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# Electroactive Fluorene-Based Polymer Films Obtained by Electropolymerization

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**Abstract :** Electrochemical oxidation is one of the most convenient ways to obtain conjugated polymer films as polypyrrole, polyaniline, polythiophene or polycarbazole. The research in the field has been mainly directed to the study of electrical conduction properties of the materials obtained by electropolymerization, often the main reason being their use as electroconducting electrodes, and very little attention has been paid to the morphological and optical quality of the films electrodeposited on flat surfaces. Electropolymerization of the monomer solution was scarcely used in the past to manufacture polymer-based light-emitting diodes (PLED), most probably due to the difficulty of obtaining defectless polymer films with good mechanical and optical properties, or conductive polymers with well controlled molecular weights. Here we report our attempts in using electrochemical deposition as appropriate method for preparing ultrathin films of fluorene-based polymers for PLED applications. The properties of these films were evaluated in terms of structural morphology, optical properties, and electrochemical conduction. Thus, electropolymerization of 4,4'-(9-fluorenylidene)-dianiline was performed in dichloromethane solution, at a concentration of 10-2 M, using 0.1 M tetrabutylammonium tetrafluoroborate as electrolyte salt. The potential was scanned between 0 and 1.3 V on the one hand, and 0 - 2 V on the other hand, when polymer films with different structures and properties were obtained. Indium tin oxide-coated glass substrate of different size was used as working electrode, platinum wire as counter electrode and calomel electrode as reference. For each potential range 100 cycles were recorded at a scan rate of 100 mV/s. The film obtained in the potential range from 0 to 1.3 V, namely poly(FDA-NH), is visible to the naked eye, being light brown, transparent and fluorescent, and displays an amorphous morphology. Instead, the electrogrowth poly(FDA) film in the potential range of 0 - 2 V is yellowish-brown and opaque, presenting a self-assembled structure in aggregates of irregular shape and size. The polymers structure was identified by FTIR spectroscopy, which shows the presence of broad bands specific to a polymer, the band centered at approx. 3443 cm-1 being ascribed to the secondary amine. The two polymer films display two absorption maxima, at 434-436 nm assigned to π-π* transitions of polymers, and another at 832 and 880 nm assigned to polaron transitions. The fluorescence spectra indicated the presence of emission bands in the blue domain, with two peaks at 422 and 488 nm for poly (FDA-NH), and four narrow peaks at 422, 447, 460 and 484 nm for poly(FDA), peaks originating from fluorene-containing segments of varying degrees of conjugation. Poly(FDA-NH) exhibited two oxidation peaks in the anodic region and the HOMO energy value of 5.41 eV, whereas poly(FDA) showed only one oxidation peak and the HOMO level localized at 5.29 eV. The electrochemical data are discussed in close correlation with the proposed chemical structure of the electrogrowth films. Further research will be carried out to study their use and performance in light-emitting devices.

**Keywords :** electrogrowth polymer films, fluorene, morphology, optical properties
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