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Magnetic Field Effects on the Polymerization of 6-*N,N*-Dioctylamino-1,3,5-triazine-2, 4-dithiol

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ABSTRACT: *Electrochemical polymerization of monosodium salt (***1b***) of 6-N, N-dioctylamino-1,3,5-triazine-2,4-dithiol on stainless steels was investigated in zero (0T), perpendicular (5T⊥), and parallel (5T//) magnetic fields which are arranged perpendicular and parallel to the direction of electrolytic current. 5T⊥ magnetic field enhances the formation rate of poly(6-N, N-dioctylamino-1,3,5-triazine-2,4-disulfide)* **2** *films but suppresses the crystallinity of* **2***. However, 5T// magnetic field enhances the formation rate and the crystallinity.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:60–64, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20257

INTRODUCTION

Electrochemical polymerization of 6-substituted-1,3,5-triazine-2,4-dithiol is a very effective method for preparing nanoscale polymer film/metal assemblies on an industrial scale. In response to the growing demand for various functions for the nanopolymer films including reactivity, insulation, chemical resistance, thermal resistance, abrasion proof etc., electrochemical polymerization conditions that can control the morphological structure of the polymer films need to be developed.

The purpose of this study is to prepare a poly (6-*N, N*-dioctylamiono-1,3,5-triazine-2,4-disulfide) **2** film with high crystallinity on stainless steel by electrochemical polymerization of monosodium salt (**1b**) of 6-*N, N*-dioctylamiono-1,3,5-triazine-2,4-dithiol in magnetic fields.

RESULTS AND DISCUSSION

Compound **1a** was a tautomer consisting of thione and thiol types. The solid **1a** is generally present as a thione type but is present as a thiol type in alkali solution. The monosodium salt (**1b**) of **1a** is considered to have both thione and thiol groups from FT-IR spectrum data [1].

In the electrochemical polymerization [2–5] of **1b,1b** is present as a dithiolate anion **1c** in 0.1 mol/dm^3 Na_2CO_3 aqueous solution (pH 11.4). **1c** in the solution diffuses to an interfacial layer following voltage application and is arranged on an anode surface. By the voltage application of 0.75–0.9V vs. SCE, **1c** releases readily two electrons at the anode to yield a dithiyl radical **1d**. Then product **2** as polymer films will be obtained by stepwise polymerization of dithiyl radicals on the anode surface (Scheme 1). The polymer film grows readily up to the order of several micrometers, although it is an insulator and not doped. This is an important feature in the electrochemical polymerization of triazine dithiols. Other dithiol compounds such as propane dithiol and benzene dithiol are never permitted to grow polymers

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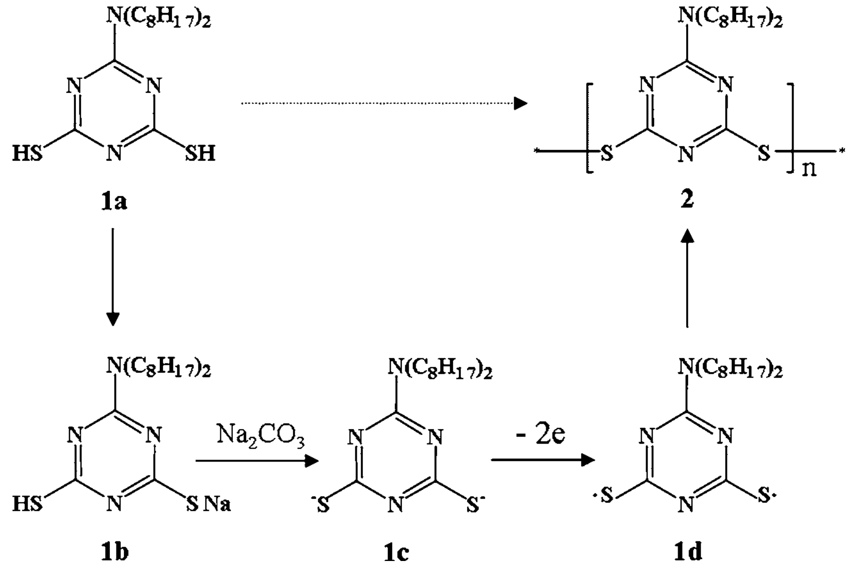


SCHEME 1 Reactions in the electrochemical polymerization of trizaine dithiols.

with high-molecular weight in electrochemical polymerization [6–8].

