

Blue Light-Emitting Polymer Prepared by Enzymatic Catalyzed Polymerization of p-Phenyl Phenol

Ma Yuguang Tang Jianguo Ma Lin Liu Shiyong Shen Jiacong

Department of Electronics Sciences, Jilin University,

Changchun, 130023, China

ABSTRACT: Photon emission properties of polyphenylphenol (PPP) which were synthesized by a newly-found enzymatic catalyst is reported. The photoluminescence peak is at about 370-420 nm excited by the light at 350 nm. The absorption band edges and photon emitting peaks of the polymer are found the conjugated lengths of the polymer dependent. In the transient luminescence measurement the lifetime of PL decay is determined to be 2.0 ns which is supposed as the evidence of polaron excitation recombination.

Traditionally, polymers have been known for their flexibility and ease of processing but not for their opto-electronic properties. Then Conducting polymers with highly extended conjugate electron system in their main chains have attracted much interest from both fundamental and practical view points. Recently, a breakthrough in conjugated polymer application is made, which the polymer can be fabricated a electroluminescent device^{1,2}. The electroluminescence originates from the recombination of polarons induced by hole and electron-injecting from the electrode, similar with photoluminescence.

In all conjugated polymers, only few shows blue emission³. In this paper, we report a novel blue emission polymer PPP prepared by enzymatic polymerization, its optical absorption and emission spectra as a function of polymer chain length and temperature are studied. By using this polymer as active layer, a light-emitting diodes was made.

PPP was peroxidase-catalyzed polymerized in dioxane(containing 20-90% aqueous buffer), the sample with difference molecular weight (3000-7000g/mol) were obtained by difference polymerization condition. The polymer

structure shown in figure 1 is demonstrated by NMR and IR spectrum.

The absorption spectra were recorded with Hitachi 500 UV-Vis double beam spectrophotometer and the fluorescence spectra with an Aminco Bowman spectrophotofluoremeter and corrected for the nonlinear response of the detector photomultiplier tube and

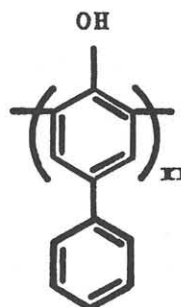


Fig.1 Molecular structure of PPP

nonuniform emission of the excitation source, a xenon lamp.

Figure 2 shows the molecular weight

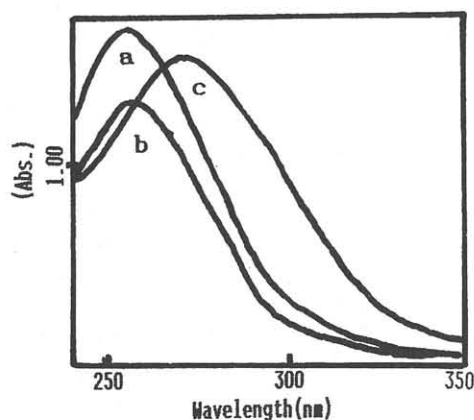


Fig.2 Absorption spectra of PPP with different molecular weight: a) 3000; b) 5000; and c) 7000 g/mol.

dependence of the absorption spectra of PPP. As evident from this figure, the absorption spectrum red-shift remarkably with increasing chain length. This means the band gap can be chemical tuned by controlling the polymer chain length. A very strong fluorescence are observed only for PPP with molecular weight 7000g/mol. The separation between the absorption and emission band (i.e. Stokes loss) are found. The fluorescence spectra of organic compounds originate from the lowest excited singlet states because the internal conversion between excited singlets is fast compared with the fluorescence emission. The fluorescent spectra of polymer in dioxane exhibit some overlapping peaks and a broad structure with a shoulder on the longer wavelength side (Fig.3). It was found that fluorescence

