

Preparation and Characterization of Poly-*N*-Vinyl Carbazole Langmuir-Blodgett Films

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Abstract

Langmuir monolayers of poly-*N*-vinyl carbazole (PNVK) were obtained by dispensing PNVK dissolved in tetrahydrofuran onto an air-water interface. Surface pressure-area isotherms of mixed monolayer of the PNVK were studied under different subphase conditions such as temperature and pH of the subphase. It was demonstrated that the monolayer of PNVK remained stable over a temperature range of 10–40°C. The area per molecule of the solid phase was found to be 31 Å². These monolayers were transferred onto indium-tin-oxide-coated glass plates and characterized by spectroscopic and electrochemical techniques.

Index Entries: LB films; conducting polymers; PNVK, cyclic voltammetry; FTIR.

Introduction

The Langmuir-Blodgett (LB) technique is an excellent method for fabricating ultrathin films that have highly ordered structure, controlled thickness, and uniform surface (1). The technique yields thickness of the films to be defined on a nanometer scale and gives rise to the possibility of a number of different molecules being incorporated onto the structure to determine its behavior under certain physical conditions. Recently, the LB technique has been used to prepare thin films of conducting polymers such as polyaniline (2), poly(*o*-anisidine) (3), and poly(3-alkylthiophene) (4). These films, based on conducting polymers, have been extensively investigated

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for various applications such as biosensors (5), chemical vapor sensors (6), and electronic devices (7). Ram et al. (8) have demonstrated that metal insulator semiconductor (MIS) devices can be fabricated by thermal evaporation of metals (Ag/Sn/Al/In) onto cadmium stearate (CdSt_2) LB films deposited on electrochemically prepared polypyrrole film. Further, it has been shown that the use of the low-temperature LB film deposition technique compared to the other method of MIS preparation results in improved junction parameters. Transfer behavior and the electrochemical characteristics of polyaniline LB films have also been studied (9). Zhu et al. (10) have described a technique for the formation of LB films of lipid-enzyme mixture by using a conventional constant-perimeter barrier trough. LB films of the regioregular poly (3-hexylthiophene) fabricated with the use of stearic acid as a surface-active molecule have been shown to possess higher electrical conductivities (11). The photocarrier mobility of the LB films of regioregular undoped poly(3-hexylthiophene)/stearic acid determined using time-of-flight technique was found to be significantly improved (12).

A number of conducting polymers have been chemically and electrochemically synthesized and characterized for various applications (13–15). Among these heterocyclic nitrogen compounds, poly-*N*-vinyl carbazole (PNVK) has been shown to display interesting electrical properties particularly for photoconduction (16). PNVK is the first known organic polymeric photoconductor. It is an insulator in the dark and becomes conductive on exposure to ultraviolet (UV) radiation. The photoconductive response can be readily extended into the visible and near-infrared region of the spectrum by incorporating sensitizing dyes or electron acceptors into the polymer. Monvernay et al. (17) have reported that the film (PNVK) grown by electrochemical technique is dependent on the nature of anion on the supporting electrolyte. Jiang et al. (18) fabricated an organic light-emitting diode with PNVK and 8-hydroxyquinoline (Alq_3). PNVK was shown to serve as a hole transport layer and Alq_3 as an emitting layer.

In the present article, we report the detailed studies on the preparation of Langmuir monolayers of PNVK. A systematic study on the temperature of the subphase/monolayer and the thickness was carried out. The actual degree of molecular order in the LB films of PNVK was accomplished using UV-visible (UV-VIS), Fourier transform infrared (FTIR), and cyclic voltammetry techniques, respectively.

