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**CHARACTERIZATION AND LUMINESCENCE PROPERTIES OF THE
DYE-DOPED POLYMER LANGMUIR-BLODGETT FILMS***

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Abstract 1,1,4,4-Tetraphenyl-1,3-butadiene (TPB) was successfully introduced into the polymer multilayer films by means of Langmuir-Blodgett (LB) technique. Results of UV-VIS spectra and X-ray diffraction showed that the uniform films had a layer structure similar to the superlattice of organic multiple quantum wells. The electroluminescence (EL) devices fabricated from the doped polymer LB films emitted blue light. Compared with the casting films, the photoluminescence (PL) and EL spectra showed that the exciton energy shifts to higher and the half-width of the emission peak becomes narrower due to exciton confinement effect.

Keywords Luminescence, Dye-doped polymer, Langmuir-Blodgett films

INTRODUCTION

Organic light-emitting devices (LEDs)^[1, 2] have attracted much attention due to their potentiality in materials and device processes. Materials used for the fabrication of LEDs can be either small molecules or polymers, in which the polymers are quite useful in fabricating LEDs due to their high mechanical strength and excellent film-forming property. Among many film-deposition methods, Langmuir-Blodgett (LB) and self-assembly (SA) techniques are very useful to process organic molecules into ultrathin multilayer films with controlled thickness and molecular architecture. However, only those amphiphilic or charged fluorescent molecules through LB^[3] or SA^[4] techniques can be used in LEDs. On the other hand, studies on multiple quantum wells (MQWs) of organic superlattices have been substantially developed^[5]. Organic crystals are bonded together by the relatively weak van der Waals force, which is insufficient to create the lattice effect, so they have prominent properties such as large photo conductivity and strong photoluminescence^[6]. Forrest and others^[7, 8] have reported the fabrication and optical characteristics of the organic MQW structure.

Recently, we used an amphiphilic grafting polymer containing a flexible hydrophilic network and hydrophobic alkyl chains to develop "Duckweed" and "Reversed duckweed" polymer LB films^[9-11] which was proved to have a more highly ordered orientation and is more stable for long term. In this paper, we introduced the dye 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) into this polymeric multilayer films by LB technique (see Fig. 1), which formed the superlattice-like structure. The TPB molecules were transferred into the uniform multilayer films confirmed by UV-VIS spectra

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and X-ray diffraction. Then the luminescence properties of the LEDs fabricated from this complex LB films were further studied.

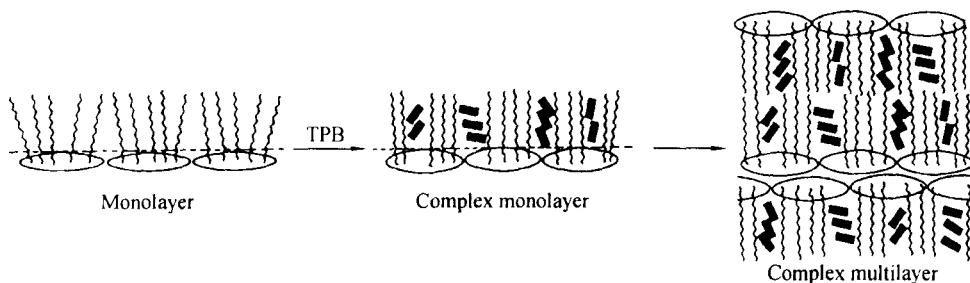
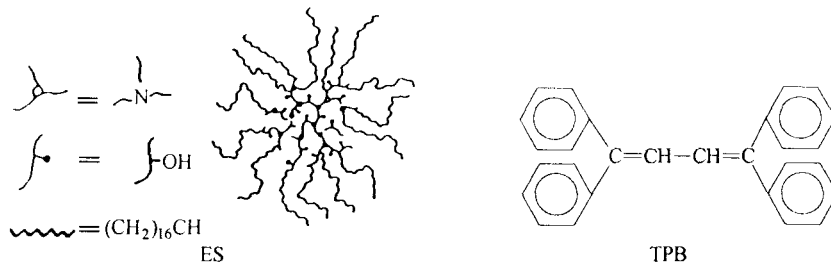


