

Electrochemical Reaction in the Polymer Plating of Triazine Dithiols

Kunio MORI,[†] Tomokazu ASAKURA, and Yoshiyuki OISHI

Chemical Engineering, Faculty of Engineering, Iwate University, Ueda, Morioka 020–8551, Japan

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ABSTRACT: The polymer plating of 6-substituted groups-1,3,5-triazine-2,4-dithiol on metal electrodes in organic solvents was studied with respect to the effect of triazine dithiols, metal electrodes, and organic solvents on electrochemical reactions. Cyclic voltammograms of 6-dioctylamino-1,3,5-triazine-2,4-dithiol (DO) on Pt plate in an acetonitrile solution of tetrabutyl ammonium hexafluoro phosphate revealed three peaks due to oxidation and reduction. The substituted groups in triazine dithiols were found to have a large influence on the reaction in polymer plating as well as their dissociation constant and oxidation potential. The type of metal electrodes was also found to affect the reactions significantly, attributable to differences in oxidation potential. Solvents accelerated the formation of radical cations for DO and bithiyl radicals for DO monosodium salt. As an overall mechanism, it was determined that thin polymer film is formed by the coupling of radical cations formed by electrochemical reaction of DO.

KEY WORDS Triazine Dithiols / Polymer Plating / Cyclic Voltammogram / Metal Electrodes / Organo Solvents / Mechanism /

Nano-scale organic thin films of metal/polymer assemblies have attracted considerable interest from the standpoint of industrial applications in areas as diverse as decorative electrodes,¹ corrosion protection,^{2,3} microelectronics,^{4,5} molecular adhesion promoters,^{6,7} and to facilitate the release of metal molds.⁸ The present authors have proposed electrochemical polymerization of 6-substituted-1,3,5-triazine-2,4-dithiol monosodium salts as an effective technique for producing metal/polymer assemblies,^{9–12} a method referred to as “polymer plating”. Polymer plating in this way is analogous to conventional metal plating.

However, prior to the development of new applications and expanding the potential applications for polymer plating, it is necessary to further investigate the unknown factors involved in this new plating process. The purpose of the present study was to investigate the relationship between the electrochemical mechanism and basic factors in polymer plating with 6-substituted-1,3,5-triazine-2,4-dithiol. Factors such as the type of triazine dithiol, metal electrodes, and organic solvents employed were examined.

EXPERIMENTAL

Materials and Reagents

Metal plates such as zinc (standard electrode potential E_0 : -0.76 V), iron (E_0 : -0.45 V), nickel (E_0 : -0.26 V), copper (E_0 : 0.34 V), and silver (E_0 : 0.85 V) were purchased from Nilako Corporation. Solvents such as acetonitrile (donor number DN : 14.1, acceptor number AN : 19.3), benzonitrile (DN : 11.9, AN : 15.5),

hexamethyl phosphoric amide (DN : 38.8, AN : 10.6), propylene carbonate (DN : 15.1, AN : 18.3), dimethylsulfoxide (DN : 26.8, AN : 19.3), dimethylamide (DN : 26.6, AN : 16.0), pyridine (DN : 33.1, AN : 14.2), proparnol (AN : 28.1), and ethanol (AN : 37.1) were obtained from commercial sources and were of reagent grade. 6-Dioctylamino-1,3,5-triazine-2,4-dithiol (DO), DO monosodium salt (DON), 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB), 6-anilino-1,3,5-triazine-2,4-dithiol (AN), and 1,3,5-triazine-2,4,6-trithiol (TT) were supplied by Sankyo Kasei Ltd. Tetrabutyl ammonium hexafluoro phosphate (TBAHP) was used as the electrolyte.

