

Photoluminescence of poly(N-vinylcarbazole) thin films deposited by dip-coating technique

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This paper is concerned with the photoluminescence (PL) study of poly(N-vinylcarbazole) (PVK) thin films deposited on the glass substrate by the dip-coating method. The PL spectra have been measured under steady state excitation (He-Cd laser, 325 nm) in the temperature range from 13 to 300 K. All the samples being studied exhibit strong luminescence in broad temperature range. The main emission PL peak has maximum at 410 nm and is attributed to the excimer emission of PVK. We have observed a small red-shift of this peak with an increase of temperature. In all the films under investigation the thermal quenching of PL has been noticed. This behaviour is determined by the closeness of carbazole groups belonging to neighbouring chains because the interaction between them leads to nonradiative transitions. The PL spectra of PVK thin films annealed under iodine atmosphere have also been investigated. We have observed a decrease of PL for these films. We have concluded that the annealing of PVK under iodine atmosphere induces its degradation.

Keywords: photoluminescence, poly (N-vinylcarbazole), thin films, dip-coating.

1. Introduction

Since the discovery of the electroluminescence of polymers, rapid progress has been made in research of these materials due to their potential applications in flat panel displays, photocells and thin field transistors. Polymer light emitting devices (PLED) have many advantages, such as: ease of colour tuning, good heat stability and simple fabrication process [1–5]. In particular, blue light emitting polymers have been investigated. One of the most intensively studied materials for blue electroluminescence emission is poly(N-vinylcarbazole) (PVK). It is a typical hole-transporting polymer which is often used in electroluminescence devices [6, 7]. As the thin polymer layers are basic components in various optoelectronic applications, it is very important to study their photophysical features. The knowledge of excited state relaxation processes

in polymers is crucial for the improvement of their optoelectronic properties. Since some defects and impurities can influence the mechanical, optical and electrical characteristics of thin polymer films, the study of polymer doping is also very important.

2. Experimental

The PVK layers were deposited on the glass substrate by dip-coating method. The PVK powder source material (Sigma Aldrich Co.) was dissolved in chlorobenzene (30 mg PVK/2.5 ml chlorobenzene). After cleaning the glass substrates were dipped in this solution at room temperature. Then, the layers were dried at room temperature under nitrogen atmosphere. Finally, the samples were heated at a temperature which was 5 K higher than the boiling point of solvent.

Photoluminescence (PL) spectra were measured using He-Cd laser ($\lambda = 325$ nm) as an excitation source and photomultiplier (R-928 HAMAMATSU) as a photodetector. The samples were placed in a closed cycle He cryostat (HC2-APD Cryogenics Inc.) and the temperature was controlled with the accuracy up to 0.1 K by a special controller (Lake Shore 330). For spectral selection the monochromator (SPM2-Zeiss) was used. Besides, the signal was processed and analyzed using a personal computer.

3. Results and discussion

Figure 1 shows PL spectra of pure PVK thin films measured at different temperatures from 13 to 300 K. These spectra are characterized by the peak at 410 nm which

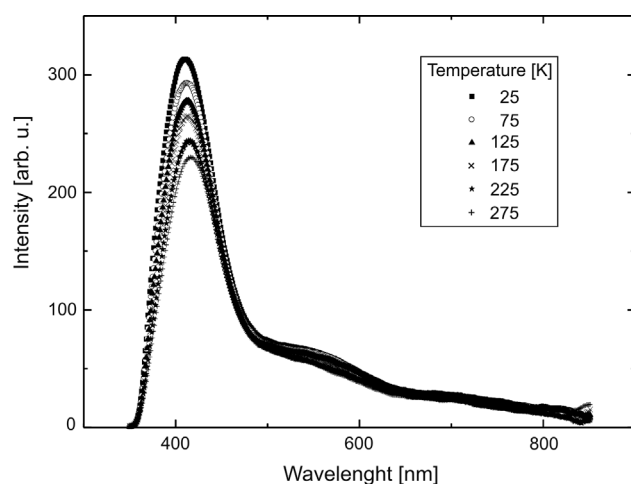


Fig. 1. PL spectra of a pure PVK layer on the glass substrate at selected values of temperature.

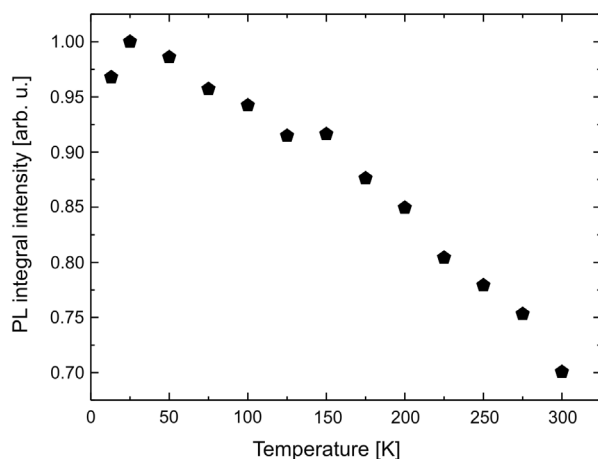


Fig. 2. Plot of the integral PL emission vs. temperature for PVK thin layer.

