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Intramolecular Dimer and Excimer Phosphorescence of Poly(2-vinylnaphthalene) and Copolymers of 2-Vinylnaphthalene and Phenyl Vinyl Ketone

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Synopsis. Phosphorescence spectra and lifetimes of poly(2-vinylnaphthalene) and copolymers of 2-vinylnaphthalene and phenyl vinyl ketone have been measured as a function of the composition ratio between the constituent benzoyl and naphthyl groups in both rigid and fluid solutions.

In a previous paper[1)] it was shown that poly(vinylnaphthalene)s exhibit fluorescence emissions ascribable to the monomer, dimer, and excimer of the constituent naphthyl groups. The purpose of the present study is to examine whether such a polymer emits the intramolecular dimer and excimer phosphorescence. Copolymers of 2-vinylnaphthalene and phenyl vinyl ketone have been employed in addition to poly(2-vinylnaphthlene). Since the formation of the intramolecular dimer or excimer is expected to depend on the naphthyl group content of copolymer, the ratio between the components of the copolymer was varied to a considerable extent. The phosphorescence spectra of these compounds were measured in both rigid and fluid solutions.

Poly(2-vinylnaphthalene) (PVN) and copolymers of 2-vinylnaphthlene and phenyl vinyl ketone (VN–PVK) were synthesized in benzene with use of azobisisobutyronitrile. The compositions of copolymer I, II, III, and IV are 9/91, 16/84, 35/65, and 75/25, respectively, in mole fraction of 2-vinylnaphthalene–phenyl vinyl ketone. Spectro-grade THF and reagent-grade MTHF were passed through an activated alumina column and distilled repeatedly (4 or 5 times) over lithium aluminium hydride or phosphorus pentaoxide.

The concentrations of the copolymer solutions were so adjusted that the absorbance at the $n \rightarrow \pi^*$ transition band was less than 0.1. The sample solutions were carefully degassed by freeze-thaw cycles. The apparatus and techniques for measuring emission spectra and monitoring the time-dependent behavior of the emissions were the same as those reported.[2,3)]

Results and Discussion

Phosphorescence Spectra in Rigid Glass. Figure 1 shows the phosphorescence spectra of VN-PVK copolymers in MTHF at 77 K. Excitation was carried out at 350 nm, where there is only the $n \rightarrow \pi^*$ absorption band of the constituent benzoyl group. The spectrum of copolymer I consists of two phosphorescence emissions. One located in the region of 400—460 nm is similar to the phosphorescence spectrum of acetophenone and ascribed to the triplet state of the benzoyl group; the other located in the region of 470—600 nm has an origin at 468 nm and is very similar to the phosphorescence spectrum of naphthalene, and is assigned to the naphthyl group. The appearance of the phosphorescence of the naphthyl group by excitation at 350 nm indicates that intramolecular triplet-triplet (T-T) energy transfer from the benzoyl group to the naphthyl group occurs effectively in the copolymer. This is supported by the fact that the emission due to the benzoyl group disappears with increase in content of the naphthyl group, which acts as an acceptor in the T-T energy transfer.

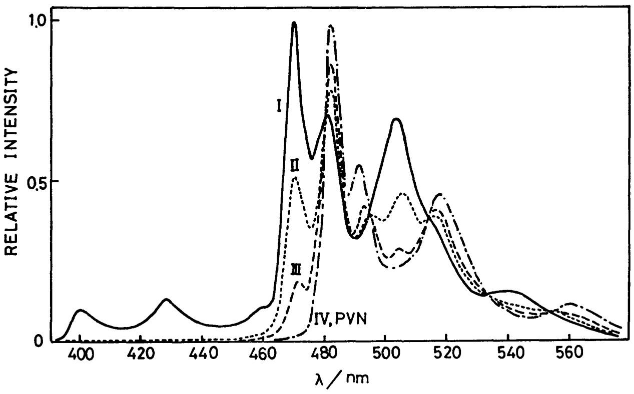

Fig. 1. The phosphorescence spectra (uncorrected) of VN–PVK copolymer I, II, III, and IV and of PVN in MTHF at 77 K obtained by exciting at 350 nm. The spectra of copolymer-IV and PVN were almost the same.

With increase in content of the naphthyl group in the copolymer the intensity of the 0-0 band at 468 nm in the phosphorescence spectrum decreases, while a new band grows at 482 nm. The intensity of the band at 482 nm is comparable to that at 468 nm for copolymer II, dominating over the latter intensity for copolymer III. On the other hand, copolymer IV and PVN give predominantly phosphorescence spectra with an origin at 482 nm which are very similar to the spectrum of the naphthalene dimer with a 0-0 band at 485 nm reported by Chandross and Dempster.[4)] From the composition dependence of the phosphorescence spectra of the copolymer and PVN, the phosphorescence spectrum with the 0-0 band at 482 nm for the copolymers and PVN can be assigned to the dimer formed between the naphthyl groups in the ground state. This leads to the conclusion that the phosphorescence spectrum of PVN in rigid glass consists almost of the dimer phosphorescence in disagreement with a previous assignment of the monomer.[5)]