Fig. 1 The possible model of the complex LB films

EXPERIMENTAL

TPB and poly(*N*-vinylcarbazole) (PVK) were purchased from Aldrich. All reagents were of analytical grade and are commercially available. The amphiphilic polymer (designated as ES) was synthesized by the method reported in our previous papers^[12, 13]. The number-average molecular weight of ES is 1.2×10^4 which was determined by means of a membrane osmometer (Model Knauer). The content of alkyl chains is 48.5 wt% with an average of 20.6 alkyl chains in each molecule.



The monolayer experiment was performed on a computer-controlled KSV-5000 instrument with a Whilhelmy plate system. The amphiphilic polymer ES and TPB were dissolved in a mixed solvent of chloroform/ethanol (volume ratio 7:3) at concentration of 2 mg/mL and 1.5 mg/mL, respectively. The aqueous subphase was deionized water. The ES and TPB solutions were mixed (volume ratio 7:1) before being spread on the water surface. The Y-type LB films were deposited on a single-crystal silica substrate for X-ray diffraction and on a quartz slide for UV-VIS measurements. The surface pressure was maintained at a constant value of 40 mN/m, the dipping speed was 10 mm/min and the upper delay 10 min for drying.

UV-VIS spectra were measured by Shimadzu UV-3100 spectrophotometer. The luminescence was measured with a Hitachi model 850 fluorescence spectrophotometer. X-ray diffraction was carried out in D/max γ_A diffractometer, with CuK_α target.

RESULTS AND DISCUSSION

The properties of the TPB doped polymer LB films can be inferred from the surface pressure (π) versus molecular area (A) isotherms (Fig. 2). The π - A isotherm of ES indicates the self-organizing ability of this amphiphilic polymer at air-water interface. It is seen from curve (a) that the polymer ES could only form a liquid-analogy monolayer due to its strong hydrophilic property. When TPB molecules were introduced into ES to balance hydrophilicity and hydrophobicity of this polymer,

curve (b) became steeper and the monolayer was in a solid-analogy state. Moreover, the molecular area decreases due to the addition of the hydrophobic TPB. Similar to our previous work^[14], the elastic polymeric amphiphiles has to change its configuration to provide enough space for TPB (see Fig. 1) when TPB was added to the monolayer. It is reasonable to imagine that the flat-shaped network will shrink in the horizontal direction and increase its thickness, so the molecular area in curve (b) decreases.

In the UV-VIS region (250 nm~700 nm) ES has no obvious absorption, but TPB has two peaks at 265 nm and 350 nm, respectively. The linear dependence of the absorption on the number of layers for these two peaks suggests that TPB is transferred to each hydrophobic layer of LB film. Furthermore, the uniform layered structure of multilayer films is proven by the X-ray diffraction pattern (Fig. 3). The pure ES multilayer films show two diffraction peaks at 1.71° and 3.52° in the small-angle region, from which the layer space can be calculated to be 2.48 nm according to the Bragg equation. For complex multilayer films, the single peak at 1.52° ($d = 5.8$ nm) is observed. We can infer one period consisting of two polymer layers. The two layers of the complex films are roughly 0.8 nm thicker than pure ES films, suggesting that the alkyl groups straighten slightly in the complex films, which fits well with the above proposed model.

