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The influence of conjugated polymer chain length on luminescence properties of ordered polymer films

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Abstract

Dependences of the photoluminescence of conjugated polymer poly(*p*-phenylene) (PPP) thin films on different lengths of polymer chain and temperatures of the samples have been studied using steady-state fluorescence spectroscopy and the time-correlated single-photon counting technique. © 1997 Elsevier Science S.A.

Keywords: Poly(*p*-phenylene); Vacuum deposition; Fluorescence; Decay curves; Polymer chains; Films

1. Introduction

Optical properties of conjugated polymers have been studied in connection with production and transport of charge carriers [1]. Since the demonstration of electroluminescence in conjugated polymers [2], significant progress has been made in improving the performance of polymer-based light-emitting diodes (LEDs). Today polymer LEDs are being seriously considered for large-area application such as alpha-numeric and flat panel displays.

The efficiency of the radiate decay in conjugated polymers has become a matter of considerable importance since the discovery that luminescence from the same singlet excited states could also be produced in thin-film LED structures. Poly(*p*-phenylene) (PPP) has attracted attention as material for a blue-emitting diodes [3,4].

This paper reports the influence of conjugated polymer chain length and substrates on luminescence properties of ordered polymer PPP films.

2. Experimental

The PPP powder was prepared according to Kovacic's method [5]. The reaction products were washed with HCl, water, methanol and then dried for 3 h at 280 °C and 30 min at 400 °C under vacuum. PPP films were vacuum-deposited on a number of substrates: non-fluorescence quartz, KBr, Si, Ge, carbon, Au or indium–tin oxide (ITO).

The deposition was performed as follows. The PPP charge (1–7 mg) was placed in a quartz ampoule and the substrate was positioned vertically or horizontally over the powder (the vacuum cell). The evaporation was carried out under a vacuum of 10^{-4} Torr with the bottom of the ampoule immersed in a heater, whose temperature was maintained at the constant level of 600–900 °C. Variation of polymer length was performed under different temperature conditions. Different methods of structure analysis (IR spectroscopy, electronography, small-angle X-ray spectroscopy) confirm the highly ordered structure of PPP films.

IR absorption spectra were recorded with a BIO-RAD Furier-IR FTS-7 spectrometer. Fluorescence spectra were investigated using a multichannel optical analyser (EG&G) with nitrogen laser excitation (337 nm). Fluorescence decay curves were measured with an Edinburgh Instruments 199 spectrofluorimeter by the time-correlated single-photon counting technique and were analysed by a least-squares iterative deconvolution method based on the Marquardt algorithm [6]. The sample studies were performed at 293 and 100 °C.

3. Results and discussion

All PPP films have a fluorescence band with three maxima at 23 041, 21 645 and 20 661 cm^{-1}. The distance between

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Table 1
The best parameters for fluorescence decay of PPP polymer films deposited onto quartz substrates. Decay law used: $B_1 \exp(-t/t_1) + B_2 \exp(-t/t_2)$

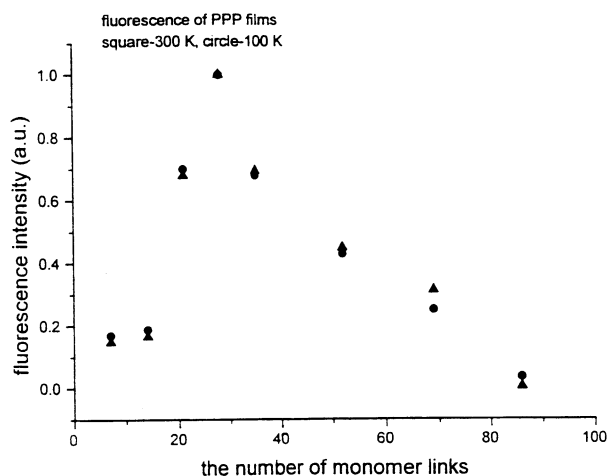| Fluorescence wavelength (nm)	No. of monomer units	τ_1 (ns)	B_1	τ_2 (ns)	B_2	Crystallized form
490	7	2.3	0.149	10.1	0.029	good
490	14	2.2	0.191	11.9	0.022	good
490	21	2.6	0.231	13.2	0.019	good
484	28	1.8	0.232	10.6	0.018	good
484	35	1.4	0.316			bad
484	52	1.2	0.352			bad
484	69	1.4	0.351			bad
516	86	1.5	0.207			bad

Fig. 1. Dependence of the fluorescence intensity on the polymer chain length.

maxima is $1400 \, cm^{-1}$ pointing to a well-developed vibration structure involving the molecular skeleton. These results are in contrast with data of Yamazaki and co-workers [7] where the fluorescence spectra of highly crystalline PPP had no vibronic structure. The influence of temperature from room temperature to 100 K did not strongly change the fluorescence spectra, excluding the decrease in re-absorption effect.

The intensities of the absorption bands of terminal monosubstituted phenyl rings (750 and 690 cm^{-1}) normalized to the intensity of the 805 cm^{-1} band are used to estimate the molecular chain length. Here we calculated the mean number of monomer units in the chain according to the expression $n = 2I_{805}/I_{690} + 2$ [8]. It was shown that PPP polymer chain length is related to the substrate temperature [9].

Fig. 1 shows the dependence of the fluorescence intensity on the polymer chain length. The curve has a maximum at about 25 units. The length of conjugate polymer chains plays the principal role in the efficiency of fluorescence. The degree of crystallinity of PPP films was investigated by the electron diffraction method. The best film order was obtained for samples with polymer chains from 7 units up to 35. The orthorhombic crystal structure for the best samples has constants: $a = 7.8 \, Å$ and $b = 5.6 \, Å$. Yamazaki and co-workers [7] obtained similar data for vacuum-deposited thin PPP films on gold-coated grids using IR spectral analysis and X-ray diffraction.

The changes of fluorescence lifetime are correlated with the changes in relative efficiency. The fluorescence decay curves were well fitted by a two-exponential law for ordered films (Table 1).

The average values for fast and slow components were 2.2 and 11.4 ns, respectively. The nature of the emitting species may be adaptable to the idea of two forms of PPP polymer (benzenoid and quinoid) [10]. It was shown that the vacuum-deposited PPP films have a strong band at 1375 cm^{-1}, associated with valent vibrations of C–C bonds linking the phenyl units in the boundary fragment between the benzenoid and quinoid structures.

Because the fluorescence efficiency of the emissive material is an upper limit for the electroluminescence efficiency of a LED, this property is directly related to the LED's power consumption. High fluorescence efficiency is desired to increase the brightness and operating lifetimes of LEDs. The fluorescence intensity dependence of the chain length has the best value at about 25–30 units for highly ordered PPP film. It has been speculated that the nature of the emitting species has two forms of PPP: other conformation defects (e.g. cissoid linkages, dihedral angles, etc.) are also possible.

Acknowledgements

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