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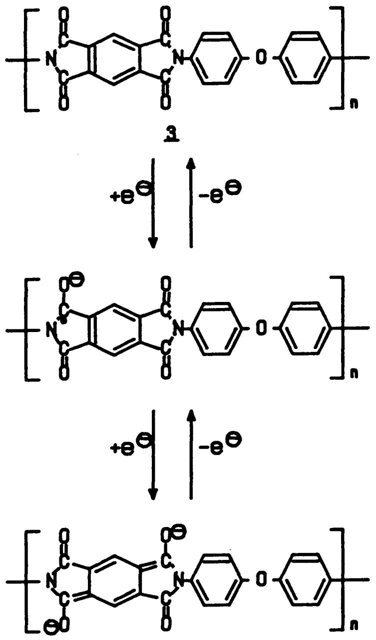
Electrochemical Behavior of Polyimide Langmuir-Blodgett Films

Yasunari NISHIKATA, Ichiro KOBAYASHI, Masa-aki KAKIMOTO,[*]
Yoshio IMAI, Yoshiki HIRATA,[†]
Katsuhiko NISHIYAMA,[†] and Masamichi FUJIHIRA[*†]
Department of Organic and Polymeric Materials,
Tokyo Institute of Technology, Meguro-ku, Tokyo
[†]Department of Biomolecular Engineering,
Tokyo Institute of Technology, Meguro-ku, Tokyo

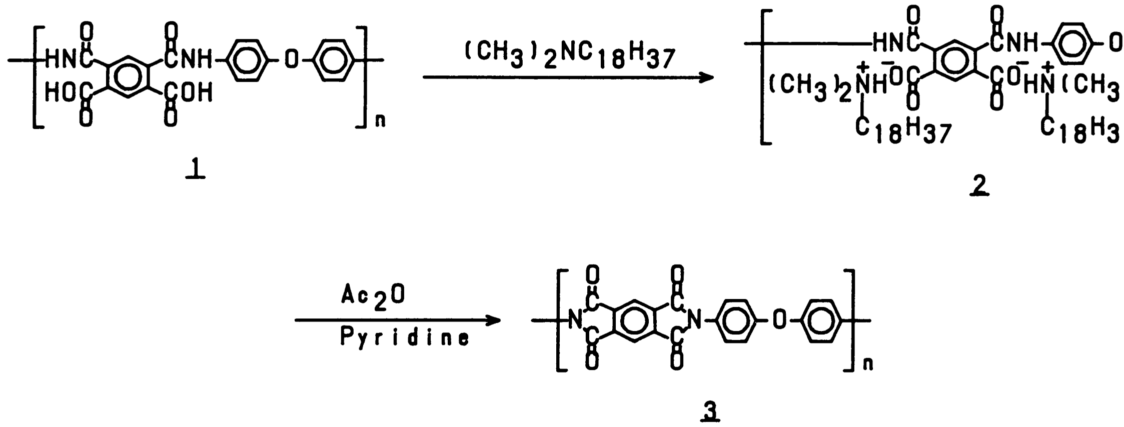
The redox reaction of the polyimide LB films themselves was examined by means of cyclic voltammetry. Both their cathodic and anodic current peaks decreased with potential cycling, and no peaks were observed after a few tens of sweeps, whereas the redox reaction was reversible in the case of polyimide cast films.

Recently, Mazur et al. reported that polyimide films (0.2 μm thick) coated on an electrode were electrochemically reduced by two distinct process, involving addition of one electron per each process to produce radical anions and dianions, respectively, as shown in Scheme 1.[1] The dianions were again oxidized to the neutral polyimides through reverse reaction. Furthermore, it was found that the cyclic voltammogram of the redox reaction was reversible in a number of repeated sweeps using the same polyimide sample. In this paper, we report an anomalous electrochemical behavior of the polyimide Langmuir-Blodgett (LB) films.[2-4]



Scheme 1.

The polyimide LB films were deposited on a glassy carbon electrode by the same procedure described in the literatures.[2-4] The monolayer film of polyamic acid alkylamine salt 2, which was prepared by mixing the solution of polyamic acid 1 and dimethyloctadecylamine at a concentration of 1 mmol/l in a 1:1 mixture of N,N-dimethylacetamide and benzene (eq. 1). Then, it was 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



