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Luminescence Properties of Epoxy Resins Modified with a Carbazole Derivative

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Summary: Luminescence properties of a new material - epoxy resin with added 9-(2,3-epoxypropyl)carbazole (REPK) were studied. Absorption and photoluminescence (PL) spectra of REPK are compared with those of poly(*N*-vinylcarbazole) (PVK). PL in REPK is shifted to shorter wavelengths. Its intensity is higher than in PVK. REPK emits light in the range from 330 nm to 470 nm. PL spectrum of REPK could be well deconvoluted for four emission bands.

Keywords: carbazole; epoxy resins; light emitting devices (LED); luminescence; polymers

Introduction

Much research has been done with organic light emitting devices (LED), especially with polymers containing carbazole groups, which have high application potential in flat panel displays.[1-3] Unfortunately, these materials suffer from inappropriate mechanical properties and their usually complex synthesis. In our study epoxy resin was used as a base material. The epoxy resin with carbazolyl groups was prepared by adding glycidyl derivative of carbazole - 9-(2,3-epoxypropyl)carbazole (EPK) (Figure 1) - to epoxy resin (R). This way we obtained a homogenous composition, which was crosslinked in the next step. In curing process we obtained a homogenous polymer with the carbazolyl group chemically bonded to the resin (REPK). Such polymer has excellent mechanical properties, high thermal stability and good chemical resistance.[4] In this paper we present some results of the luminescence measurements (absorption and photoluminescence (PL)) performed on thin layers of REPK.

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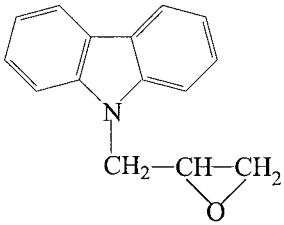

Figure 1. 9-(2,3-epoxypropyl)carbazole (EPK).

Experimental

The sample was prepared as a mixed composition, which contains 10 wt. % of EPK (R10EPK), using low-molecular-weight commercial epoxy resin – Ruetapox 0162 (Bakelite AG). Glycidyl derivative of carbazole was obtained by the reaction of carbazole with epichlorohydrin.[5] The modifier was dried to constant weight and powdered in a ceramic mortar. In the next step, components were mixed mechanically and then kept at 333 K for 24 h. Isophoronediamine (Euredur 46-Ciba) was used as a curing agent. Thin films (1.300 μm thick layers) were deposited from acetone solution on a glass substrate for absorption spectra and on a copper substrate for luminescence spectra. The obtained layers were then cured at room temperature and post-cured at 363 K for 24 hours. The finished material is homogeneous, amorphous, with 2-3% content of crystalline phase.

The PL and absorption measurements were carried out in an optical cryostat. The samples were excited using a 75 W xenon arc lamp installed in a high-intensity illumination system. Luminescence intensity was monitored using an SP150 spectrograph connected to the LN/CCD-1024E camera (chip format 1024x256, spectral range 190-1080 nm). The CCD camera is cooled with liquid nitrogen to reduce the dark current. Temperature of CCD chip is stabilized with a controller between 143 K to 203 K. The samples during PL measurements were excited by UV light (at 282 nm and 286 nm) in air at room temperature. The wavelength resolution of the measurements was about 0.4 nm. The obtained spectra were numerically calibrated with respect to wavelength and intensity.

Results

The absorption spectrum of R10EPK is presented in Figure 2. Its shape is similar to the absorption spectrum of poly(*N*-vinylcarbazole) (PVK).[6] The absorption edge for this material is ca. 360 nm. PL in R10EPK appears in the wavelength range from 330 nm to 470 nm. PL and absorption spectra are symmetrical, crossing at about 348 nm (Figure 3). Therefore the distance between singlet states S_{00} and S_{10} is about 3.4 eV. The intensity of PL for R10EPK is dependent on the thickness of the sample. It reaches a maximum for about 5 μm of the sample thickness, becoming constant for the sample thickness larger than 16 μm. Analogous measurements were performed for PVK for the same size and the same thickness of samples. The PL intensity of R10EPK is higher than intensity of PVK (Figure 4).

PL emission spectrum of R10EPK has a complex structure. To describe its shape more quantitatively, it was deconvoluted numerically giving four emission bands: 352 nm (maximal intensity), 366 nm, 377 nm and 395 nm. It was assumed that the bands have Gaussian shape. The deconvolution is shown in Figure 5.

