STUDIES OF THE TEMPERATURE DEPENDENT PHOSPHORESCENCE OF POLY(N-VINYLCARBAZOLE)

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Phosphorescence lifetimes and spectra of solid films of poly(N-vinylcarbazole) (PVCA) have been examined over the temperature range from 77°K - 298°K. At 77°K the usual phosphorescence emissions at 490 nm and 518 nm are observed but the intensity of the higher energy emission is much more temperature sensitive than the lower so that only the 518 nm signal remains at 298°K. The activation energies for radiative decay of these two signals are 0.6 kcal/mole (490 nm) and 2.9 kcalmole (518 nm). If, as has been previously supposed, these two emissions are from trapped triplet species, then these energies represent the respective trap depths. An unexpected result is that the mobile triplet energy level in solid PVCA is calculated to be about 20,500 cm^{-1} from these results whereas the N-alkyl carbazolyl chromophore has a lowest triplet energy of about 23,000 cm^{-1}.

The solid films of PVCA are cast from solution using either benzene or methylene chloride as solvent. Usually the films are air-dried but unmistakable increases in delayed luminescence intensity are observed after heating an air-dried film overnight in a vacuum oven. Although delayed luminescence from PVCA films has been detected up to about 175°K, the spectra obtained in this study are apparently the first examples of room temperature delayed luminescence from this polymer. Air-dried films from methylene chloride or films cast from either solvent and then vacuum dried give easily detected spectra at room temperature. Since neither benzene nor methylene chloride have quantum states accessible from the mobile PVCA triplet, it is concluded that the residual solvent molecules disrupt the formation of trap sites in the polymer leading to decreased intensities of phosphorescence and delayed fluorescence.