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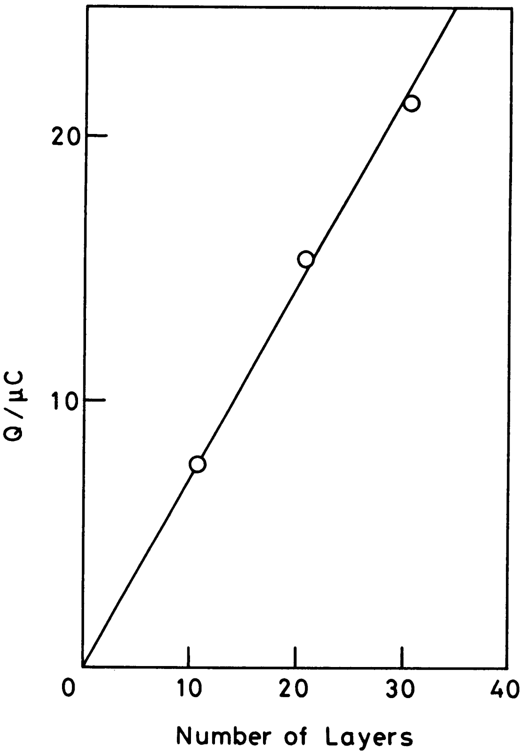

Fig. 1. Dependence of electric charge (Q) on number of layers of the LB film of polyimide 3 calculated from the first sweep of the cyclic voltammogram in acetonitrile saturated with KPF_6.

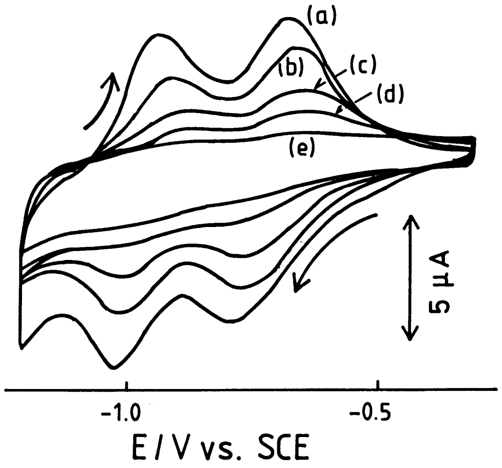

Fig. 2. Change in cyclic voltammogram of the LB film of polyimide 3 (11 layers) at a scanning rate of 300 mV/s in 0.1 M KCl aqueous solution with a number of scans; (a) 1, (b) 5, (c) 10, (d) 15, and (e) 20.

at a drawing rate of 10 mm/min for the upward trip and 100 mm/min for the downward trip at a surface pressure of 20 mN/m and < 5 mN/m, respectively. Under these conditions, the deposited film should have the Z type structure. The LB film of 2, thus obtained, was converted to the LB film of polyimide 3 by the treatment with a mixture of acetic anhydride and pyridine. Electrochemical measurements were carried out under nitrogen atmosphere at 25 °C using a Nikko Keisoku NPGFZ-2501A potentio-galvanostat. A glassy carbon rod and a saturated calomel electrode (SCE) were employed as the counter and the reference electrodes, respectively.

The first and the second redox potentials of voltammogram of polyimide 3 was observed at -0.83 and -1.28 vs. SCE in acetonitrile saturated with KPF_6, and -0.75 and -1.00 in 0.1 M KCl aqueous solution, respectively. The formers were the same values measured in the case of thick polyimide films.$^{1)}$

Figure 1 shows the dependence of electric charge (Q) on number of layers of the polyimide LB film calculated from the first sweep of the cyclic voltammogram in acetonitrile saturated with KPF_6. The high reaction efficiency was proved by the fact that a density of the molecules on the surface of the electrode calculated from Q (6.5 X 10^{11} repeat unit/mm^2) was in good agreement with the density calculated from the surface area-surface pressure isotherm (7.14 X 10^{11}) of the monolayer film of polyamic acid salt 2 prepared at air-water interface.$^{2)}$ The linear relationship in Fig. 1 indicated that most of the imide carbonyls participated in the redox reactions in spite of increasing the number of layers.

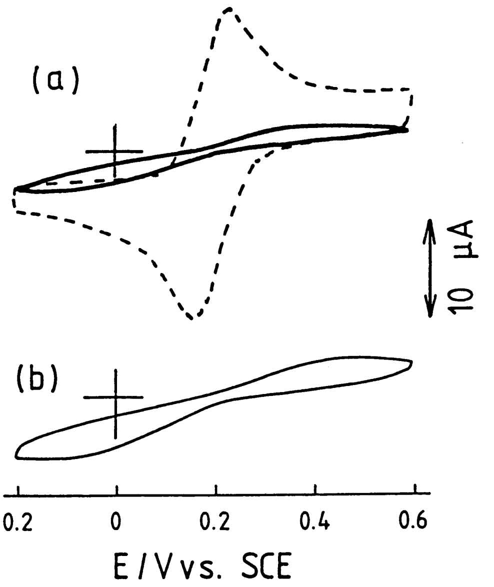

Fig. 3. Cyclic voltammograms of $K_4[Fe(CN)_6]$ aqueous solution (1 mM $K_4[Fe(CN)_6]$- 100 mM KCl). (a): Measured by the uncoated electrode (dotted line) and measured by the coated electrode with 11 layers of polyimide LB film before the electrochemical redox reaction of polyimide 3 itself (solid line). (b): Measured by the same polyimide coated electrode of (a) after the electrochemical redox reaction of polyimide 3 itself.

