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Photoluminescence Study of Langmuir-Blodgett Films of Blend Poly 3-(2-(5-Chlorobenzotriazole)Ethyl) Thiophene

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The multilayer Langmuir-Blodgett (LB) films of poly 3-(2-(5-chlorobenzotriazole)ethyl) thiophene (PCBET) blended with amphibious arachidic acid (AA) were prepared and characterized. The photoluminescence intensity of the blend film was enhanced as the AA increased by a certain amount. The PCBET excimers were not formed in the blend LB films.

Keywords: polythiophene derivative; LB film; photoluminescence

INTRODUCTION

In recent years, Langmuir-Blodgett (LB) films of polymers for LEDs application have been given much attention^[1]. Until now one of the best interesting candidate polymers for LEDs is polythiophene(PT) derivative^[2]. The blend polymer systems have the unique advantage of simplicity among macromolecular systems. Generally polymer alone is not well suited for manipulation by the LB technique, and pure luminescent molecules have problems of the fluorescence quenching of concentration, but its mixed system with model amphibious molecules

can be used to prepare homogeneous LB film. In this paper, the thin multilayer (LB) films of poly 3-(2-(5-chlorobenzotriazole)ethyl) thiophene (PCBET) blended with amphibious arachidic acid (AA) were prepared and characterized.

EXPERIMENTAL

The PCBET that has an electron-withdrawing moiety in the side chain was synthesized as reported in previous paper^[2]. Surface pressure-area (π -A) isotherm and film deposition were performed on a LB balance. A 4.0×10^{-6} M solution was spread onto an aqueous subphase. The floating molecules were compressed at a speed of 10 mm/min. The LB multilayer were prepared on ITO-glass by Y-type method at a pressure of 23 mN/m.

RESULTS AND DISCUSSION

The π -A isotherms of PCBET and PCBET/AA (1:4) are shown in Figure 1. In the case of pure PCBET LB film, the mean area of repeating unit of polymer is 15 \AA^2 . It is only a little bigger than the value 14.7 \AA^2 that is the area of the thiophene ring calculated from the Corey-Pauling-Koltum (CPK) model^[3]. This result led us to deduce that after PCBET formed a condensed monolayer one PCBET chain is compressed into a mass limited in about size of a thiophene ring on the air-water interface. In ref.4, the mean molecular areas of five poly (3-alkylthiophene)s are in the range of $4.2\text{--}9.5 \text{ \AA}^2$. It is obvious that they are much smaller than 14.7 \AA^2 (CPK value). Comparing with above results, it seems that PCBET has a better behavior similar to the amphibious character than poly (3-alkylthiophene)s on air-water

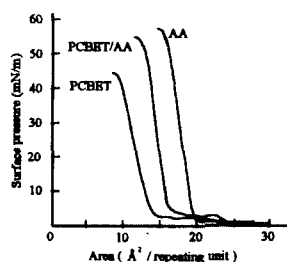


FIGURE 1. The surface pressure-isotherms of PCBET, AA and mixed systems PCBET/AA in 4.0×10^{-3} molar (1:4 ratio).

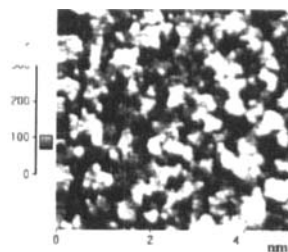


FIGURE 2. AFM image of LB film

interface. After mixing with AA, the area of repeating unit of LB becomes larger (16.5 Å^2), because the long alkyl chain can improve environment of polymer to subphase and prevent PCBET from folding at the air-water interface during the compression. The stable condensed monolayers of both pure and blend BCBET were formed on subphase in Figure 1. The monolayer of pure PCBET collapses at 43 mN/m , but the blend monolayer has a higher collapse pressure. The mean transfer ratio of pure PCBET of LB film is ~ 0.78 . The PCBET can form a condensed monolayer on the air-water interface compared with poly (3-alkylthiophene)s^[4], but the Langmuir film on the subphase could not sufficiently be transferred to substrate. It is explained that the molecular structure feature such as thiophene ring is not well hydrophilic.

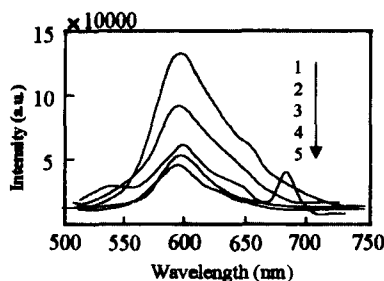


FIGURE 3. The PL spectra of LB films of PCBET/AA at different blend ratios: (1) 1:4, (2) 1:2.5, (3) 1:0, (4) 1:5, (5) 1:6. Excitation wavelength: 422 nm .

However the blend monolayer can be easily transferred onto the substrate and the mean transfer ratio is ~ 0.95 . The PCBET and AA are not miscible at the molecular level. They formed a microstructure with domains, which was proved by the AFM images shown in Figure 2. Figure 3 shows the PL intensity of PCBET mixed with AA at different mixing ratios and the effect of both aggregates and excimers of PL of the emissive polymer. The PL intensity of curve 2 (1:2.5 ratio of PCBET/AA) is stronger than that of curve 3 (1:0 ratio). The intensity of curve 1 (1:4 ratio) is much stronger than that of pure PCBET (curve 3). The intensity of curve 5 (1:5 ratio) becomes smaller. Clearly the well mixed system can enhance the fluorescence intensity even though the concentration of PCBET becomes low compared to the pure PCBET. The emission intensity increases initially, then reaches the maximum as the PCBET has an optimum-mixing ratio, and finally decreases again. The PCBET excimers, which appeared in the PCBET LB films at ~ 680 nm region^[2], were formed in the 18 layer pure PCBET and blend LB films. The peaks at 600 nm and 680 nm are attributed to molecule aggregates and excimers, respectively.

Acknowledgments

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