originates from the low-energy intrachain excimer recombination [8, 9]. Other broadened bands are much weaker and can be caused by the formation of dimers and some conglomerates in solid state. The main maximum shifts to lower energies when the temperature increases (from 410 nm at 13 K to 416 nm at room temperature). The character of this red-shift is similar to typical inorganic semiconductors [10]. While the temperature increases the integral intensity of spectra decreases. The thermal quenching of luminescence is separately shown in Fig. 2. It is clearly seen that the increase in temperature of 250 K reduces integral intensity by about 25%. This reduction is mainly caused by the increase of probability of nonradiative transitions at

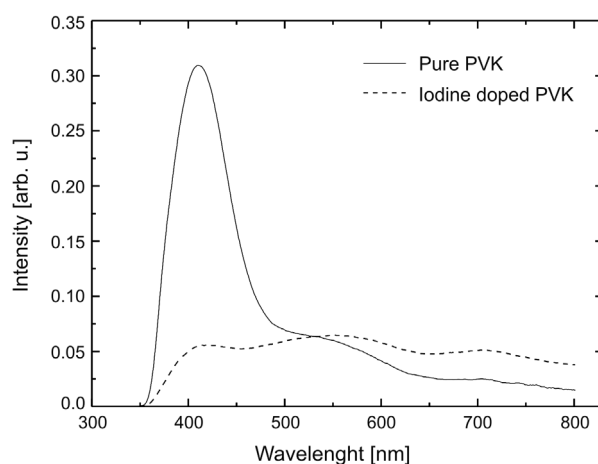


Fig. 3. PL spectra of a pure PVK layer and iodine-doped layer on the glass substrate at 13 K.

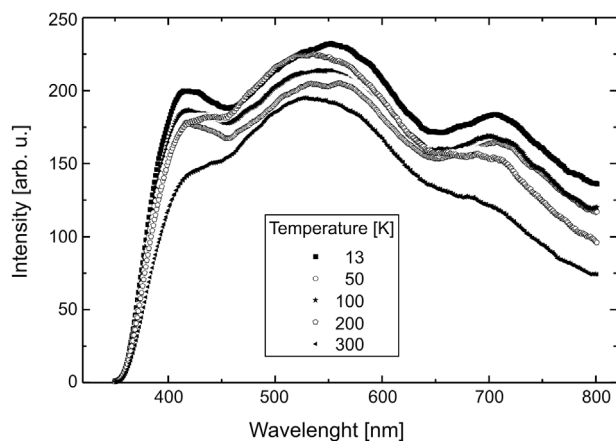


Fig. 4. PL spectra of iodine-doped PVK layer at different temperatures.

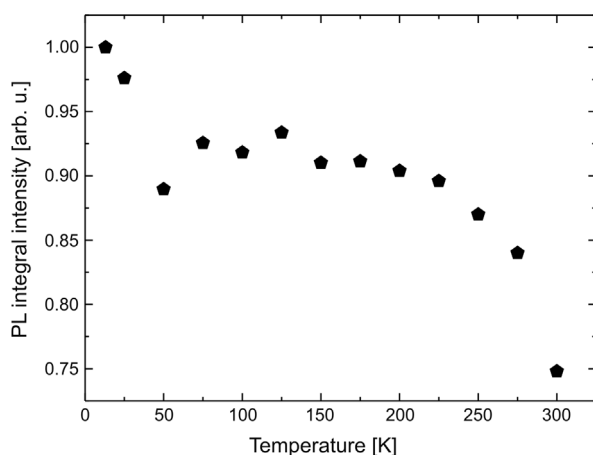


Fig. 5. Plot of the integral PL emission vs. temperature for iodine-doped PVK layer.

higher temperatures. These transition paths in PVK layers, leading to the luminescence quenching, can be determined by the interaction between carbazole groups belonging to neighbouring polymer chains.

One of the most extensively studied subjects has been the doping of PVK by different guest materials [11, 12]. In order to study the influence of iodine doping on optical properties of PVK layers we have annealed PVK under iodine atmosphere. The PL spectra of pure PVK and iodine doped films at 13 K are presented in Fig. 3. It can be seen that the reduction of the main PL peak takes place in doped layer whereas other bands are insignificantly enhanced. Since the large decrease of PL occurs in doped film even at low temperature we have concluded that the annealing of PVK under iodine atmosphere degrades the excimers.

Besides, we suppose that the iodine doping is conducive to formation of new conglomerates.

The temperature dependence of doped films has also been investigated. In Fig. 4, the temperature dependence of PL spectra of such a layer is shown. Figure 5 presents a plot of the integral intensity of iodine-doped film versus temperature. This dependence is quite different from pure PVK. The integral emission of iodine doped film decreases with an increase of temperature above 50 K. Then it is nearly constant and decreases significantly at room temperature. Such a dependence can be determined by the new energy states, introduced to PVK by doping, and energy transfers between them.

4. Summary

We have presented temperature photoluminescence studies of poly(*N*-vinylcarbazole) layers deposited on the glass substrate by the dip-coating method. The results obtained show strong dependence of PL properties of PVK on temperature. The thermal quenching in typical PVK thin layer has been observed. This behavior can be explained by interaction between carbazole groups belonging to neighbouring chains leading to nonradiative transitions. The PL spectra of PVK thin films annealed under iodine atmosphere have also been studied. We have observed a considerable decrease of PL for these films at all temperatures. We have concluded that the annealing of PVK under iodine atmosphere induces the degradation of its excimer states.

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