Figure 1 shows the effect of the magnetic field on the relationship between the polymer film weight and polymerization time for the electrochemical polymerization of **1b** (1 mmol/dm^3) on SUS304 plates at 20°C and 0.2 mA/cm^3. In zero (0T) magnetic field, the polymer film weight increased in proportion to the square root of the polymerization time according to a parabolic law [9]. The parabolic law relationship indicates that the rate-determining step is the diffusion process of the monomer. Diffusion control in the electrochemical polymerization is recognized under conditions such as low-monomer concentration (1 mmol/dm^3) of **1b**, low-temperature (20°C), and high-current density (0.2 mA/cm^2) [5]. In the present case, dithiyl radicals formed by the emission of electrons to the anode may cause stepwise polymerization with low-formation rates to yield amorphous polymer films which are disordered (I_{2927}/I_{2853} ratio: 2.2) and packed [9] with low density (density: 1.08 g/cm^3), low crystallinity (peak intensity at $2\theta = 3.30°$: 220 cps), and low-molecular weight (M_n, 4.2×10^4).

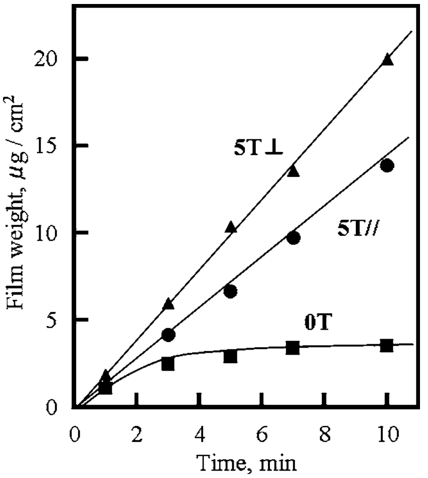


FIGURE 1 Effect of the magnetic field on the relationship between the polymer film weight and polymerization time for the electrochemical polymerization of **1b** (1 mmol/dm^3) on SUS304 plates at 20°C and 0.2 mA/cm^3.

In the 5T⊥ and 5T// magnetic fields, the polymer film weight increased in proportion to the polymerization time according to a linear law [9], though the electrochemical polymerization time was elongated. The linear relationship indicates that **1c** was carried and packed readily in the interfacial layer with high concentration due to the effect of the magnetic fields, which are generated as solution flows in the neighborhood of interfacial layer. **1c** is always present with high concentration in the neighborhood of interfacial layer forming a layered structure. The rate-determining step, therefore, is the charge transfer process emitting electrons from **1c** to the anode to yield **1d**.

The magnetic fields are considered to have an effect by changing the rate-determining step from the mass transfer process to the charge transfer process for the electrochemical polymerization of **1b** on the SUS304 plates. The mass transport effect in the 5T⊥ magnetic field, which means that the magnetic flux density is perpendicular to the direction of electrolytic current density, is greater than in the 5T// magnetic field, which means the magnetic flux density is parallel to the direction of the electrolytic current density. Aogaki et al. [10] reported that the perpendicular magnetic field causes a magnetohydrodynamic (MHD) effect for electrochemical reactions, induced by the Lorentz force. The Lorentz force is generated by the magnetic field perpendicular to the direction of the electrolytic current, and brings solution flows by convection to the electrode surface, which prompts mass transport markedly. Since the MHD effect strongly enhances mass transport by convection into the interfacial layer, the rate-determining step for the formation of polymer films in a perpendicular magnetic field becomes the charge transfer process obeying a linear law.

In general, the 5T// magnetic field does not result in an MHD effect for the electrochemical reactions because the magnetic flux density is parallel to the direction of the electrolytic current density and the Lorentz force is not generated. However, in the electrochemical polymerization of **1b**, the 5T// magnetic field enhanced the formation rate of the polymer films, as shown in Fig. 1. Aogaki et al. [11] report that the parallel magnetic field prompts local mass transport by the vortexes in the interfacial layer. This is called the micro-MHD effect. Therefore, it can be sufficiently explained that in the electrochemical polymerization of **1b**, the 5T// magnetic field increases polymer film weight with time obeying the linear law.

