SHORT COMMUNICATIONS

Effect of 6-Dioctylamino-1,3,5-triazine-2,4-dithiol Concentration on the Polymer Plating on Iron Plates

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The formation of polymer thin films on metal surfaces has attracted considerable interest as a nano-scale technology with potential industrial applications as well as for functional surface control. Nano-scale organic thin films of polymer/metal assemblies have become of interest in a range of potential applications, including decorative electrodes,[1] corrosion protection,[2,3] microelectronics,[4,5] releasing properties[6] and molecular adhesion promoters.[7,8] Some applications require the formation of nano-scale polymer films which are highly aligned and closely packed on metal surfaces.[2–6]

The authors have developed effective surface finishing technology that improves various surface characteristics through polymer plating of 6-substituted-1,3,5-triazine-2,4-dithiols (triazine dithiols).[9–13] Polymer plating is a method for coating metal surfaces and results in triazine disulfide polymers by electrochemical processing of triazine dithiols on anode surfaces.[14,15] However, in the polymer plating, it is difficult yet to obtain polymer films on which morphology is sufficiently controlled. The formation of highly aligned and closely packed polymer films on metal surfaces should be investigated to control the morphological structure of polymer films.

The purpose in this paper is to control the morphological structure of polymer films by investigating the effect of the concentration of 6-dioctylamino-1,3,5-triazine-2,4-dithiol mono sodium (DON) on the polymer film weight, current density, current efficiency and molecular weight in the polymer plating of DON in $0.1 \, mol/dm^3$–Na_2CO_3 aqueous solution on iron plates.

EXPERIMENTAL

Materials and Reagents

Iron test samples $(0.2 \times 30 \times 60 \, mm)$ were cut from a commercial ingot purchased from Nilako Corporation. The samples were sanded with emery paper (#3000, $5 \, \mu m$) and then finished with polishing paste (particle, $2 \, \mu m$). The average surface roughness after processing was in the range of 0.1–$0.2 \, \mu m$. The iron test plates were degreased by ultrasonic cleaning in acetone and dried with a hot-air drier, before testing.

DON was prepared by the reaction of 1,3,5-triazine-2,4,6-trichloride with dioctylamine and NaSH, according to the method described in a previous paper.[16]

Polymer Plating

The electrochemical polymerization of DON, also referred to as called polymer plating was performed using an electrochemical measurement apparatus (Hokuto Denkou Co. Ltd. HD-3000) as described previously.[14,15] The electrolytic cell was equipped with a working electrode (Iron plates), counter electrode (Pt plate $0.2 \times 30 \times 60 \, mm$) and reference electrode (saturated calomel electrode, SCE) and filled with an electrolytic solution containing DON and $0.1 \, mol/dm^3$–Na_2CO_3 in water. Polymer plating was conducted without agitation.

Measurement

Polymer film weight was determined by measuring the difference in plate weight before and after polymer plating, using a Mettler AT250 electronic scale (measurement accuracy: $\pm 0.005 \, mg$). The thickness of the polymer films was determined using a JASCO M-150 ellipsometer (Jasco, Tokyo, Japan). Current

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efficiency (CE) was calculated from following equation:

$$\text{CE}/\% = \text{Wp}/\text{Wt}, \quad \text{Wt}: F \times i \times t/26.8$$

where Wp is a found polymer weight deposited on iron plates and Wt is a theoretical polymer weight calculated from the gram equivalent (F) of 6-dioctyl-amino-1,3,5-triazine-2,4-dithiol (DO), i is a current density and t is plating time. Molecular weights were determined by gel permeation chromatography (GPC, Shimadzu GPC SWRH8 2A) using THF sample solutions prepared by immersing the polymer-plated iron plates in THF for 5 min at 30 °C and Showadex GPC columns (KF-802.5, 804, and 805: exclusion limited molecular weight, 10×10^5). FT-IR spectra were measured using a Nippon Denshi FT-IR, IR-5500 (Nippon Denshi Co. Ltd.), by high-performance reflection absorption spectroscopy (IR-RAS). Small-angle X-ray diffraction pattern was recorded on a Rigaku Denki instrument (SLK-2000). The X-ray radiation source (Cu Kα, $\lambda = 0.154$ nm) was operated at 50 kV and 300 mA.

RESULTS AND DISCUSSION

In the electrochemical polymerization, the morphological structure of polymer films formed on metal electrodes may be influenced by the formation process of polymer films and the properties of monomers. It is considered that the film formation process depends on the concentration of a monomer (here, DON) and current density. In a previous paper,[15] we described that the film weight increases with a low formation rate up to a 0.001 mmol/dm^3 of DON concentration but with very high formation rate over this concentration, when the polymer plating is conducted with an 0.2 A/m^2 of current density. Difference in the formation rate of polymer films due to the DON concentration suggests that in rate determining step in the polymer plating.