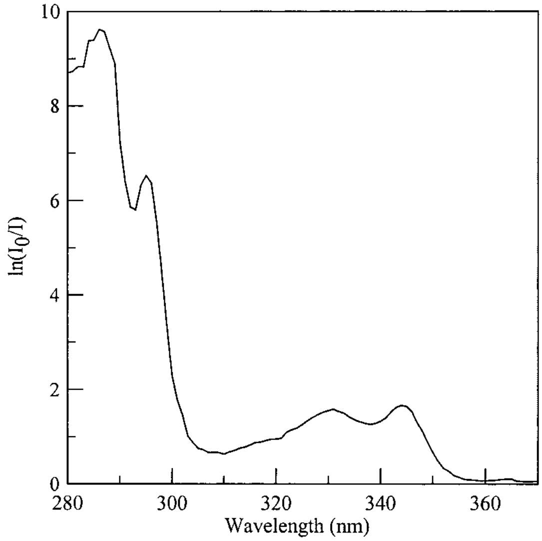

Figure 2. Absorption spectrum of an R10EPK thin film at room temperature.

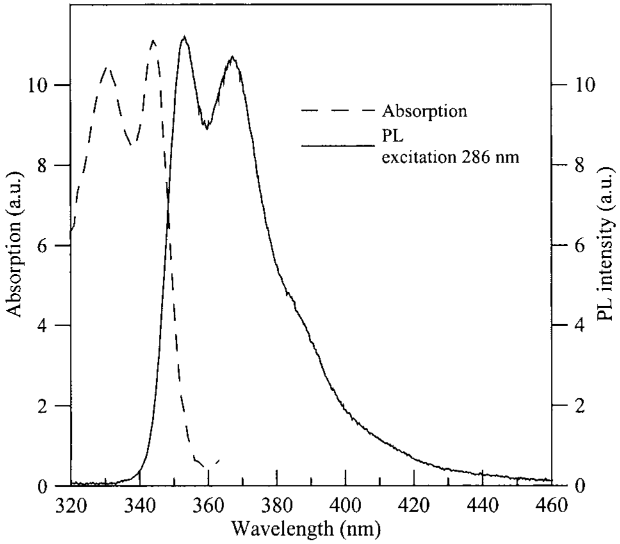

Figure 3. Absorption and photoluminescence spectra of R10EPK thin film at room temperature. PL spectrum measured after excitation at 286 nm.

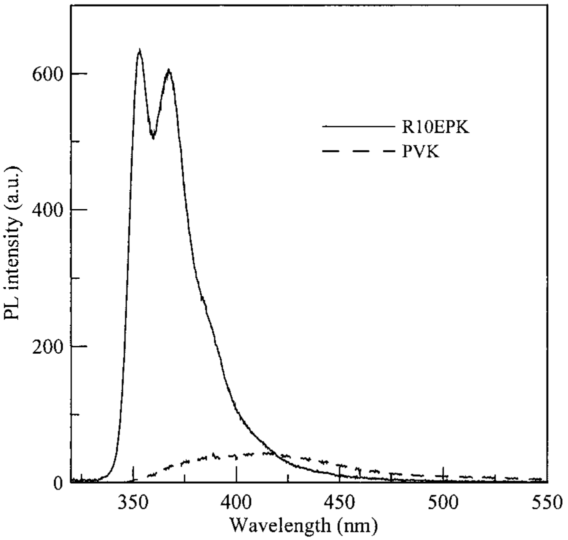

Figure 4. Photoluminescence spectra of R10EPK and PVK thin films at room temperature. Excitation at 282 nm.

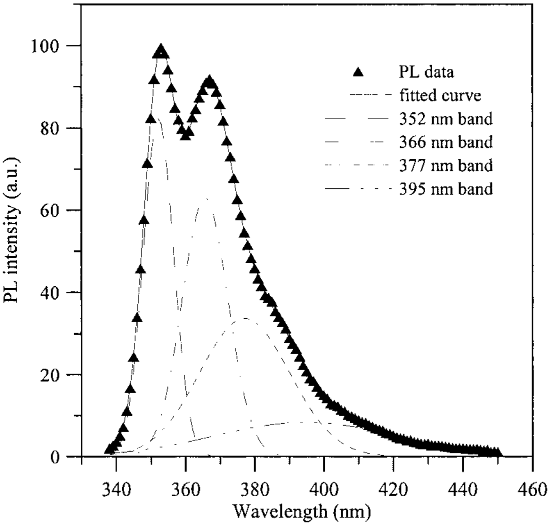

Figure 5. PL spectrum of an R10EPK thin film at room temperature excited at 286 nm. The spectrum is fitted with four emission bands.

Conclusions

Luminescence properties of a new material – R10EPK – were studied and compared with the known PVK polymer. Although absorption spectra of these two materials are similar, PL in R10EPK has greater intensity than in PVK. It is also shifted to shorter wavelengths with an effective range from 330 nm to 470 nm. The distance between singlet states S_{00} and S_{10} was found to be about 3.4 eV. PL emission spectrum of R10EPK has a complex structure. It can be represented as a sum of four Gaussians having maxima at 352 nm, 366 nm, 377 nm and 395 nm. Presumably these emission bands are related to vibrational levels of the singlet state S_0 of EPK. A very high PL efficiency of this material together with its excellent mechanical properties makes it a promising candidate for LED applications. This will be the aim of our further studies.

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