The difference in the magnetic fields suggests a change in the crystallinity of the polymer films deposited because polymer films increase with time obeying the linear law. Figure 2 shows the diffraction patterns of the polymer films, which were formed by polymerization time of 20 min, obtained by low angle X-ray diffraction measurements. For the electrochemical polymerization of **1b** in zero and 5T magnetic fields, a sharp peak can now be seen at near $2\theta = 3.30^\circ$ while the intensity of peaks is markedly different in each case. The differences in peak intensities indicate differences in the degree of crystallinity of the polymer films. In the polymer film crystals, the layer spacing distance between layer surfaces is approximately 2.7 nm which is the same as for Y-type LB films [3]. The 5T⊥ magnetic field yielded a lower peak intensity than the zero magnetic field. Thus, the 5T⊥ magnetic field suppresses the growth of triazine disulfide polymer crystals more than a zero magnetic field during the polymerization process. The 5T⊥ magnetic field markedly increases the formation rate but decreases crystallinity because it enhances the transport of **1c** in the solution by the MHD effect but causes disorder in the arrangement of **1c** in the neighborhood of interfacial layer by the MHD effect. In other words, as the arrangement is disordered by convection, the crystallinity of the polymer films decreases. In both zero and 5T⊥ magnetic fields, weak peaks at $2\theta = 3.30^\circ$ (2.67 nm) and $2\theta = 3.29^\circ$ (2.67 nm) in the X-ray measurements of the polymer films were observed (Scheme 2). These peaks suggest that the crystallinity of **2a** and **2b** is very low because both the triazine ring and octyl chains are oriented in the horizontal direction leaning slightly to the surface.

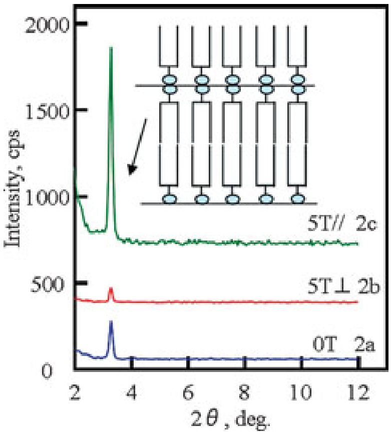
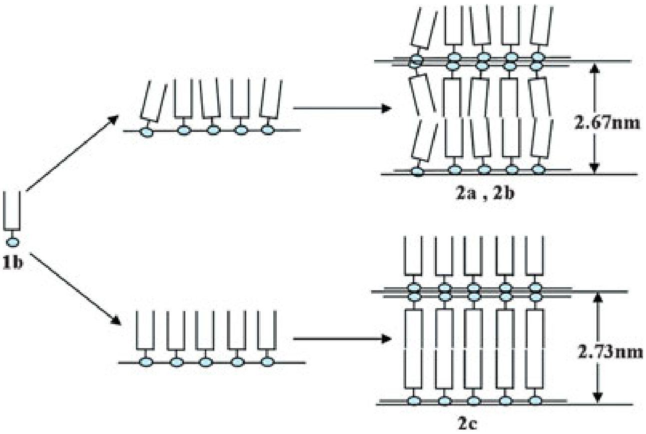


FIGURE 2 X-ray diffraction patterns for DO polymer films (**2a**, **2b**, **2c**) obtained in the electrochemical polymerization of DON (1 mmol/dm^3) for 20 min at 20°C in 0.1 mol/dm^3 Na_2CO_3 aqueous solution.

On the other hand, the 5T// magnetic field promotes the crystallinity of polymer films more than the zero and 5T⊥ magnetic fields in the polymerization process, because vortexes generated by the micro-MHD effect markedly enhance the arrangement (I_{2927}/I_{2853} ratio: 1.8) and packing (density: 1.15 g/cm^3) of **1c** in the interfacial layer. In the small-angle X-ray diffraction measurement of **2c** (Scheme 2) in the 5T// magnetic field, a peak at $2\theta = 3.23^\circ$ (distance between layer surfaces: 2.73 nm) was



SCHEME 2 Polymer assembly models for the electrochemical polymerization of triazine dithiols in the 0T, 5T⊥, and 5T// magnetic fields.

observed with very great peak intensity (1100 cps), suggesting that the crystallinity of **2c** on the plates is very high because both the triazine ring and octyl chains are at right angles to the horizontal direction. The 5T// magnetic field yields vortexes vertical to the electrode surface, and these vortexes result in the arrangement and packing of the triazine ring and octyl chains at right angles.

As described above, in the electrochemical polymerization of **1b**, the 5T⊥ magnetic field is very effective for enhancing the formation rate of the polymer films; however, it suppresses crystallinity of the polymer films. The 5T// magnetic field is very effective to enhance both the formation rate of the polymer films and the growth of the polymer film crystals.