Materials and Methods

PNVK, obtained from Polysciences (Germany), and tetrahydrofuran (analytical grade; Merck) were used directly without purification. Stearic acid was recrystallized from acetone three times. Deionized water was obtained from a Millipore (model RST-10) water purification system. Pressure-area isotherms of PNVK monolayer were recorded using a Joyce-Loebl (LB) trough (Model-4). Temperature of the subphase was controlled by

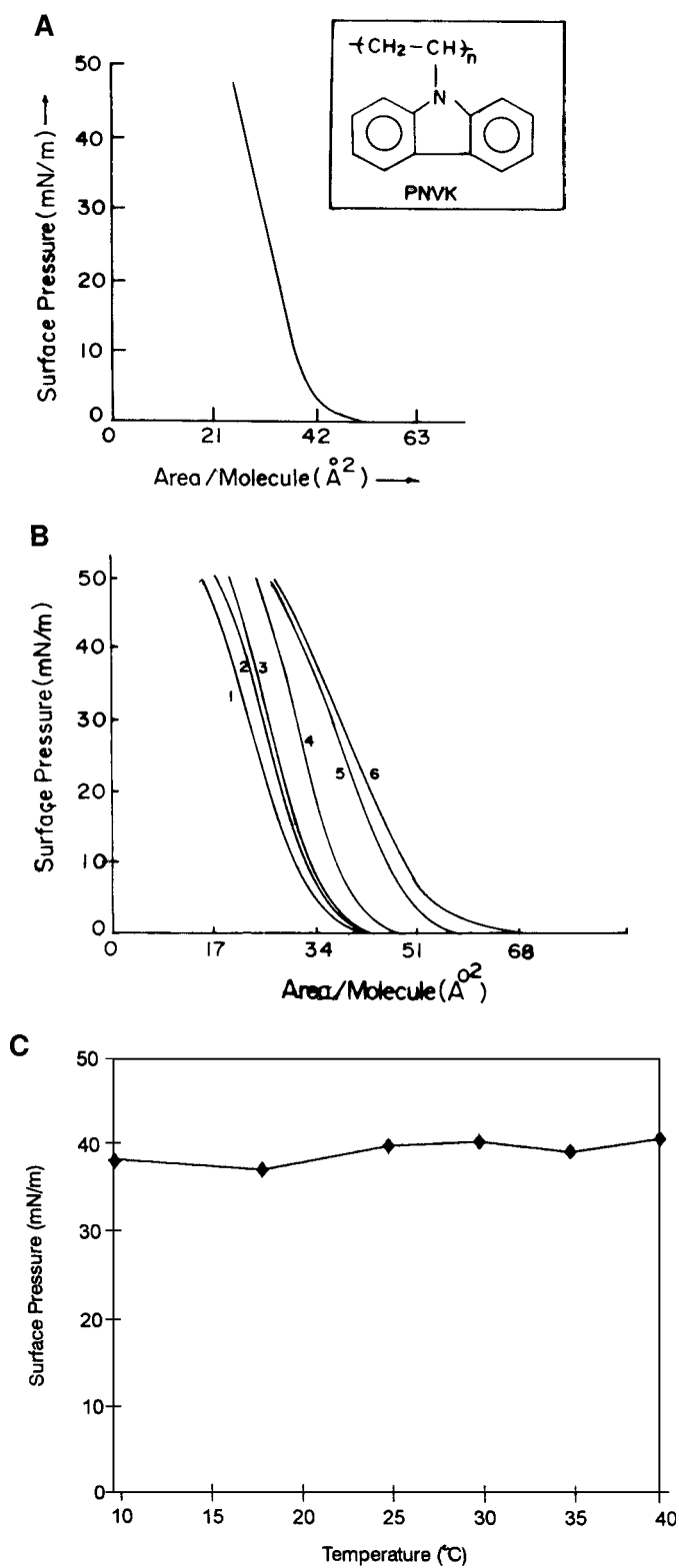
using a refrigerated regulator (Model E4870; Bio-Rad). A 5×10^{-3} mM solution of PNVK in tetrahydrofuran and 2 mM solution of stearic acid in tetrahydrofuran were mixed in a 1:1 ratio and sonicated for about 1 h. The resulting solution was filtered with a solvent-resistant filter (0.5 μ m) before use. This solution was spread uniformly on the water subphase using a μ L syringe. After complete evaporation of the solvent, the floating layer on the subphase was compressed at 40 mm/min, and pressure-area isotherms were recorded at 10, 15, 20, 28, 35, and 40°C. The Langmuir monolayers of PNVK were transferred onto an indium-tin-oxide (ITO)-coated glass plate at a surface pressure of 30 mN/m and 30°C. The speed of the dipping head was maintained at 3.5 mm/min.

