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ELECTROCHEMICAL POLYMERIZATION IN LANGMUIR-BLODGETT FILM OF NEW AMPHIPHILIC PYRROLE DERIVATIVES

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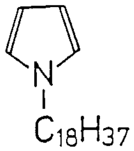
ABSTRACT Electrochemical polymerization in Langmuir-Blodgett multilayers of amphiphilic pyrrole derivatives resulted in anisotropic conducting thin films having alternate conducting and insulating layered structure.

As a promising electronic material, much attention has been recently directed to conducting polymers (1). Up to date, most of the polymers had amorphous structure with isotropic properties since no or little steric regulation of the polymerization was designed. Some anisotropic and specific properties would be gifted with the conducting polymers when the molecular arrangement in polymerization is fairly controlled (2). Our aim is to design a new type of conducting polypyrrole thin film by Langmuir-Blodgett technique, which is expected to have highly anisotropic conductivity due to a laminated structure of alternate conducting and insulating layers (3-5). The polymerization in a Langmuir-Blodgett film is also effective for stabilizing a monolayer (multilayer) (6). Here, we present a preliminary report on preparing anisotropic conducting polymer thin films by Langmuir-Blodgett technique and electropolymerization.

The amphiphilic pyrrole derivatives (7), 1, 2, and 3, were synthesized according to the following routes: 1 and 2 were obtained by N-alkylation of pyrrole and 4-methylpyrrole-3-carboxylic acid with stearylbromide, respectively. 3 was given by reaction of stearyl crotonate with toluenesulfonylmethyl isocyanide (8,9). All pyrrole monomers were electropolymerized in CH_3CN containing tetrabutylammonium perchlorate (TBAP) or $LiClO_4$ under potentiostatic condition (1.1-1.3 V vs SCE). The resulting polymers showed typical cyclic voltammograms characteristic of doping-undoping



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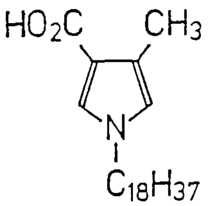

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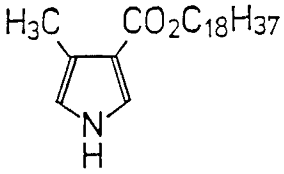

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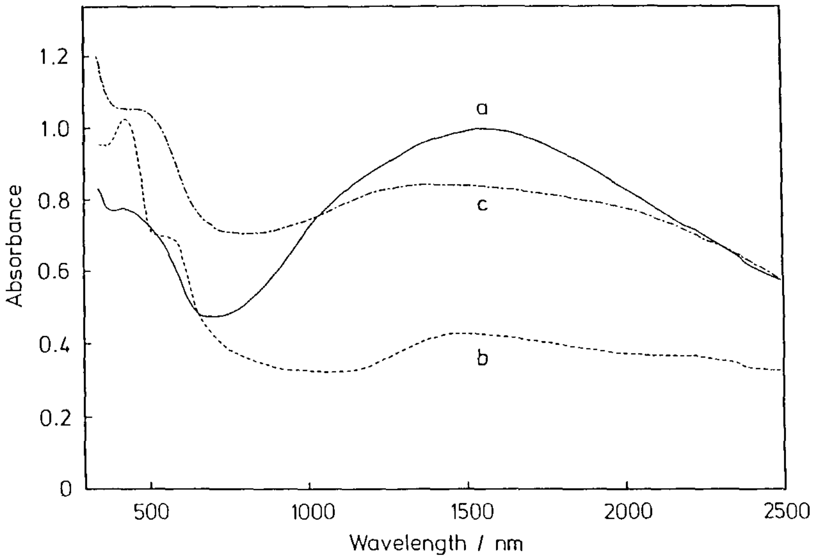

Fig. 1. Visible and near-IR absorption spectra of (a) (———) amorphous **poly-3** electropolymerized on an ITO electrode in 0.1 mol/l LiClO$_4$ CH$_3$CN containing 0.1 mol/l **1**, (b) (--------) the electro-reduced **poly-3** at 0.4 V v SCE in 0.1 mol/l LiClO$_4$ CH$_3$CN (the undoped **poly-3**), and (c) (—·—·—) the mixed **3**-**4** (2:1) multilayer (300 layers) on a silated ITO electrode after electro-oxidation in 0.1 mol/l LiClO$_4$ CH$_3$CN at >1.0 V vs. SCE.

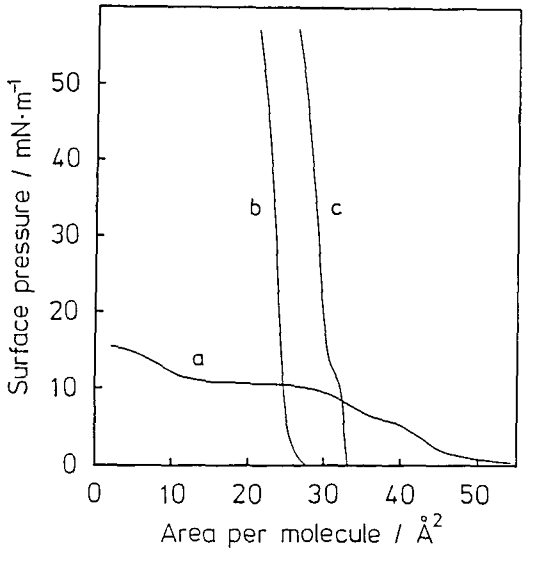

Fig. 2. Surface pressure-area isotherms for (a) the mixed **1**-**4** (1:1) monolayer, (b) the mixed **2**-**4** (2:1) monolayer, and (c) the mixed **3**-**4** (2:1) monolayer. (a) on 1N HCl subphase (pH 0.4) at 18 °C. (b),(c) on 1 mmol/l KH$_2$PO$_4$-Na$_2$PO$_4$ neutral subphase (pH 6.85-6.95) at 17 °C

process (10). The dc-conductivity of the polymers were 1.8x10^{-3} S/cm for **poly-1**, 1.5x10^{-3} S/cm for **poly-2**, and 2.0x10^{-2} S/cm for **poly-3**. The spectro-electrochemical measurement of the polymers on ITO electrodes showed reversible doping-undoping processes at 1000-1500 nm region, for example, as Fig. 1(a)(b) shows.