EXPERIMENTAL

Cyanuric chloride, dioctylamine, NaSH, and ethanol were purchased commercially with reagent grades. Melting points were determined in a capillary apparatus. The weight of a polymer film was determined by measuring the difference in plate weight before and after the electrochemical polymerization using a Mettler AT250 electronic scale (measurement accuracy: ±0.005 mg). Infrared spectra were recorded on Jasco FT/IR 7300 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC 400 (400 MHz). Elemental analysis was run in a Perkin–Elmer model 2400 CNH analyzer. Molecular weight (M_n: number average) of polymers was determined by gel permeation chromatography with a Tosoh HLC-8220 GPC system on the basis of polystyrene calibration in tetrahydrofuran. Small-angle X-ray diffraction patterns were recorded using 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.

Synthesis of 6-N,N-Dioctylamiono-1,3,5-triazine-2,4-dithiol **1a**

Compound **1a** was prepared by the reaction of cyanuric chloride, dioctylamine, and NaSH as follows, according to the method described in a previous paper [12]. The stirring ethanol solution of cyanuric chloride (0.1 mol) was added dioctylamine (0.102 mol) at −5°C over period of 60 min. And then the reaction mixture was added dropwise methanol solution of NaOH (0.1 mol) over period of 60 min. After the solvent was removed under vacuum, the residue was extracted with ether to yield 6-*N, N*-dioctylamiono-1,3,5-triazine-2,4-dichloride. To the dimethylformamide solution (200 mL) of the dichloride, NaSH · 2H$_2$O aqueous solution (23 g, 2.6 mol in 50 mL H$_2$O) was added dropwise for 30 min at 40°C. The reaction mixture was poured into water and then neutralized with 1 wt% HCl aqueous solution to pH 4 to precipitate a white solid. The solid was recrystallized from ethanol–hexane to obtain a colorless crystallinity solid **1a** (31.1 g). Yield: 81%, mp 94–95°C MS *m/z(%)*: 385 (M$^+$ + 2), 383 (M$^+$, 100). ^{1}H NMR (CDCl$_3$) δ 0.86 (t, $J = 6.6$ Hz, 6H, C—CH$_3$), 1.19–1.32 (m, 20H, C—CH$_2$—C), 1.45–1.60 (m, 4H, C—CH$_2$—C), 3.51 (q, $J = 7.2$ Hz, 4H, N—CH$_2$—C). IR (KBr): 3161 (NH), 2957 (CH$_3$), 2924 (asymm. CH$_2$), 2854 (sym. CH$_2$), 1601 (—CSNH—), 1531 (C=N), 1497 (C=N), 1277 (C—N), 1178 (C—N), 1137 cm^{-1} (C=S). Anal. Calcd for C$_{19}$H$_{36}$N$_4$S$_2$: C, 59.33; H, 9.43; N, 14.57; S, 16.67%. Found: C, 59.41; H, 9.38; N, 14.60; S, 16.61%.

*Synthesis of Monosodium Salt (***1b***) of 6-N,N-Dioctylamiono-1,3,5-triazine-2,4-dithiol*

Compound **1a** (0.05 mol) and NaOH (0.052 mol) was dissolved in ethanol (100 mL) stirring in a beaker. After insoluble parts were filtered, the solvent was removed under vacuum to give a mixture of a white solid and ethanol. After the mixture was poured into ether (100 mL), the solid **1b** (19.5 g) was collected. Yield: 96%, d.p. >250°C MS *m/z* (%): 405 (M$^+$ + 4), 405 (M$^+$ + 2), 403 (M$^+$, 100). The IR spectrum of **1b** showed bands at 3110 (NH), 2957 (CH$_3$), 2930 (asymm. CH$_2$), 2857 (symm. CH$_2$), 1636 (—CSNH—), 1544 (C=N), 1511 (C=N), 1252 (C—N), 1224 (C—N), and 1143 cm^{-1} (C=S). Anal. Calcd for C$_{19}$H$_{35}$N$_4$S$_2$Na: C, 56.12; H, 8.68; N, 13.78; S, 15.77%; Found: C, 56.08; H, 8.73; N, 13.84; S, 15.72%.