Absorbance of the LB films was measured by using a UV-VIS spectrophotometer (Shimadzu 160A). FTIR spectra of PNVK LB films were recorded on an FTIR spectrophotometer (Nicolet 510P). Cyclic voltammetric experiments of PNVK LB films were conducted on an electrochemical interface (SI1286; Schlumberger). For cyclic voltammetry, the LB films of PNVK were placed in a solution of LiClO_4 (0.5 M) in acetonitrile and then subjected to repeated cyclic sweeps of potential.

Results and Discussion

Figure 1A shows the surface pressure-area (π -A) isotherm of PNVK at a surface temperature of 28°C and pH 5.6. The gas-liquid transition is clearly visible in this pressure-area isotherm. Gas-liquid phase transition occurs when area per molecule changes from 42 to 38 \AA^2 , and liquid-solid phase transition occurs when area per molecule changes from 38 to 31 \AA^2 . Figure 1B shows the variation in area per molecule as a function of temperature of the subphase. It can be seen that on increasing the temperature of a subphase, area per molecule increases. It is clear that the nature of the various pressure-area isotherms remains the same, indicating thermal stability of Langmuir monolayers of the PNVK on the surface of water. Figure 1C shows that the surface-pressure of liquid-solid phase transition increases on increasing subphase temperature. As the temperature increases from 10 to 40°C, surface pressure increases from 22 to 35 mN/m. These results are in agreement with the fact that on increasing the temperature, the intermolecular distance increases, resulting in increased film area. Thus, increased pressure is required to obtain the desired solid phase.

Transfer characteristics can be studied by using cumulative transfer parameter (CTP) as given by Dhanabalan et al. (9). It can be seen from Fig. 2 that there is a nonlinear dependence of CTP on the number of strokes. Up to 20 layers the slope is almost equal to 1; this result shows that the CTP is equal to the number of strokes, and after 20 layers there is variation in slope indicating Y-type deposition up to 20 layers followed by poor Z-type deposition above 20 layers. Figure 3 shows the FTIR spectra of LB films of PNVK obtained for 10 (curve 1), 20 (curve 2), 30 (curve 3), 35 (curve 4), and 40 (curve 5) monolayers. The peaks can be seen at 2200, 1950, 1550, 1450, 1250, 780, and



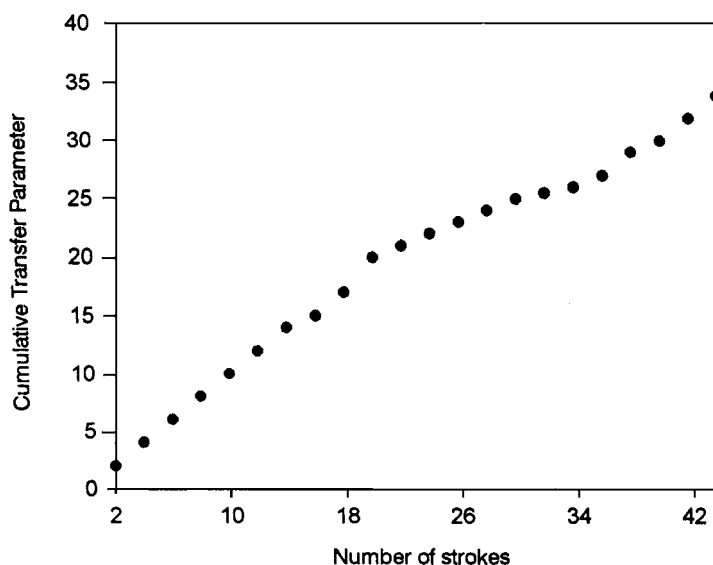


Fig. 2. Variation in cumulative transfer parameter vs number of strokes on ITO-coated glass substrate. Films were transferred at 25 mN/m, pH 5.6, and 30°C.