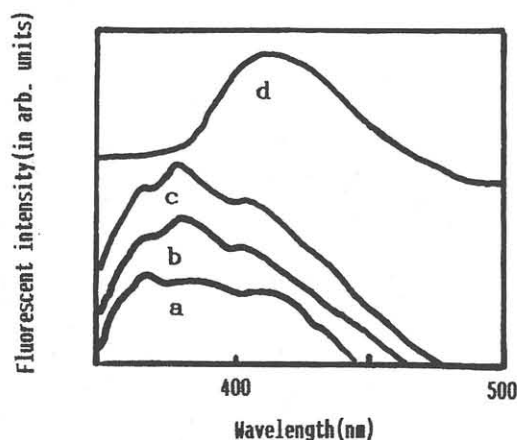


Fig.3 Fluorescent spectra of PPP in dioxane solution: a) 1×10^{-4} g/ml, b) 2×10^{-4} g/ml, c) 4×10^{-4} g/ml, d) in film.

intensity at 376nm become weaker with

decreasing polymer concentration. In general, this indicated that there exist intermolecular excimers. An approximate analysis of the shoulder on the longer wavelength side of PPV indicates the existence of one or two weak bands with vibrational frequencies 1300 ± 100 and $1500 \pm 100 \text{ cm}^{-1}$. These vibrational frequencies observed in the present case show a close agreement with the infrared bands at 1275 and 1524 cm^{-1} measured by our group and assigned as ring stretching vibrations. In films, a blue emission (420nm) is obtained, which is very different with it in solution, it indicated that the micro-surrounding affect the band gap and the recombination of polarons. The temperature dependence of luminescence intensity is more clearly indicated in Fig.4. That is, with increasing temperature the emission intensity decreases. That is due to the increased probability of non-radiative recombination.

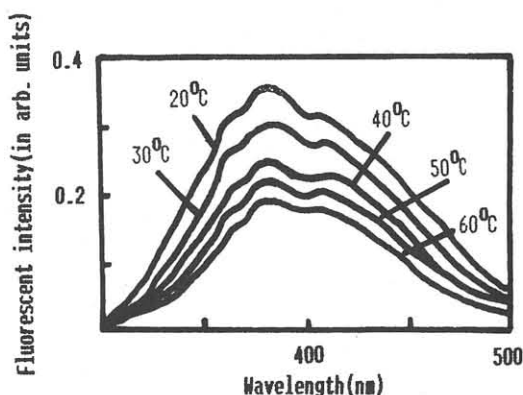


Fig.4 Fluorescence of PPP at various temperatures

The time resolved PL was also measured by a pulsed mode-locked Nd:YAG laser and the SHG of the Nd:YAG pumped dye laser (200 to 300 nm) and a streak camera. The laser pulse width is 15 ps which is much shorter than the PL decay. The lifetime of PL decay measured to be 2.0 ns, which is supposed as the evidence of polaron excitation recombination fluorescence.

The relatively high quantum yield for photoluminescence (about 50%) suggests the possibility of achieving polymer dye lasers using this polymer as the active chromophore. The research for other application for blue light-emission LEDs with this polymer as active layer is in progress in our laboratory. Fig. 5 shows the structure of the LEDs. The LEDs were fabricated by spin coating a PPP films in ITO electrode on glass substrate. Then a Mg electrode was attached to polymer

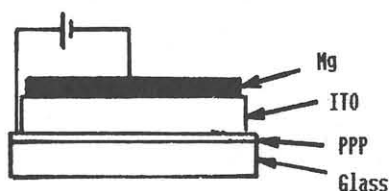


Fig. 5 Configuration of PPP light-emitting diode

layer, the emitting area in the devices was 4mm^2 . Current-voltage characteristics were measured by an electrometer. A pronounced rectification effect was observed in the device (Fig. 6). EL emission was observed only

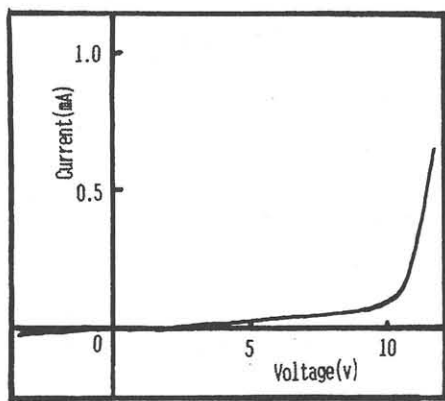


Fig. 6 Current-voltage characteristics of PPP light-emitting diode

in forward bias. The emission at 10V, was clearly observable in a darkness room with the naked eye. But the lifetime of emitting is very short, which is about 5s.

Acknowledgments

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