To confirm the rate determining step due to difference in DON concentration, the relationship between film weight and plating time was investigated at various DON concentrations as shown in Figure 1. In low DON concentrations such as 0.1 and 0.3 mmol/dm^3, a polymer film weight increased in proportion to the square root of plating time according to a parabolic law. This indicates that rate-determining step for the formation of polymer films is on the diffusion process. It is considered that there are two diffusion process in the rate-determining step. One is the process that DO anions diffuse from outer Helmholtz plane to the inner Helmholtz plane in an electric double layer. Here, DO anions do not aggregate at all because the concentrations are low. Another is the process that active sites diffuse in the inner plane, which do not also aggregate
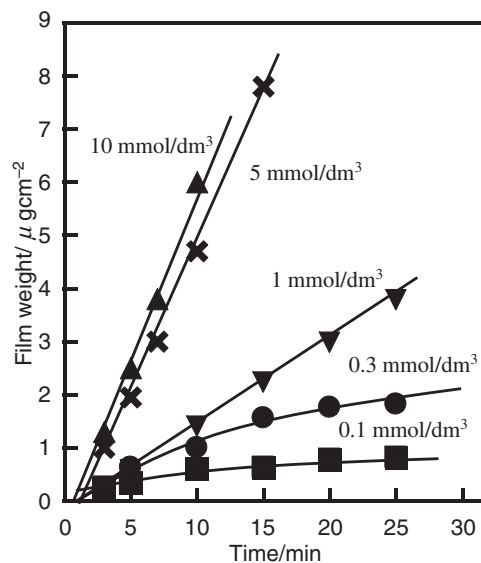
Figure 1. Effect of plating time and DON concentration on polymer film weight in the polymer plating of DON in 0.1 mol/dm^3–Na$_2$CO$_3$ aqueous solution at 40 °C. Current density: 0.1 A/m^2.

at all. Here, the active sites mean DO thiyl biradicales, which are formed by emitting an electron to anode when DO anions are reached in the inner Helmholtz plane. The DO thiyl biradicals are randomly situated far apart from each other in the low DON concentration. They polymerize consecutively diffusing and colliding each other on the two-dimensional plane (inner Helmholtz plane) to yield 6-dioctylamino-1,3,5-triazine-2,4-disulfide polymers. The formed disulfide polymers deposit on anode surfaces losing its solubility to produce polymer films which are disordered and packed with low density because the concentration of formed polymers is low and strong molecular force does not work between the polymer molecules. The triazine ring and octyl chains in polymer films lie down on the surfaces since the contact angles of polymer films are low.[15] As a result, it is considered that a polymerization rate is low and the polymer film is amorphous since it is aggregated irregularly and heterogeneously on the iron surface.
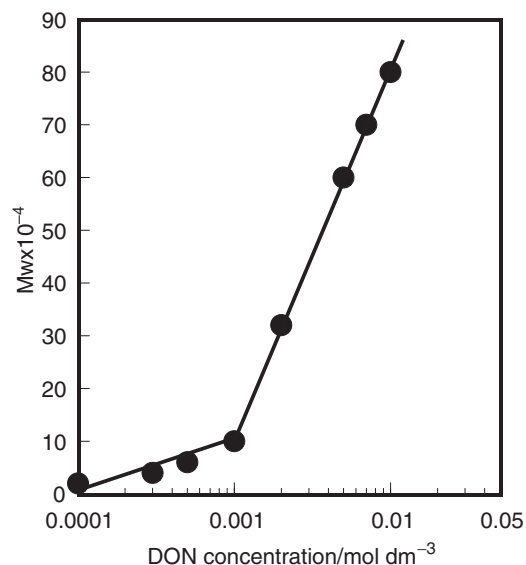
On the other hand, in high DON concentrations such as 1, 5 and 10 mmol/dm^3, polymer film weight increased in proportion to plating time according to a linear law. The application of linear law means that in high DON concentrations, DO anions were packed closely in both inner and outer Holmholtz planes. Closely packed DO anions do not diffuse in the inner Holmholtz plane forming a layer structure. The rate-determining step, therefore, is on the charge transfer process emitting electrons form DO anions to anodes. That is, in high DON concentrations, DO anions are arranged and ordered regularly with high concentration forming a layer structure of DO anions in the
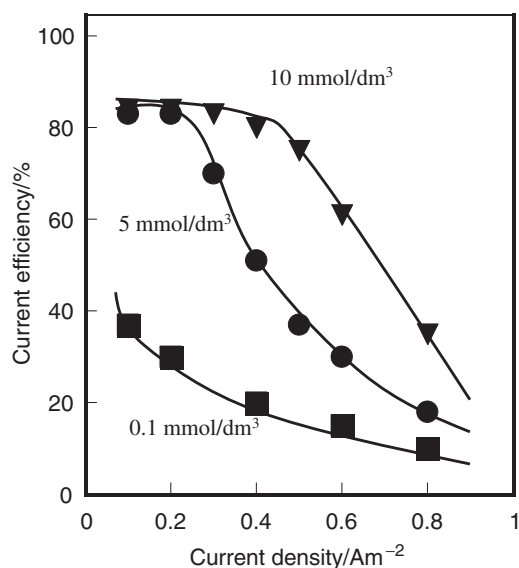
Figure 2. Effect of current density and DON concentration on current efficiency in the polymer plating in $0.1 \, mol/dm^{-3}$–Na_2CO_3 aqueous solution for 10 min at 40 °C.