535 cm^{-1} , respectively. The peak at 1250 cm^{-1} is accompanied by a sharp shoulder at 1450 cm^{-1} corresponding to the C-N stretching mode, whereas another sharp peak at 1550 cm^{-1} is owing to the presence of aromatic C=C and C-C stretching modes. In addition, another broad signal at 2100–2200 cm^{-1} arises owing to the aliphatic C-C chain. Figure 4A shows the UV-VIS spectrum of freshly prepared PNVK LB films deposited onto ITO-coated glass plate as a function of monolayers. The LB films of PNVK show a sharp absorption peak at 346 nm. The peak seen at 346 nm is owing to the π - π^* transition (bonding to antibonding transition). The linear relationship obtained (Fig. 4B) between absorbance at 340 nm and the number of layers indicates a uniform layer-by-layer transfer of PNVK.

Cyclic voltammetry studies were carried out in acetonitrile by taking PNVK LB films cast onto ITO glass plates as working electrode, platinum plate as a counterelectrode, and standard calomel electrode as a reference electrode using 0.5 M LiClO_4 as an electrolyte. The electrode was subjected to a sweep potential between 1.25 and -0.6 V at different scan rates. Figure 5A shows the cyclic voltammogram of 10–40 monolayers of PNVK LB films obtained at a scan rate of 50 mV/s. It can be clearly seen that oxidation potential was shifted anodically with increasing number of monolayers. A plot of oxidation current vs number of monolayers of PNVK LB films

Fig. 1. (*opposite page*) (A) Pressure-area isotherm of monolayer of PNVK at 28°C when PNVK was dissolved in tetrahydrofuron; (B) variation in pressure-area isotherm of PNVK LB films as a function of temperature: 10°C (curve 1), 15°C (curve 2), 20°C (curve 3), 28°C (curve 4), 35°C (curve 5), and 40°C (curve 6). (C) Variation in surface pressure of solid phase condensation with temperature.

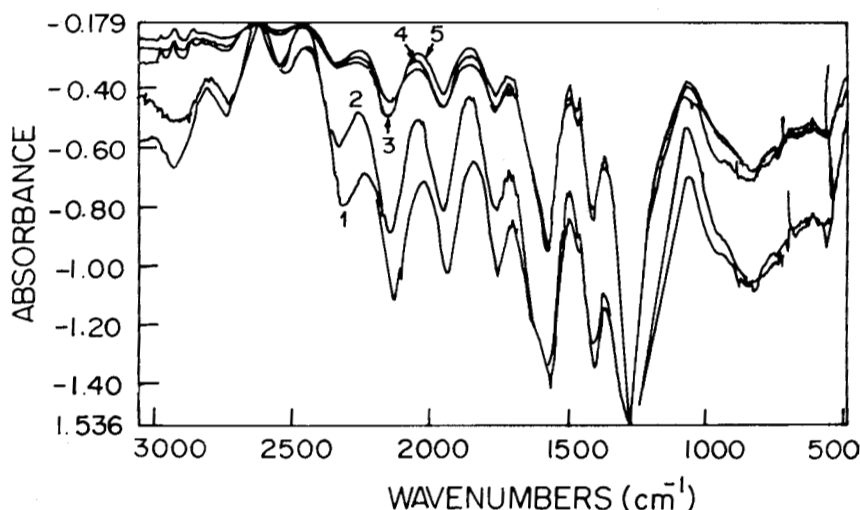


Fig. 3. FTIR spectra obtained as a function of the number of monolayers of PNVK LB films: curve 1, 10 monolayers; curve 2, 20 monolayers; curve 3, 30 monolayers; curve 4, 35 monolayers; curve 5, 40 monolayers.

(Fig. 5B) reveals that the oxidation current increased linearly with increasing number of monolayers. It is clear (Fig. 5C) that oxidation potential stabilized (0.78 V) after the deposition of 35 monolayers of PNVK LB films.