The decay of the phosphorescence observed at 480 nm of copolymer I in MTHF at 77 K gives a single exponential curve with a lifetime 2.7 s. However, two exponential decays are observed in each of the copolymers II—IV. A relatively fast decaying component appears in addition to the slowly decaying component corresponding to the component of copolymer I. The contribution of the fast decaying component increases with increase in content of the naphthyl group. Since copolymer I shows mainly the monomer phosphorescence and the intensity ratio of the dimer to monomer phosphorescence in copolymers II—IV increases with the content of the naphthyl group, it is obvious that the fast and slow components correspond to the dimer and monomer phosphorescence of the naphthyl groups, respectively. The lifetimes of the triplet monomer and dimer are 2.1 and 0.6 s for copolymer II, 2.3 and 0.5 s for copolymer III, and 2.0 and 0.5 s for copolymer IV.

With the change of copolymer from I to IV, the lifetime of the monomer decreases from 2.7 to 2.0 s, while that of the triplet dimer remains 0.5 s. The decrease in lifetime of the monomer phosphorescence can be explained in terms of the quenching of the monomer emission by the dimer species through T-T energy transfer.

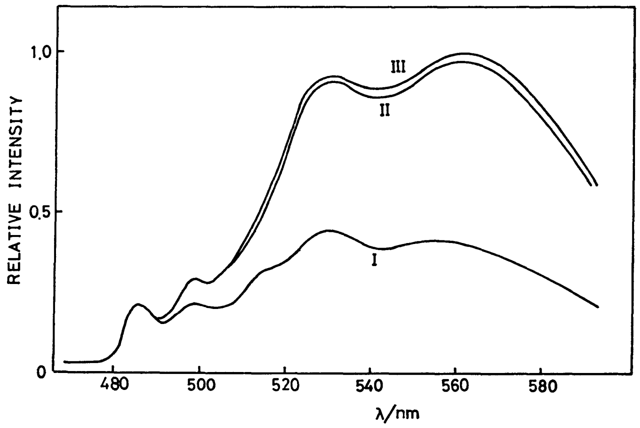

Fig. 2. The phosphorescence spectra (corrected) of VN–PVK copolymer I, II, and III in fluid THF solution at 187 K obtained by exciting at 350 nm.

Phosphorescence Spectra of the Copolymers in Fluid Solution. Figure 2 shows corrected phosphorescence spectra of the copolymers in fluid THF solution at 187 K. Each of these spectra consists of a structured spectrum with a 0-0 band at 485 nm and a broad, structureless spectrum with intensity maximum at *ca.* 550 nm. The former phosphorescence spectrum is attributable to the emission of the dimer of the naphthyl groups in the polymer since it is similar in position to the spectrum of the dimer of the naphthalene nuclei in rigid glass,[4] and in general $\pi\leftarrow\pi^*$ phosphorescence spectra of compounds such as naphthalene, phenanthrene, and quinoxaline remain almost unchanged in the position of the 0-0 band when the sample is changed from rigid glass solution to fluid.[2,3,6]

The broad emission spectra are attributed to the phosphorescence from the excimer of the naphthyl group in the polymers. This assignment is in line with the following experimental results: (1) The broad emission spectra of the copolymers correspond to the excimer phosphorescence spectra of naphthalene and its derivatives,[2,3] and 1,3-di(1-naphthyl)propane[7,8] in fluid solution. (2) The excitation spectra obtained by monitoring the emission at 560 nm of the copolymers agree with the absorption spectra. (3) No broad emission spectra are observed in rigid glass at 77 K. (4) The lifetimes of the emissions are of the order of 10^{-4} s.

In the fluid solution at 187 K, the decay curves of the phosphorescence emissions of all the copolymers obtained by monitoring at 500 nm consist also of two exponentiallg decaying components. The results are shown in Fig. 3 where the reciprocal lifetimes of the two decaying components are plotted as a function of the composition of the copolymer. The monitoring wavelength dependence and VN–PVK composition dependence of the contribution of the two components indicate that the two components, fast and slow, are attributable to excimer and dimer phosphorescence, respectively. The lifetime of the dimer phosphorescence with a relatively slow decay, 3×10^{-4} s, is independent of the composition of the copolymer, while that of the excimer phosphorescence decreases rapidly, reaching a constant value of 5×10^{-5} s as the content of the naphthyl group increases.

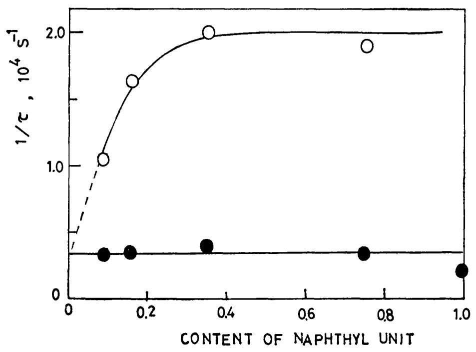

Fig. 3. The reciprocal lifetimes of the phosphorescence of VN–PVK copolymers as a function of VN–PVK composition. The measurements were carried out in fluid THF solution at 187 K. ○ corresponds to the reciprocal lifetime of the excimer and ● that of the dimer.

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