

EFFECT OF SUBSTITUTION AND AGGREGATE STATE ON OPTICAL PROPERTIES OF POLYVINYL CARBAZOLE

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A comprehensive study of the optical properties (absorption, photoluminescence (PL) and excitation of photoluminescence (EPL) spectra) was performed for solutions and films with thickness in the range of 30-100 nm of poly-vinylcarbazole (VC) polymers and copolymers with substituents to both the polymer chain and directly to carbazole molecule. We choose compounds, which, recently, were used for the development of polymer composites of polymethine dyes with high photosensitivity in a wide spectral range [1] including the near-infrared region [2].

The absorbance measurements for the chloroform solutions and the drop-cast films from same solutions on quartz substrates showed that changing in the aggregate state (going from solution to the film) results in a small red shift (8-10 meV) of the absorption band maxima, slight decrease in the half-width of the absorption bands in the films of the copolymers of VC with octylmethacrylate (OMA), and, practically, no change for the ratio of the intensities of the absorption bands in the films and solutions.

We have established that the attachment of OMA group to VC polymer significantly increases solubility, ductility and molecular ordering in solid state (in the films) for the derivatives in comparison with neat VC polymer. This also affects the energy maxima of bands and the intensities of the bands for excimer PL. In all the films, we have observed three bands of excimer PL, which are more split in VC-OMA copolymer. The latter shows both an improvement of the molecular ordering in the films of iodine- (I-VC-OMA) and benzene- (7V-BC-OMA) VC-OMA derivatives in comparison with non-OMA analogues (I-VC and 7V-BC) and a change in the structure of polymer aggregates (complexes) in the films.

Changes in the spectra due to the substitution of VC polymer are highly dependent on a size (volume) of the substituents. Since the attachment of iodine leads mainly to significant red shift (0.132 eV) of $^1A \rightarrow ^1L_a$ electronic transitions polarized along the long axis of the polymer molecules [3], without significant change in the band intensities. The attachment of bulky benzene groups leads to significant increase in both the intensity of a high energy $^1A \rightarrow ^1L_b$ transitions polarized along the short axis of VC molecule and red shift (0.388 eV) of low energy $^1A \rightarrow ^1L_a$ transitions. Moreover, the substitutions results in blue shift of the energy position of the EPL spectra (the range of absorbance for $^1A \rightarrow ^1L_b$ transitions).

Obtained data can be used to develop new methods of further increase of photosensitivity for polymer composites in a wide spectral range.

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[2] Ya.Vertsimakha, A.Verbitsky, A.Ishchenko, V.Syromyatnikov, I. Pomaz, Effect of Polymer Molecular Structure on Photosensitivity of Composites Films Based on Infra-Red Polymethine Dye, Mol. Cryst. Liq. Cryst. 536 pp. 99, 2011.

[3] V.M.Yashchuk, Fotonika Polimeriv, Publ. "Kyivskij Universitet", 2004, pp. 112.