CHEMISTRY LETTERS, pp. 861-864, 1989.

Evaluation of Defects of Polyimide Langmuir-Blodgett Films by Electrochemical Method

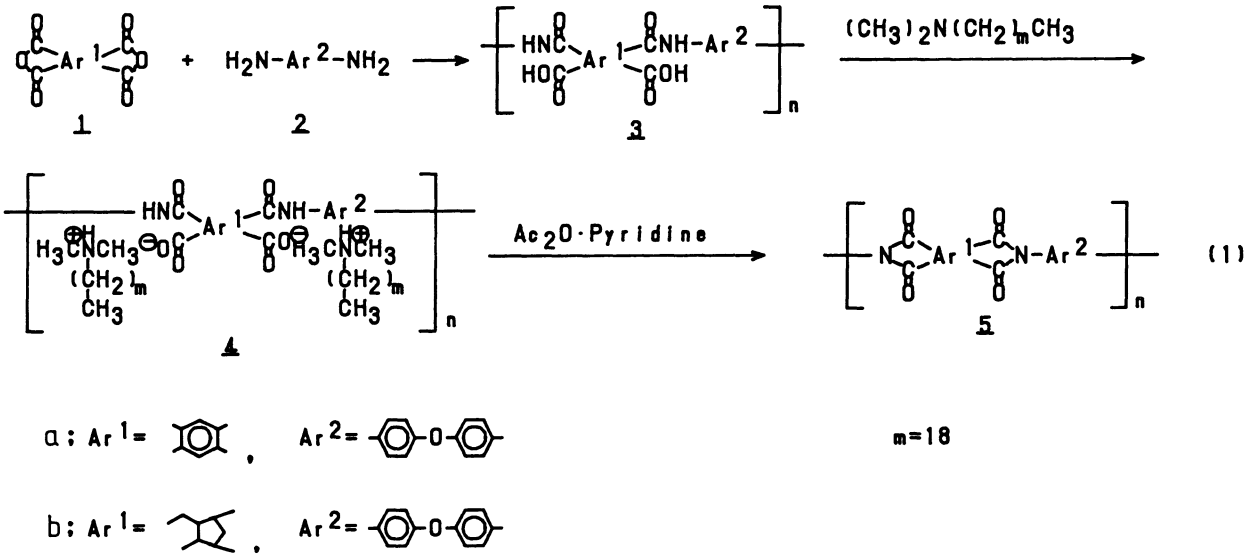
Yasunari NISHIKATA, Masa-aki KAKIMOTO,* Atsushi MORIKAWA, Ichiro KOBAYASHI, Yoshio IMAI, Yoshiki HIRATA,† Katsuhiko NISHIYAMA,† and Masamichi FUJIHIRA*†

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

†Department of Biomolecular Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

The defects of the polyimide LB films deposited on glassy carbon electrodes were examined by means of cyclic voltammetry of the redox couple of potassium ferri- and ferrocyanide in aqueous solution. The degree of defects of the polypyromellitimide LB films was apparently less than that of the cadmium arachidate LB film. The polyimide derived from aliphatic tetracarboxylic acid afforded the ten-layer LB films possessing no detectable defects.

We have reported the preparation of ultra-thin films of polyimides and poly(p-phenylene vinylene)s using Langmuir-Blodgett (LB) technique.[1-4] Because these condensation polymers were neither amphiphilic nor hardly soluble in organic



solvents, a new preparative method for LB films, "Precursor Method", was developed, in which the LB films of amphiphilic precursor polymers with long-alkyl chain were prepared first, and then, these precursor polymers was converted to the desired polymers on the substrate with removal of the long-alkyl chain. For instance, the polyimide LB films were prepared as follows (eq. 1): 1) the preparation of monolayer films of polyamic acid long-chain alkylamine salts 4 at air-water interface, 2) the deposition of the monolayer films onto appropriate substrates giving polyamic acid long-chain alkylamine salt LB films (precursor LB films), and 3) the chemical treatment of the deposited films with a mixture of acetic anhydride and pyridine to form polyimide LB films. The monolayer thickness of the polyimide LB films was about 0.4-0.6 nm due to the absence of alkyl spacer chains, which depends on their chemical structures.[5] Furthermore, the LB films had characteristics such as high thermal stability up to 200 °C, high chemical resistance, and excellent electrical properties.