On neutral subphases, the monolayer of pure **1**, and the mixed monolayer of **1** and octadecane **4** were unstable and no increase of surface pressure could be detected. The stability of the mixed monolayer **1**-**4** was slightly improved by using acidic subphase (0.1-1.0 N HCl) so as to increase hydrophilicity of pyrrole moiety of **1** However, poor reproducibility in Π-A isotherm (Fig. 2(a)) and low maximum collapse pressure (<15 mN/m) were not satisfactory for successive deposition of the multilayer. On the other hand, the Π-A isotherms of the mixed monolayer of **2**-**4** (2:1), and that of **3**-**4** (2:1) were very stable and reproducible. Even on neutral subphase, distinct and sharp built-up points of surface pressure were observed and the maximum collapse pressure reached >50 mN/m (Fig. 2(b),(c)). These observations were due to stronger hydrophilicity at pyrrole moiety of **2** and **3** than the case of **1**. The different limiting areas in the Π-A isotherms of **2** and **3** would be explained by the different orienting angles between the hydrophilic pyrrole plane and the water/air interface. More than 300 layers of the mixed monolayer, **2**-**4** and **3**-**4**, could be deposited on a silated quartz plate or a silated ITO electrode (transfer ratio = 0.9-1.1) as Y-type films (pure water subphase, 30 mN/m, 20 °C).

The potentiostatic electrolysis (>1.0 V) of the mixed **3**-**4** (2:1) 200- or 300-layers on a silated ITO electrode in CH_3CN containing $LiClO_4$ resulted in considerable color change of the multilayer from semitransparent white to reddish brown. A broad absorption around 1500 nm, as Fig. 1(c) shows, was considered to be characteristic of an ordinary doped polypyrrole. Additionally, the ATR-IR absorption band at 780 cm^{-1}, assigned to C-H out-of-plane bending at 2 and 5 positions in a pyrrole ring, disappeared after electro-oxidation of the multilayer. These spectroscopic observations strongly suggested that the pyrrole moiety in the LB multilayer was electro-polymerized into polypyrrole structure. The X-ray diffraction (XRD) pattern (12) of the electro-oxidized **3**-**4** multilayer (200 layers) showed a sharp diffraction peak at $2\theta=6.07°$, which was almost similar to that before electro-oxidation ($2\theta=6.22°$). The multilayers before and after electropolymerization would have 56.7 Å and 58.1 Å of bilayer d spacing respectively, as was expected from their layered structures (11). No peaks in this region were observed for amorphous **poly-3** electropolymerized on an electrode. We hence speculated that most of the layered structure, alternate conducting polypyrrole and insulating long-alkyl-chain layers, would be preserved even after electropolymerization. Preliminarily, the electro-polymerized **3**-**4** LB film had much highly anisotropic dc-conductivity (12) by ca. 10 orders. ($\log \sigma_{\parallel}=-1$, $\log \sigma_{\perp} \leqq -11$) The present LB film will provide not only new conducting thin film for an electronic device but also a stabilizing material for a functional LB film. A detailed study on polymerization mechanisms and LB film structures is in progress.

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References and notes

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7. Theses monomers were identified by elementary analyses and ^{1}H-NMR spectra. **1**: $C_{22}H_{41}N$, C,0.82(calcd., 0.80);H,0.13(0.15);N,0.04(0.05);^{1}H-NMR δ($CDCl_3$), 0.87(3H,t),1.03-1.53(32H,m),3.82(2H,t),6.08(2H,t),6.57 (2H,t); **2**: $C_{24}H_{43}NO_2$, C,0.76(0.76);H,0.12(0.11);N,0.04(0.04); ^{1}H-NMR, δ ($CDCl_3$), 0.87(3H,t),1.03-1.66(32H,m),2.27(3H,s),4.16(2H,t),6.45(1H,br.), 7.29(1H,t),8.53(1H,br.s); **3**: $C_{24}H_{43}NO_2$, C,0.76(0.76);H,0.12(0.11);N,0.04 (0.04); ^{1}H-NMR, δ ($CDCl_3$), 0.86(3H,t),1.03-1.63(32H,m),2.27(3H,s),4.17 (2H,t),6.45(1H,br.s),7.30(1H,t)
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10. $E_{1/2}$=0.75 V vs SCE (**poly-1**), 1.08 V (**poly-2**), 1.11 V (**poly-3**).
11. Assuming that the observed peaks in XRD patterns were assigned to 4th-order reflection, the resulting lattice constants meant bilayer d spacing of Y-type LB film.
12. The dc-conductivity parallel to a multilayer ($\sigma_{/\!/}$) was measured by thrusting four pin-electrodes into a multilayer and the conventional van der Pauw method. The dc-conductivity in the perpendicular direction ($\sigma_{\perp}$) was measured by putting a LB film between two ITO electrodes (ca. 1 cm^2).

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