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Preparation and Characterization of DBSA Doped Polyaniline Thin Films

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Stable monolayer of the polyaniline(PAn) doped with dodecyl benzenesulfonic acid(DBSA) can form on the pure water surface. The multilayer ultrathin film can be successfully deposited by Langmuir-Blodgett(LB) technique onto CaF₂ substrate. The limiting mean molecular area and collapse pressure observed are 0.066 nm² and 35 mN m⁻¹, respectively. The multilayer LB film and casting film were all characterized by IR and UV-Vis-NIR spectroscopies.

Keywords: DBSA doped polyaniline; LB film; casting film; characterization

INTRODUCTION

Polyaniline(PAn), an important kind of conducting macromolecular material, is being attracted much attention on its preparation of ordered ultrathin film in recent years^[1-3]. But there are only a few papers presented about that of LB film till now, owing to its requirement of amphiphilicity and processibility of the material in preparation of LB film. In order to solve this question, dodecyl benzenesulfonic acid (DBSA) was used as the dopant to improve the film-forming of polyaniline. This doped polyaniline had good solubility in chloroform. In this paper, the preparation and characterization

results of dodecyl benzenesulfonic acid doped polyaniline(PAn-DBSA) LB film are presented. The characterization comparisons of the LB film with the casting film are also given.

EXPERIMENTAL SECTION

DBSA acid doped polyaniline(PAn-DBSA) was provided by Y. H. Geng. Chloroform of A.R. grade was used as the spreading solvent. Hydrophilically pretreated CaF_2 were used as the substrates. Surface pressure-mean molecular area isotherm determination and multilayer LB film deposition were carried out using KSV-5000 system at $20.5 \pm 0.1^\circ\text{C}$. The LB multilayer film was deposited as Y-type with 21 layers. The surface pressure and dipping speed were kept at 23 mN m^{-1} and 10 mm min^{-1} . IR and UV-Vis-NIR spectra were obtained from Bio-Rad FTS-135 and P-E Lambda 9 spectrophotometers.

RESULTS AND DISCUSSION

Surface pressure-area isotherm and multilayer film deposition

The titled polymer could form stable monolayer on the air-water interface. The limiting molecular area for each repeating unit is about 0.066 nm^2 , which is smaller than those of pure PAn(0.08 nm^2 ^[2], 0.20 nm^2 ^[3]) and substituted PAn($0.23\text{-}0.27 \text{ nm}^2$ ^[1]). Except that it is related to the processibility of the different solvents and different polymerization method of PAn, the folding of the PAn chains is also a probable reason. The collapse pressure of the monolayer is about 35 mN m^{-1} .

UV-Vis-NIR spectra

Figure 1. is the UV-Vis-NIR spectra of PAn-DBSA. There are a strong

absorption band at 444 nm and a small broad band at 860 nm in PAN-DBSA chloroform solution (Fig.1a). These are the characteristic bands of the doped polyaniline, assigned to the lattice absorption of the polaron^[4]. The absorption band at 325 nm is the π - π^* electron transition of the conjugate aromatic ring which is rather weak and flat. In the near infrared region, there is a continuously increasing "free-carrier tail" which indicates that the PAN chain is in the expanded state.

For the casting film (Fig.1b), we can see that the relative ratio of absorption intensity at 444 and 325 nm changed obviously. The band at 325 nm is the strongest absorption peak. And the carrier tail does not go up, indicating that the expanded extent of PAN chain is decreased. After the PAN chain was orderly oriented by LB technique (Fig.1c), the absorption band at 325 nm occurred a little red shift. The intensity of 445 nm absorption peak is further decreased. And the 860 nm band is not distinguished perfectly. However, a new broad and symmetric absorption band at ~620 nm occurred. It is considered to be the electron transition of quinoid unit^[5] which is the characteristic band of pure polyaniline. This suggests that some of the dopant DBSA molecules were ripped out of the PAN chains during the compressing process of PAN-DBSA monolayer. The absorbance after 1000 nm is declined, showing that the PAN chain in LB film is in the compact state.

IR spectra

Figure 2. is the IR spectra of the PAN-DBSA films. According to the assignment of PAN^[6], the bands in LB film(Fig.2b) at 1572, 1493, 1300, 1244, 1033 and 1007 cm^{-1} are the vibrations of $\nu_{\text{C-C}}$ (quinoid unit), $\nu_{\text{C=C}}$ (benzoid unit), $\nu_{\text{C-N}}$, $\nu_{\text{C-N}}$, $\delta_{\text{C-H}}$ and $\delta_{\text{C-H}}$ (in-plane), respectively. As comparison with the casting film(Fig.2a), the peaks in LB film are more sharp. This indicates that the PAN-DBSA molecules are oriented orderly in

LB film. The intensity and position of the absorption bands also changed obviously. Especially the characteristic peak of doped PAn at 1150 cm^{-1} in casting film shifts 25 cm^{-1} to lower frequency. It is considered to be derived from the more ordered structure in LB film. After this LB film was heated in 150°C for 1 hour, this band shifted to 1143 cm^{-1} (Fig.2c). This result suggests that the heating treatment destroyed the ordered packing of PAn-DBSA to some extent.

The new small peak at 1372 cm^{-1} occurred in LB film is the C-N stretching vibration in quinoid unit of PAn intrinsic state. This gives further evidence indicating that the doped PAn molecule occurred partially dedoped during the compressive process of PAn-DBSA monolayer. This result is coincidence with that of the UV-Vis-NIR spectra.

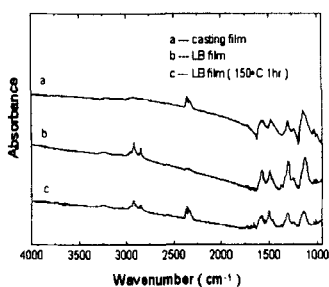
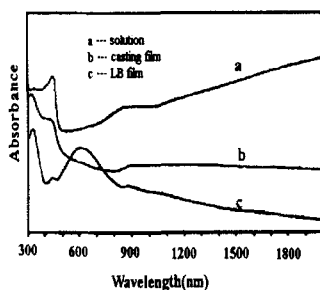


FIGURE 1 UV-Vis-NIR spectra FIGURE 2 IR spectra

References

- [1] M. Ando, Y. Watanabe, T. Iyoda, K. Honda and T. Shimidzu, *Thin Solid Films*, **179**, 225 (1989).
- [2] A. Dhanabalan, R. B. Dabke, N. Prasanth Kumar, S. S. Talwar, S. Major, R. Lal and A. Q. Contractor, *Langmuir*, **13**, 4395 (1997).
- [3] N. E. Agbor, M. C. Petty, A.P. Monkman and M. Harris, *Synth. Met.*, **55-57**, 3789 (1993).
- [4] Y. N. Xia, J. M. Wiesinger, and A. G. MacDiarmid, *Chem. Mater.*, **7**, 443 (1995).
- [5] Y. Furukawa, T. Hara, Y. Yyodo and I. Harada, *Synth. Met.*, **16**, 189 (1986).
- [6] J. S. Tang, X. B. Jing, B. C. Wang and F. S. Wang, *Synth. Met.*, **24**, 231 (1988).