Procedure for the Polymerization of **1b**

Monomer **1b** was polymerized electrochemically on an anode (SUS304 plates, 0.2 × 30 × 60 mm, average roughness 4 nm) for 10 min at 20°C at a current density of 0.20 mA/cm^2, using an electrochemical measurement apparatus (Hokuto Denkou Co. Ltd., HD-3000) as described previously [13] to deposit poly(6-*N, N*-dioctylamiono-1,3,5-triazine-2,4-disulfide) **2a** on the plate in a low yield. The electrolytic cell was equipped with a working electrode (SUS304 plates), counter electrode (Pt-plate 0.2 × 30 × 60 mm), and a reference electrode (saturated calomel electrode, SCE) and filled with an electrolytic solution containing **1b** (1 mmol/dm^3) and 0.1 mol/dm^3 Na$_2$CO$_3$ in water. A polymer obtained on the plates was completely dissolved in tetrahydrofuran, and then the concentrated solution was used for the measurement of number average molecular weight (M_n) and elemental analysis. Yield: 3.2 μg/cm^2(24%). mp 220–225°C MS *m/z(%)*: 383 (M$^+$ + 2), 381 (M$^+$, 100). The density of polymer film **2a** was about 1.08 g/cm^3. M_n: 4.2×10^4; The small-angle X-ray diffraction patterns of **2a** showed a peak at $2\theta = 3.30^\circ$ indicating a distance between layers of 2.67 nm. The IR spectrum (RAS method) of **2a** showed bands at 2954 (CH_3), 2927 (asymm. CH_2), 2853 (symm. CH_2), 1566 (C=N), 1538 (C=N), 1331 (C–N), 1301 (C–N), and 1143 cm^{-1} (C=S), and the I_{2927}/I_{2853} ratio was 2.2. Anal. Calcd for $C_{19}H_{34}N_4S_2$: C, 59.64; H, 8.96; N, 14.64; S, 16.76%; Found: C, 59.68; H, 8.92; N, 14.59; S, 16.81%.

Procedure in Perpendicular Magnetic Field for the Polymerization of 1b

Monomer **1b** was polymerized electrochemically on an anode (SUS304 plates, 0.2 × 30 × 60 mm, average roughness 4 nm) for 10 min at 20°C at a current density of 0.20 mA/cm^2 in perpendicular magnetic field, by placing an electrolytic cell in the bore of a superconducting magnet (JMTD-5T 3000M-PC Japan Magnet Technology Inc.) and using a potentiostat/galvanostat (Hokuto Denko HA-20) connected to an X-Y-recorder (Riken Denshi F-3DP). A five-tesla (5T) homogeneous magnetic field was applied perpendicular to the electrolytic current in the JMTD-5T 3000M-PC magnet (5T⊥). A polymer **2b** obtained in 5T⊥ magnetic field was investigated about various properties as follows. Yield: 20.2 μg/cm^2 (87%). mp 226–231°C. The density of polymer film **2b** was about 1.07 g/cm^3. M_n: 6.3×10^4. The X-ray diffraction patterns of **2b** showed a peak at $2\theta = 3.31^\circ$ indicating a distance between layers of 2.67 nm. The IR spectrum (RAS method) of **2b** showed bands at 2954 (CH_3), 2924 (asymm. CH_2), 2853 (symm. CH_2), 1544 (C=N), 1502 (C=N), 1311 (C–N), and 1291 (C–N), and the I_{2927}/I_{2853} ratio was 2.3.

Procedure in Parallel Magnetic Field for the Polymerization of 1b

Monomer **1b** was polymerized electrochemically on an anode (SUS304 plates, 0.2 × 30 × 60 mm, average roughness 4 nm) for 10 min at 20°C at a current density of 0.20 mA/cm^2 in parallel magnetic field, by placing an electrolytic cell in the bore of a superconducting magnet (JMTD-10T100M, Japan Magnet Technology Inc.) and using a potentiostat/galvanostat (Hokuto Denko HA-20) connected to an X-Y-recorder (Riken Denshi F-3DP). A five-tesla (5T) homogeneous magnetic field was applied parallel to the electrolytic current in the JMTD-10T100M magnet (5T//). A polymer **2c** obtained in 5T// magnetic field was investigated about various properties as follows. Yield: 14.5 μg/cm^2(63%). mp 238–244°C. The density of polymer film **2c** was about 1.15 g/cm^3. M_n: 12.5×10^4. The X-ray diffraction patterns of **2c** showed a peak at $2\theta = 3.23^\circ$ indicating a distance between layers of 2.73 nm. The IR spectrum (RAS method) of **2c** showed bands at 2957(CH_3), 2930 (asymm. CH_2), 2857 (symm. CH_2), 1568 (C=N), 1542 (C=N), 1334 (C–N), and 1304 (C–N) and the I_{2927}/I_{2853} ratio was 1.8.

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