Figure 3. Effect of DON concentration on the molecular weight of weight average (M_w) in the polymer plating in 0.1 mol/dm^3–Na_2CO_3 for 10 min at 40 °C.

inner Holmholtz plane to yield DO thiyl biradicals emitting electrons to anode. The closely packed and active DO thiyl biradicals on the two-dimensional plane are predicted to cause readily stepwise polymerization with very high formation rates to yield highly aligned and closely packed polymer films with high density because active sites are packed in close proximity to one another on the two-dimensional plane. The formed disulfide polymers are deposited on anode surfaces keeping the layer structure to produce polymer films which are ordered and packed with high density and then polymer films grow repeating the above process.

In order to confirm polymerization mechanism, relationship between current density and current efficiency is investigated as shown in Figure 2. A 100% of current efficiency means that a found quantity of electricity was used completely for the formation of polymer films. The current efficiency less than 100% indicates that side reactions occurred including the decomposition of water, the decomposition of disulfide polymers with hydrogen generated, and the oxidation of electrode. Current efficiency at low DON concentration ($0.1 \, mmol/dm^3$) was very low even at a 0.1 A/m^2 of current density and then decreased with current density. It is possible that in the low DON concentration, polymer films have a low molecular weight because disulfide polymers react readily with hydrogen generated by the side reaction. At high DON concentrations (5 and $10 \, mmol/dm^3$), current efficiency indicates a high value (about 83%) up to a certain current density (0.3 or 0.5 A/m^2) and then decreased. The reason that current efficiency stops at 83% is not al-

ways for side reactions. In the polymerization on the two-dimensional plane, current efficiency does not always reach 100% because monomers not to meet the growth end radicals of polymers are necessarily present on the same plane.[17] The decreases in current efficiency due to an increase in current density is also for the reason that excess quantity of electricity to monomers is used for the side reactions. The side reactions occur mainly in the process that monomers diffuse to the inner Holmholtz plane form the outer Holmholtz plane when the gram-equivalent of monomers situated in the inner Holmholtz plane for charge transfer is smaller than the quantity of electricity used. The proportion of the gram-equivalent of monomers to the quantity of electricity used is determined by monomer concentrations when current density is constant. Therefore, monomer concentrations have a great effect on current efficiency, influencing the formation rate of polymer films and its morphological structure. Figure 3 shows the relationship between weight-average molecular weight (M_w) and DON concentrations. In a low DON concentration less than $0.001 \, mmol/dm^3$, M_w increased with DON concentrations with a low level, but in a high DON concentration more than $0.001 \, mmol/dm^3$, with a high level. In the low DON concentration, M_w did not become high because polymers deposit on the surface before sufficient growth and disulfide polymer chains are readily reduced with hydrogen which is generated by the decomposition of water. At high DON concentrations, M_w increases markedly because active DO thiyl biradicals are closely packed in two-dimensional surface forming a layer structure and cause polymerization with very high

Table I. The formation conditions of polymer films and their properties

DON mmol/dm^3	Current Density A/m^2	Time nm	Film Thickness nm	Density g/cm^3	$M_w \times 10^{-4}$	Layer Spacing Distance nm
0.3	0.1	20	340	1.08	4.1	—
5	0.1	20	700	1.22	60	26.7

rate. The quantity of electricity applied is not used at all to cause the side reaction and mainly is used only to transfer charges.

Table I shows that difference in DON concentrations is reflected to the properties of polymer films. The polymer plating for 20 min at 40 °C with 0.3 mmol/dm^3-DON concentration and a 0.1 A/m^2 of current density provides a 340 nm of polymer films with a 1.08 g/cm^3 of specific density and a 6.2×10^4 of M_w. This condition leads to the step wise polymerization with very low rates. The polymer film does not show a peak on X-ray measurement and indicates a 2.4 of CH$_2$a/CH$_2$s ratio at FT-IR measurement, suggesting amorphous morphological structure. The polymer plating for 13 min at 40 °C with 5 mmol/dm^3-DON concentration and a 0.1 A/m^2 of current density provides a 700 nm of polymer films with 1.22 g/cm^3 of specific density and a 75×10^4 of M_w. This condition leads to step wise polymerization with very high rate. The polymer film showed a sharp peak at $2\theta = 3.30°$ (Half width: 0.19, Intensity: 220 cps) in X-ray measurement indicating a 26.7 nm of layer spacing distance[14] and indicated a 1.95 of CH$_2$a/CH$_2$s ratio at FT-IR measurement, suggesting highly ordered and closely packed morphological structure and a crystalline polymer film like a Y-type LB film.[14,15]

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