Polymer Plating

The 6-substituted-1,3,5-triazine-2,4-dithiols were plated on metal plates^{9,10} using a potentiostat/galvanostat (HA-20, Hokuto Denko) with a linear scanner (HB-103, Hokuto Denko) and X-Y recorder (F-3DP, Riken Denshi) as described previously.^{9–12} The electrolytic cell contained a working electrode (steel plate: $0.2 \times 30 \times 60$ mm), counter electrode (Pt plate: $0.2 \times 30 \times 60$ mm), and reference electrode (saturated calomel electrode, SCE) connected with salt bridge (0.1 M $[\text{C}_4\text{H}_9]_4\text{NClO}_4$)¹³ and was filled with an electrolytic solution containing 6-substituted-1,3,5-triazine-2,4-dithiol and TBAHP in organic solvents. The metal plates (average roughness less than 0.02 μm) were polished to a mirror-like surface with diamond paste (0.2 μm). The weight of deposited polymer was determined from the difference in plate weight before and after polymer plating using a Mettler AT250

[†]To whom correspondence should be addressed (Tel: +81-19-621-6320, E-mail: kuni@iwate-u.ac.jp).

electronic scale (measurement accuracy: ± 0.005 mg). Cyclic voltammetry was performed using the same potentiostat/galvanostat, linear scanner and X-Y recorder.

Measurements

The average molecular weight (M_w) was determined by gel permeation chromatography (GPC; SWRH8 2A, Shimadzu) using tetrahydrofuran (THF) solutions prepared by immersing the treated iron plates in THF for 30 min at 30 °C using Showadex GPC columns (KF-802.5, 804, and 805; exclusion limited molecular weight, 5×10^5) An ultraviolet detector (254 nm) was used to detect organic compounds.

RESULTS AND DISCUSSION

Polymerization Potential

Information regarding oxidation-reduction potential is essential for investigating electrochemical reactions. Figure 1 shows cyclic voltammograms for DO on a Pt plate in an acetonitrile solution of TBAHP. In the first cycle, scanning from -1.0 to 1.3 V vs. SCE revealed a clear oxidation peak (peak 1) at 1.10 V vs. SCE, possibly corresponding to the oxidation potential of DO. The small current observed for iron plates in Na_2CO_3 aqueous solution⁹ at about 0 V vs. SCE was not observed in

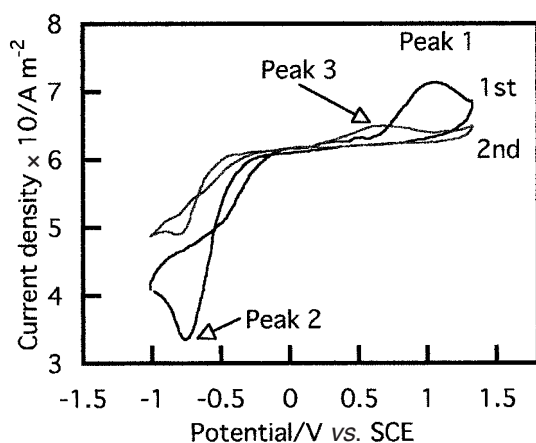


Figure 1. Cyclic voltammograms on Pt plate in the AN solution of TBAHP (0.05 mol dm^{-3}) and DO (1 mmol dm^{-3}) at 20 °C.

the present experiments, attributed to the electrochemical stability of the Pt electrode and organic solvents employed. A reduction peak (peak 2) was seen at -0.7 V vs. SCE when the potential was scanned from 1.3 to -1.0 V vs. SCE. In the second cycle, the oxidation peak (peak 3) weakened and shifted to 0.6 V vs. SCE.

A number of cyclic voltammogram was recorded (Table I) in order to elucidate the electrochemical reactions indicated by these peaks. Table I (1) shows a cyclic voltammogram for polymer-plated Pt plates processed in the acetonitrile solution of TBAHP without DO. The oxidation peak at 0.6 V vs. SCE and the reduction peak at -1.0 V vs. SCE are not present in this system, indicating that there is no current and hence that no oxidation or reduction occurs during the electrodeposition of triazine dithiol films on Pt plates. Therefore, the oxidation and reduction observed in Figure 1 are attributable to the presence of DO.

