presence of a ground-state species that, when excited, emits the second-excimer-like high-energy fluorescence. (We, however, cannot exclude the possibility of some excimer emission being buried underneath the dominating high-energy trap emission.)

When dispersed in a polystyrene (PSt) matrix (0.2 wt %), PtBVN exhibits, as expected, a larger extent of monomer emission plus some excimer and high-energy trap emission (Figure 2). When emission from P(tBVN-*co*-St) dispersed in PSt (ca. 5 wt %) is assumed to be mostly monomeric and is subtracted from the above spectrum, we obtain the residual spectrum shown in Figure 2, which can be further divided into high-energy trap emission and excimer emission, assuming that the peak at 345 nm is essentially due to the high-energy emission observed with PtBVN film (Figure 1).

In fluid solution, the high-energy trap emission is much less pronounced. For example, when excitation is carried out at 308 or 323 nm, the observed emission is mostly monomeric even in a poor solvent such as ethyl acetate (Figure 3). The absorption spectrum, however, shows a band around 340 nm, excitation of which affords emission (in the wavelength region ≥350 nm) identical with the high-energy trap emission of the PtBVN film.

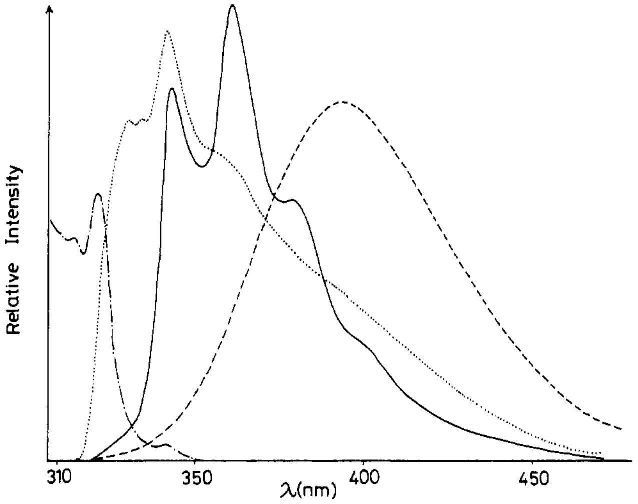

Figure 1. Fluorescence spectra of PtBVN and PVN at room temperature: (—) PtBVN film, $\lambda_{ex} = 308$ nm; (···) PtBVN in tetrahydrofuran (5×10^{-4} mol/L in chromophore concentration), $\lambda_{ex} = 308$ nm; (---) PVN film, $\lambda_{ex} = 302$ nm; (-·-) excitation spectrum of PtBVN film, $\lambda_{em} = 364$ nm.

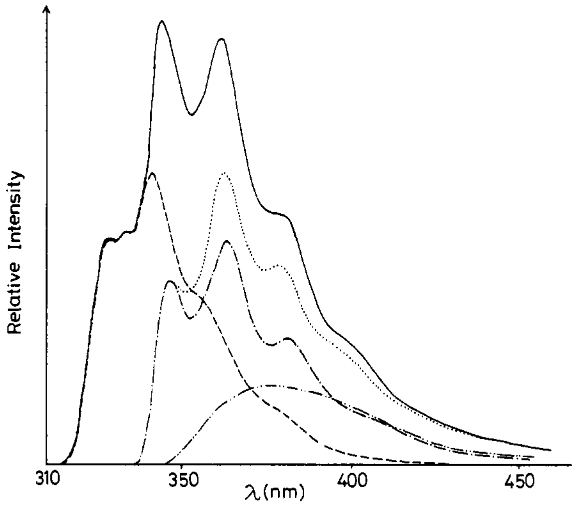

Figure 2. Fluorescence spectra of PtBVN and P(tBVN-*co*-St) in PST at room temperature, $\lambda_{ex} = 290$ nm: (—) PtBVN (0.2 wt %) in PSt; (---) P(tBVN-*co*-St) (5 wt %) in PSt, normalized at 333 nm; (···) difference of the preceding two spectra; (-·-) high-energy trap emission normalized at 345 nm; (-··) difference of the preceding two spectra.

The absorption spectra of samples showing the high-energy trap emission are nearly identical with that of P(tBVN-*co*-St) in PSt or in tetrahydrofuran except for the weak 340-nm absorption. Thus, the concentrations of the high-energy trap appears to be rather low even in the case of PtBVN film. As a result the dominant high-energy trap emission observed with PtBVN film suggests efficient trapping of monomer excitation energy at the trap sites via intra- and/or intermolecular energy migration and transfer.