Conclusion

It has been shown that stable Langmuir monolayer of PNVK can be formed by dispensing PNVK dissolved in tetrahydrofuran at the air-water interface. It has also been demonstrated that the monolayers of PNVK are stable over a temperature range of 10–40°C. The area per molecule of solid phase was found to be 31 Å². Detailed experiments regarding application of PNVK LB films to biosensors are presently in progress at our laboratory.

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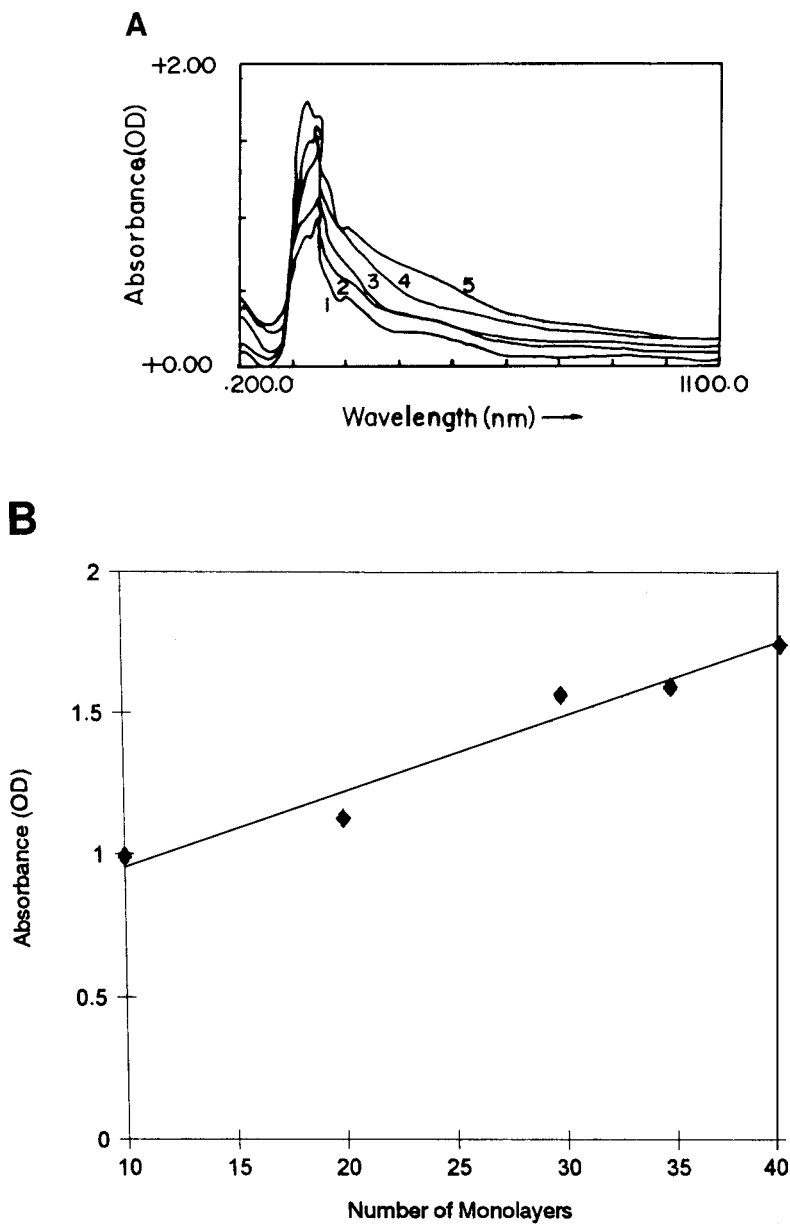


Fig. 4. **(A)** Variation in UV-VIS absorption of PNVK LB films as a function of number of monolayers; curve 1, 10 monolayers; curve 2, 20 monolayers; curve 3, 30 monolayers; curve 4, 35 monolayers; curve 5, 40 monolayers. **(B)** Absorbance as a function of number of monolayers of PNVK. OD, optical density.