Table I (2) shows cyclic voltammograms for DO on Pt plates in an acetonitrile solution of TBAHP, scanned from 1.3 to -1.0 V vs. SCE. The -0.7 V vs. SCE reduction peak and 0.6 V vs. SCE oxidation peak were observed in this case, but the oxidation peak at 1.1 V vs. SCE (peak 1) was absent. The oxidation peak at 0.6 V vs. SCE is attributed to DO derivatives formed by the reduction at -0.7 V vs. SCE, as described below.

Table I (3) shows the cyclic voltammogram for DON on a Pt plate in an acetonitrile solution of TBAHP. In forward scanning, DON dissociates as an anion in the acetonitrile solution. An oxidation peak (peak 3) at 0.6 V vs. SCE is therefore assigned to the electrochemical oxidation of the anion of DON. This reaction was investigated in more detail by scanning DO on Pt plates from 1.3 to -0.5 V vs. SCE as shown in Table I (4). Only peak 1 was observed in both the first and second cycles, indicating that only the oxidation corresponding to peak 1 proceeds when no reduction occurs. That is, only the oxidation of DO occurs, forming radical cations.

The current density at peaks in cyclic voltammograms is proportional to the concentration gradients of electrolytes on an electrode surface and the electrolyte

Table I. Cyclic voltammograms in the electrolytic solutions

No.	Working Electrode	Scanning width /V vs. SCE	Electrolytic solution ^b	Scanning direction ^a	Peak potential / V vs. SCE	
					Oxidation	Reduction
(1)	DO polymer-plated Pt plate	$-1 \sim 1.3$	ACN solution of TBAHP	Anode	–	–
(2)	Pt plate	$-1 \sim 1.3$	ACN solution of TBAHP and DO	cathode	0.6	-0.7
(3)	Pt plate	$-1 \sim 1.3$	ACN solution of TBAHP and DON	Anode	0.6	–
(4)	Pt plate	$-0.5 \sim 1.3$	ACN solution of TBAHP and DO	Anode	1.12	–

^aScanned potential in defined direction from open circuit potential. ^bTBAHP: 0.05 mol dm^{-3} . DO: 1 mmol dm^{-3} .

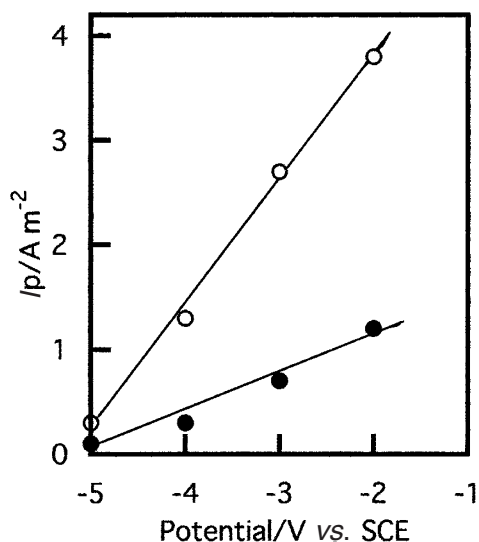


Figure 2. Relation between current density at peaks 1 and 3 and the concentration of DO in the cyclic voltammogram of DO on Pt plate in the ACN solution of TBAHP (0.05 mol dm^{-3}) and DO (1 mmol dm^{-3}) at 20°C , which is obtained by the scanning potential between -1.0 and 1.3 V vs. SCE in positive or negative directions. (○); peak 1, (●); peak 3.

concentration in solution.¹⁴ The relationship between the current density at peaks 1 and 3 and the concentration of DO for plating DO on a Pt plate in an acetonitrile solution of TBAHP is shown in Figure 2. The current densities at peaks 1 and 3 can be seen to increase proportionally with DO concentration, and the gradient at peak 1 is higher than that at peak 3. This is because oxidation at peak 1 is directly related to the DO concentration, whereas oxidation at peak 3 relates indirectly to the DO concentration. That is, the latter oxidation peak relates directly to the anion of DO, which is formed by the reduction of DO during scanning from 1.3 to -1.0 V vs. SCE . Figure 3 shows the effect of potential on film weight and the average molecular weight in the polymer plating of DO on Pt plate in the acetonitrile solution of TBAHP. The highest film formation rate and film molecular weight were achieved at a potential of 1.12 V vs. SCE . Therefore, the polymerization potential in the polymer plating of DO on Pt plates was confirmed to be 1.12 V vs. SCE .