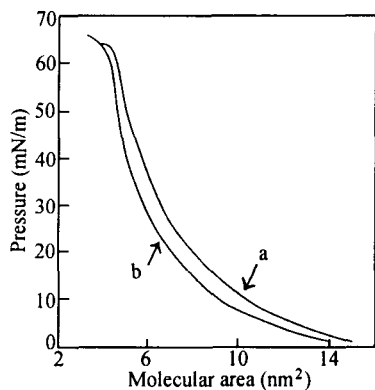


Fig. 2 Surface pressure (π) versus molecular area (A) isotherms of the LB monolayer
a) pure ES monolayer; b) TPB-doped ES monolayer

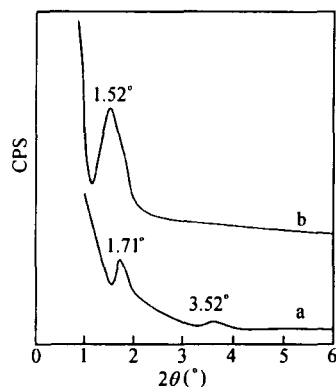


Fig. 3 X-ray diffraction patterns of 30 layers LB films
a) pure ES monolayer; b) TPB-doped ES monolayer

ES is an insulating polymer with large energy gap, so the hydrophilic network of the complex LB films can be used as the energy barrier and the hydrophobic part with TPB acts as the energy well, which has the high ordered structure similar to the superlattice structure of organic multiple quantum wells^[15].

The TPB-doped polymer LB films were used to fabricate LEDs. The LB films were transferred onto a PVK-coated indium-tin-oxide (ITO) glass substrate with a sheet resistance of $20\Omega/\square$ (see Fig. 4). An aluminum electrode was vacuum deposited on the LB films at 10^{-6} Torr. The deposition rate was maintained at 0.1~0.2 nm/s. When the LED of ITO/3-bilayers LB film/Al was driven by an applied voltage of 6 V, a blue emission was observed and the device exhibits maximum brightness of about 45 cd/m^2 at 11 V.

The PL and EL spectra of these dye/polymer LB films are shown in Fig. 5. Compared with the casting films (curve a), the PL emission peak of the LB films (curve b) shifts 10 nm towards lower wavelength and its half-width (65 nm) narrows about 20 nm. Our previous work showed that the emission peaks of PL spectra for TPB did not change with the variation of its concentration either in chloroform solution or in polymer thin films, so we think that the difference of PL spectra between the two above mentioned films resulted from the quantum confinement effect^[16] of the

between the two above mentioned films resulted from the quantum confinement effect^[16] of the superlattice structure: the excitons in TPB layer are isolated by the hydrophilic network of ES. The EL spectra are basically identical with the PL emission, but the variation of the EL intensity with the layer number is not similar to its PL intensity, which increases with increasing layer number. Only if the complex LB film has three-period layers, can the EL intensity reach its maximum at the same applied voltage, which indicates that the excitation formation mechanism is different between PL and EL process. With increasing layer number, the resistance also increases and leads to difficulty in carrier injection, so the EL efficiency of the complex LB films decreases.

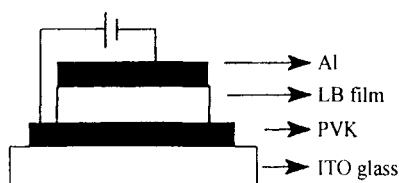


Fig. 4 Configuration of the LED device

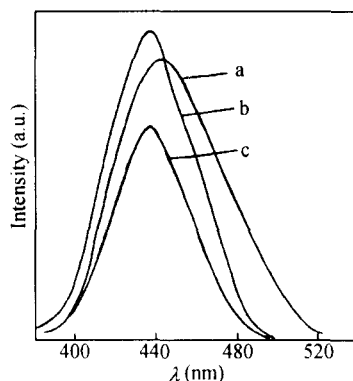


Fig. 5 PL and EL spectra of TPB-doped polymer thin films
a) PL of casting film, b) PL of LB film, c) EL of LB film

Summarizing, we have used LB technique to fabricate a new kind of LEDs with a structure similar to superlattice. Compared with the casting films, its PL and EL spectra both showed the spectral narrowing and the emission energy shifting to higher energy. It is indeed a good method to fabricate LEDs with superlattice structure.

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