The defects of LB films are one of the big problem especially in practical uses. Although some methods such as electron microscopy and metal decoration technique have been applied to detect the defects,[6] we adopted an electrochemical redox reaction which is carried out on the surface of the electrodes, and readily monitored by the cyclic voltammetry. The degree of defects of the LB films which cover the electrode surface should be readily evaluated, because the redox reaction proceeds only when the electrolyte ions come in contact with the electrode surface through the defects. This paper deals with the electrochemical evaluation of defects of the polyimide LB films by redox reaction in aqueous solution.

The monolayer films of polyamic acid alkylamine salts 4 were transferred on a glassy carbon disk electrode (3 mm diameter, 7.06 mm^2 surface area), which was inclined in 45 ° against the normal direction, using a SAN'ESU model FSD-20 LB equipment at a drawing rate of 10 mm/min for the upward trip and 100 mm/min for the downward trip at a

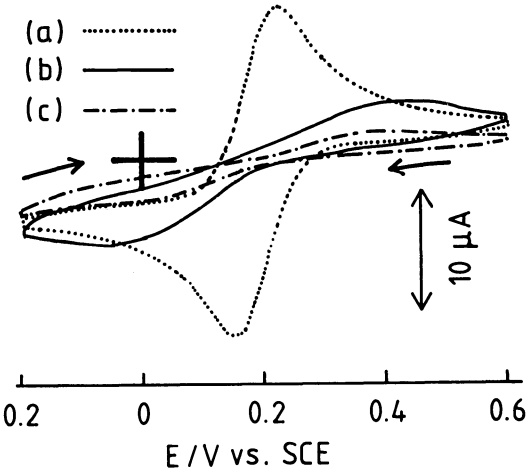


Fig. 1. Cyclic voltammogram of $K_4[Fe(CN)_6]$ aqueous solution. Electrodes, (a) Uncoated glassy carbon electrode (area 19.6 mm^2), (b) coated with cadmium arachidate LB film (3 layers, 7.5 nm thick), (c) coated with LB film of polyimide 5a (11 layers, 5 nm thick), were used. $K_4[Fe(CN)_6]$ (1 mM)- KCl (100 mM) aqueous solution was used as electrolyte. Scan rate was 100 mV/s.

surface pressure of 20 mN/m and < 5 mN/m, respectively. Under these conditions, the deposited films should have the Z type structure. The LB films of 4, thus obtained, were converted to the LB films of polyimides 5 by the treatment with the mixture of acetic anhydride and pyridine. On the other hand, the Y-type LB film of cadmium arachidate on the same electrode was prepared at a drawing rate of 10 mm/min at a surface pressure of 35 mN/m for both upward and downward trips. Electrochemical measurements were carried out under nitrogen atmosphere at 25 °C using a Nikko Keisoku NPGFZ-2501A potentiogalvanostat. A glassy carbon rod and a saturated calomel electrode were employed as the counter and the reference electrodes, respectively.

The redox reaction between potassium ferri- and ferrocyanide was employed for the present work. The dotted line in Fig. 1 shows the cyclic voltammogram of potassium ferrocyanide recorded using the uncoated electrode. The cyclic voltammograms recorded with the electrode coated with 3 layers of cadmium arachidate (7.5 nm thick) and 11 layers of polyimide 5a (5 nm thick) showed apparent decrease of the redox peak currents and increase of the redox peak-to-peak separation, which indicated that contact of the ferrocyanide ion with the surface of the electrode was restricted. In the electrodes deposited with two different types of LB films, the polyimide LB film had lower degree of the defects than the cadmium arachidate had. Such coating ability of the polyimide LB film may be caused by its amorphous nature.[7)]