Triazine Dithiols

Polymer plating of triazine dithiols is thought to proceed due to the facile generation of the radical cation of triazine dithiols (monomers), as shown above. Table II shows the relationship between the dissociation constant of triazine dithiols and the potential at peak 1 in the polymer plating of triazine dithiols on a Pt plate in an acetonitrile solution of TBAHP. The dissociation constant of triazine dithiols differs according to the substituted groups. Oxidation peaks are estimated to be

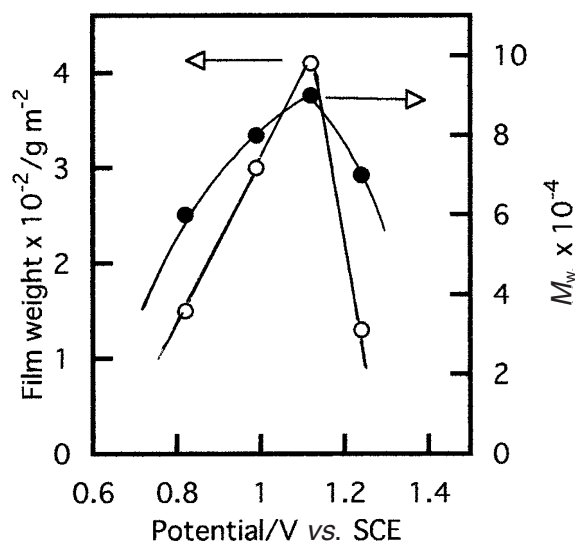


Figure 3. Effect of potential on film weight and the average weight of molecular weight (M_w) in the polymer plating on Pt plate in the AN solution of TBAHP (0.05 mol dm^{-3}) and DO (1 mmol dm^{-3}) for 10 min at 40°C . (○); Film weight, (●); M_w .

Table II. Relation between the pKa triazine dithiols and potential at peak 1 in the cyclic voltammogram of DO (1 mmol dm^{-3}) on Pt plate in the AN solution of TBAHP (0.05 mol dm^{-3}) at 20°C

	pKa	Ep/ V vs. Ag/AgCl
DB	4.1	1.01
DO	4.3	1.12
AN	5.5	1.86
TT	6.5	1.98

related to the dissociation constant of triazine dithiols in polymer plating. The ease of formation of radical cations in triazine dithiols is similar to the ease of dissociation of thiol groups. Therefore, in polymer plating of triazine dithiols, electropolymerization of DO is promoted by the formation of radical cations of triazine dithiols.

Metal Electrodes

The electrode material is known to influence the electrochemical reaction as a result of differences in delivery and acceptance of electrons. Figure 4 shows cyclic voltammogram of DO on various metal electrodes in the acetonitrile solution of TBAHP at 20°C . The oxidation peaks corresponding to the oxidation potential at peak 1 described above, were shifted to anode side in the order of silver, copper, nickel, and zinc in the polymer plating of DO in the acetonitrile solution of TBAHP, indicating an activation overpotential. The activation overpotential increased with the electron affinity of metals in the polymer plating of DO. Metal electrodes with high electron affinity including silver and copper facilitate the polymer plating of triazine dithiols, effectively increasing oxidation current at low po-

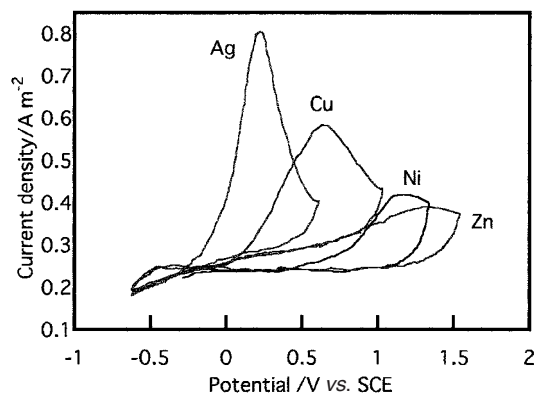


Figure 4. Cyclic voltammogram of DO (1 mmol dm^{-3}) on various metal electrodes in the acetonitrile solution of TBAHP (0.05 mol dm^{-3}) at 20°C .