To date, several papers have been published in which emissions similar to that found in the present study are reported.[8-11] In most of these studies, however, the authors

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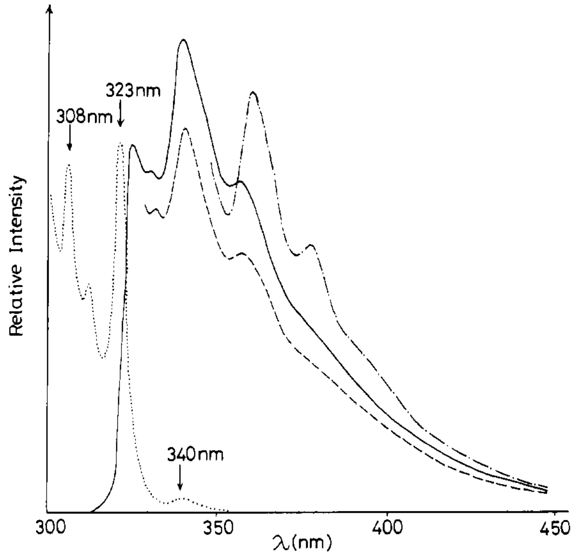

Figure 3. Fluorescence spectra of PtBVN in ethyl acetate (5 × 10^{-5} mol/L in chromophore concentration) at room temperature: (—) λ_{ex} = 308 nm; (– – –) λ_{ex} = 323 nm; (–·–) λ_{ex} = 340 nm; (···) absorption spectrum of PtBVN in ethyl acetate.

neglected the possibility of second-excimer-like traps giving the emission. For example, while Frank and Gashgari were examining polymer blend compatibility, they observed emission, nearly identical with observed here, from PVN in the thermodynamically good host matrix poly(isopropyl methacrylate).[8] Similar emissions were also observed from a film of an alternating copolymer of 2-vinylnaphthalene and methyl methacrylate[9] and from a film prepared from the polymer of general structure $-[CH(C_6H_5)CH_2CH_2CH(C_6H_5)(CH_2)_n]-$.[10] Irie et al. also reported similar emission from poly(1-vinylnaphthalene) in a thermodynamically poor solvent, i.e., cyclohexane.[11] They attributed the emission to that from "dimer" formed by the increased chromophore interaction and conformational rigidity in the poor solvent. Our preliminary study on poly[(2-naphthyl)alkyl methacrylate] films also revealed that a second-excimer-like fluorescence identical with that observed here is emitted by poly[1-(2-naphthyl)ethyl methacrylate], which has methyl groups, unfavorable for excimer-forming interaction, that are located near the naphthalene chromophores. The films of other polymers with linear alkyl chains, e.g., poly[(2-naphthyl)methyl methacrylate] and poly[2-(2-naphthyl)ethyl methacrylate], afforded mostly excimer emission.[12]

Therefore, high-energy trap formation is quite general in polymers having pendant aromatic chromophores. The only requirement appears to be that chromophores be separated, by steric or other structural causes or by extensive host–guest polymer interpenetration, by distances longer than that for excimer-forming interaction and further that chromophores be fixed in place by decreased chain mobility as in a film or in a poor solvent. Since the stabilization due to charge resonance interaction, both in the excited state and in the ground state, appears to be rather small compared with that of excitation resonance in a low-energy excimer,[1] the above geometric requirement needs to be fulfilled before the high-energy trap can form and emit prior to dissociation to excited- and ground-state monomers or conversion to the more stable low-energy excimer. A more complete study including the temperature dependence of the high-energy trap emission is in progress and will be reported in a future publication.

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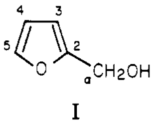
^{13}C NMR Study of Cured Furfuryl Alcohol Resins Using Cross Polarization and Magic-Angle Spinning

Resins prepared from furfuryl alcohol (I) are of considerable interest.[1-4] The formation process of uncured resins has been studied extensively and is relatively well understood in terms of the following reactions:[2,3]



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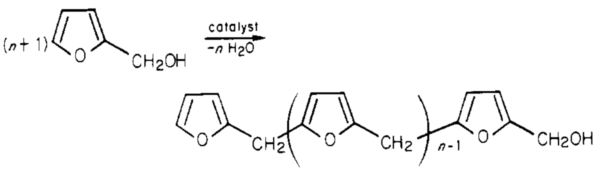
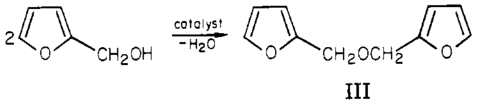


(1)

II



(2)

III

Knowledge of the curing process(es) of these resins by heating, with or without a catalyst, is less detailed.

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