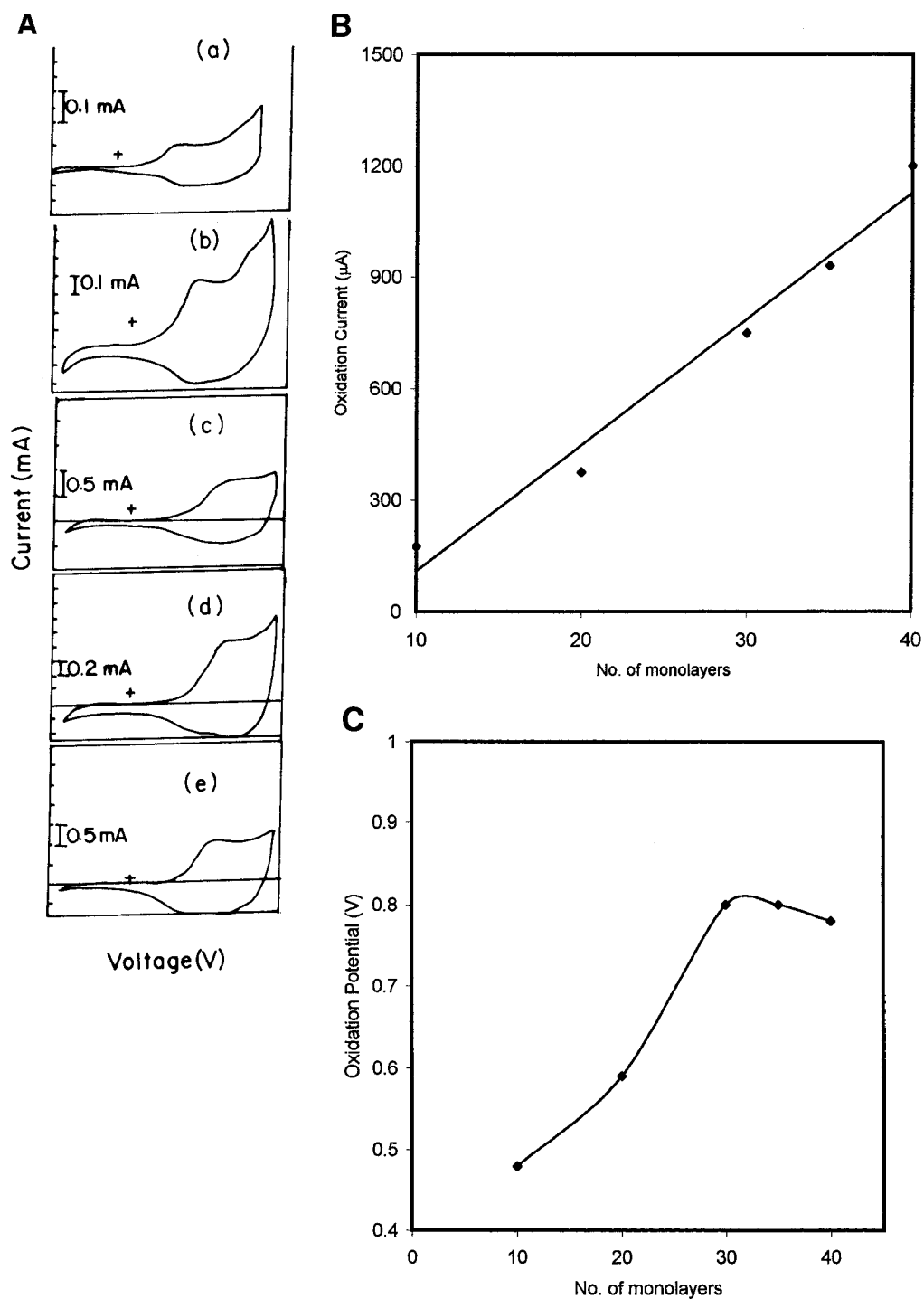


Fig. 5. **(A)** Cyclic voltammogram of PNVK LB films: (a) 10 monolayers, (b) 20 monolayers, (c) 30 monolayers, (d) 35 monolayers, (e) 40 monolayers; **(B)** variation in oxidation current with number of monolayers of PNVK LB films; **(C)** variation in oxidation potential with number of monolayers of PNVK LB films.

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