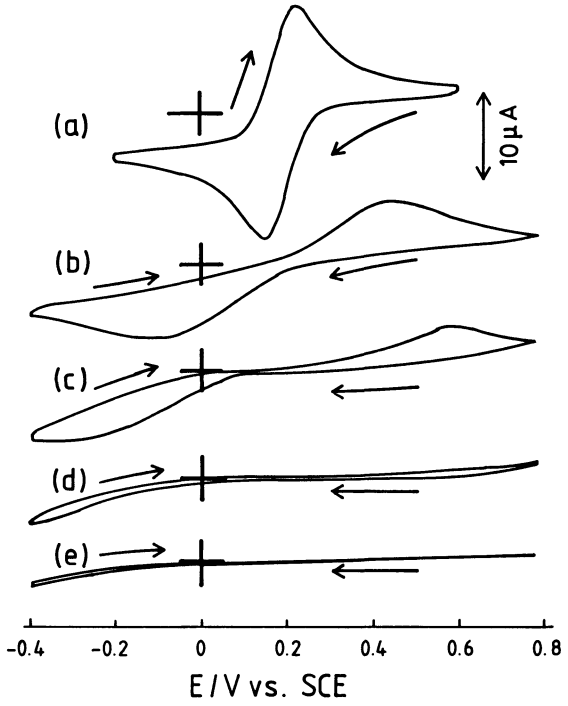


Fig. 2. Cyclic voltammogram of $K_4[Fe(CN)_6]$ aqueous solution. Electrodes, (a) Uncoated glassy carbon electrode (area 19.6 mm^2), (b-e) coated with polyimide LB film of 5b: (b) 1 layer, (c) 3 layers, (d) 6 layers, and (e) 10 layers, were used. $K_4[Fe(CN)_6]$ (1 mM)- KCl (100 mM) aqueous solution was used as electrolyte. Scan rate was 100 mV/s.

In the next stage, the same measurement was carried out with polyimide 5b, which consisted of aliphatic tetracarboxylic dianhydride. The cyclic voltammograms observed with changing the number of layers are shown in Fig. 2. A fair degree of defects was observed with the LB film of low number of layers, which may

be explained by the direct influence of the roughness of the electrode surface. Decreasing of the redox peak current and increasing of the peak-to-peak separation were observed with increasing the number of layers. The ten-layer LB film of 5b was found to be sufficient for covering the surface of the electrode with no detectable defects. The excellent coating ability may be attributed to the flexible aliphatic structure of tetracarboxylic acid unit.

Thus, the cyclic voltammetry is one of the convenient methods for the evaluation of defects of LB films. The results suggested that the polyimide LB films possessed low degree of defects compared with the LB films of fatty acids, and the degree was depended markedly on the chemical structure of the polyimides employed.

References

1) M. Suzuki, M. Kakimoto, T. Konishi, Y. Imai, M. Iwamoto, T. Hino, Chem. Lett., 1986, 395.
2) M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto, T. Hino, Chem. Lett., 1986, 823.
3) M. Kakimoto, M. Suzuki, Y. Imai, M. Iwamoto, T. Hino, "Polymers for High Technology, Electronics and Photonics", edited by M. J. Bowden and S. R. Turner, p. 484 ACS Symposium Series 346, American Chemical Society, Wachington, DC (1987).
4) Y. Nishikata, M. Kakimoto, and Y. Imai, J. Chem. Soc., Chem. Commun., 1988, 1040 (1988).
5) Y. Nishikata, T. Konishi, A. Morikawa, M. Kakimoto, and Y. Imai, Polym. J., 20, 269 (1988).
6) M. Vandevyver, Thin Solid Films, 159, 243 (1988).
7) S. Isoda, H. Shimada, M. Kochi, and H. Kambe, J. Polym. Sci., Phys. Ed., 19, 1293 (1981).

(Received February 9, 1989)