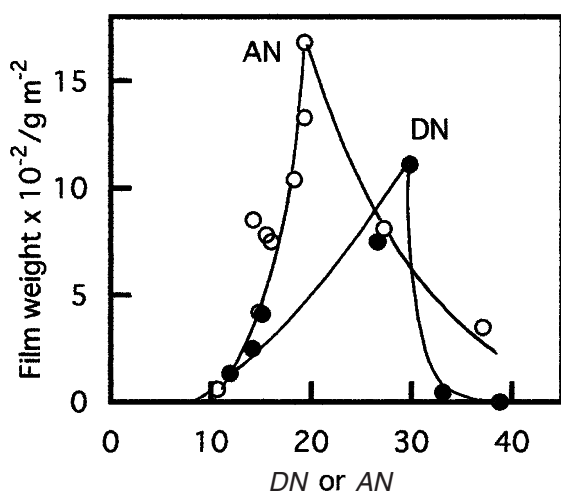


Figure 5. Relation between the donor number (DN) or the acceptance number of solvents (AN) and film weight in the polymer plating of DO or DON (1 mmol dm^{-3}) on Pt plate in the organic solution of TBAHP (0.05 mol dm^{-3}) for 20 min at 40°C . Potential: 1.2 V vs. SCE .

tential. Metals such as nickel and zinc, which have low electron affinity, prevent the production of DO radical cation, decreasing oxidation current at high potential. The above results indicate that in the polymer plating of DO in organic solvents, the effect of metal electrodes is the easy of charge transfer from DO to metal electrodes.

Solvents

The radical cations are considered to form as a reaction intermediate in the polymer plating of triazine dithiols, as described above. If this process of formation of radical cations is correct, the polymer plating of triazine dithiols will be influenced by the solvent employed. Figure 5 shows the relationship between the donor number or acceptor number of solvents and film weight for the polymer plating of DO or DON on Pt plate. No correlations between film weight and the acceptor number, dielectric constant, dipole moment, and polarizability of solvents were recognized. Film weight

has a tendency to increase markedly with the donor number of solvents up to 30, and then decrease rapidly with donor number over 30. Good correlations between both were recognized at donor numbers below 30, attributable to enhanced dissolution of radical cations of DO by the hydrogen cations in the solvent. This reconfirms that radical cations play a significant role in the polymer plating of DO. In solvents with donor numbers over 30, polymerization is markedly inhibited because the radical cations react easily with the solvent.

No correlations between film weight and donor number, dielectric constant, dipole moment, and polarizability of solvents were recognized in the polymer plating of DON on Pt plates. However, good correlations between film weight and acceptor number were recognized in solvents with donor numbers below 20, in this case due to facile dissolution of the DON anion. In solvents with donor numbers over 20, the polymer film weight was lower due to reaction of the thiyl radicals with the solvent.

Electrochemical Reaction

Based on the above results, the reactions at peaks 1, 2, and 3 are shown in Figure 6. The reaction at peak 1 occurs on the anode to afford DO polymer, and is considered to proceed as follows. DO provides two electrons to the anode (Pt plate) to produce the radical cations of DO (reaction 1). The radical cations then couple to afford a DO polymer (reaction 2). For peak 2, the reaction for which occurs on the cathode to yield the anion of DO, proceeds as given by reaction 3. That is, DO gains two electrons to become the DO anion. The reaction at peak 3 occurs on the anode in the presence of the DO anion to afford DO polymer (reactions 4 and 5). That is, the anion of DO transfer two electrons to the anode to generate the thiyl radicals of DO, which then couple to produce the DO polymer.