In the next stage, the cyclic voltammetry was carried out repeatedly to determine the reversibility of the redox reaction of polyimide LB film. Figure 2 shows the cyclic voltammograms of every five sweeps in 0.1 M KCl aqueous solution. It was interesting that both cathodic and anodic currents were decreased sweep by sweep, and finally, no redox peaks could be detected. Because it was feared that the polyimide LB film came off from the surface of the electrode in such a case, the cyclic voltammetry of potassium ferrocyanide was attempted to clarify the surface of the electrode.$^{5)}$ In the beginning, the cyclic voltammetry of potassium ferrocyanide was carried out using the electrode coated with the polyimide LB film (11 layers) sweeping the potential from -0.2 V to +0.6 V vs. SCE. As shown in Fig. 3a, the cyclic voltammogram recorded with the electrode coated with polyimide showed apparent decrease of the redox peak currents and increase of the redox peak to peak separation, compared with the cyclic voltammogram measured with the uncoated electrode, which indicated that contact of the ferrocyanide ion with the surface of the electrode was restricted. Next, the electrode was immersed in 0.1 M KCl aqueous solution, and recorded the multi-sweep cyclic voltammograms of the polyimide LB film itself until the current could not be detected by scanning the potential from -1.2 V to 0 V. The cyclic voltammogram (Fig. 3b) was recorded using the electrode after the cyclic voltammetry of the polyimide LB film. The fact that almost the same cyclic voltammogram was obtained before and after the cyclic voltammetry of polyimide itself suggested that the polyimide LB film did not come off from the surface of the electrode.

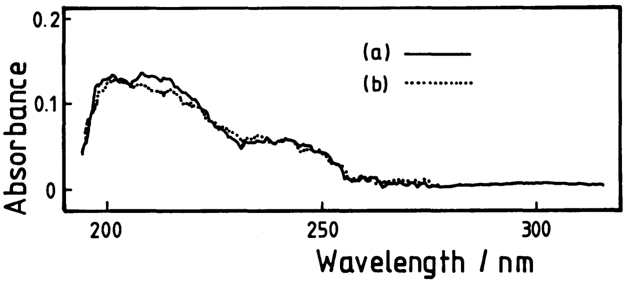

Fig. 4. Absorption spectra of polyimide LB film measured, (a) before, and (b) after the electrochemical redox reaction of polyimide 3 itself.

To get further evidence of existence of the LB film on the electrode surface, the electrode was changed from the glassy carbon to a quartz coated with a thin layer of gold metal. The absorption spectra before and after the cyclic voltammetry of the polyimide LB film (Fig. 4) indicated that not only the LB film was attached on the surface of the electrode but also the chemical structure remained unchanged through the redox reaction of the polyimide. It is necessary that the supporting electrolyte comes into the LB film to induce the redox reaction of polyimide. The decay of the currents in the cyclic voltammogram suggested that the permeation of the supporting electrolyte into the LB film was gradually blocked during the reaction, and the blocking of the permeation remained unchanged by standing the electrode at room temperature for one week.

Thus, the electrochemical redox peaks of polyimide decayed after several tens of potential sweeps, although the high efficient redox reaction was observed in the first sweep of the potential. In other words, the polyimide LB films which blocked the ion permeation were readily obtained by the simple electrochemical redox treatment. This may be ascribed to a unique annealing phenomenon caused by the electrochemical redox reaction.

References

1) S Mazur, P. S. Lugg, and C. Tarnitzky, J. Electrochem. Soc., 134, 346 (1987).
2) M. Suzuki, M. Kakimoto, T. Konishi, Y. Imai, M. Iwamoto, and T. Hino, Chem. Lett., 1986, 395.
3) M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto, and T. Hino, Chem. Lett., 1986, 823.
4) M. Kakimoto, M. Suzuki, Y. Imai, M. Iwamoto, and T. Hino, "Polymers for High Technology, Electronics and Photonics," ed by M. J. Bowden and S. R. Turner, ACS Symposium Series 346, American Chemical Society, Wachington, DC (1987), p. 484.
5) Y. Nishikata, M. Kakimoto, A. Morikawa, I. Kobayashi, Y. Imai, Y. Hirata, K. Nishiyama, and M. Fujihira, Chem Lett., 1989, 000.

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