CONCLUSION

The polymer plating of 6-substituted-1,3,5-triazine-2,4-dithiols on metal electrodes in organic solvents was examined, and the relationships between the electrochemical mechanism and basic factors such as the type of triazine dithiol, metal electrode and organic solvent were established. Cyclic voltammograms of DO on Pt plate in an acetonitrile solution of TBAHP revealed three peaks, assigned to oxidation and reduction. Based on this analysis, it was suggested that polymer film is formed by coupling of radical cations. The substituted group in the triazine dithiols was found to have a significant effect on the polymer plating process due to differences in dissociation constant and oxidation po-

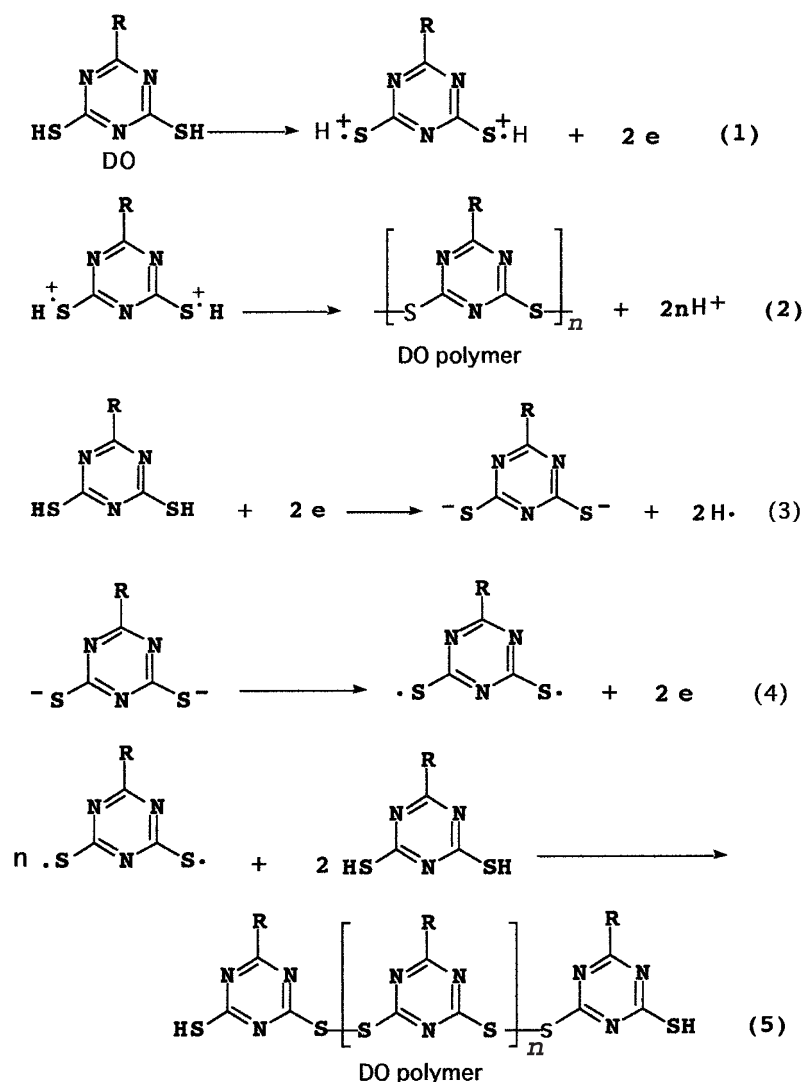


Figure 6. Reactions corresponding to peaks 1, 2, and 3 in the cyclic voltammograms of on Pt plates in the ACN solution of TBAHP and DO.

tential. The type of metals used for the electrode was also found to influence polymer plating significantly because deposition was promoted with an increase in the electron affinity of metal electrodes. The deposition rate was found to increase with solvent donor number up to 30 for DO and with increasing acceptor number up to 20 for DON, above which deposition was increasingly inhibited.

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