# Light reflection at polyaniline films and
# its application to a kinetic study of polymer chain conformation

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**Abstract**

Light reflection at polymer-coated electrodes is studied for polyaniline and its derivatives. Reflected light intensity is found to vary with the applied potential for the two reasons: one is absorption of light due to coloring of the oxidized polymer film and the other is light scattering which is concerned with a polymer chain conformation upon oxidation. A new method based on the potential dependence of light reflection is proposed for studying kinetics of conformational changes of polymer chains. The rate constants evaluated are found to be 0.05-8 $s^{-1}$, depending on the film thickness and pH of the solution.

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**Introduction**

An increasing number of studies have been devoted to fabrications of artificial muscles or soft actuators, which consist of soft matters showing deformations in response to external stimuli such as electricity and light irradiation. Gels, elastomers, co-polymers, and nanotubes supported on, or between, metallic layers are potential candidates for the development of the biomimetic actuators [1-5]. Among them, π-conjugated polymers are well known to expand/contract upon electrochemical oxidation/reduction. Such dimensional changes induced by the electrochemical stimulus originate from an incorporation of solvated dopant ions into the film and/or a conformational change of π-conjugated chains. A number of studies have been carried out on the potential-induced deformations of conducting polymers in order to fabricate novel actuators [6-11]. Polyaniline (PANI) and its derivatives are a family of conducting polymers that exhibit a significant extent of deformations at low voltages. They have been investigated intensively by a research group of Kaneto as a key material for developing soft actuators with a large strain and fast response [12-16].

Recently, we have found a new type of potential-induced changes in film property of PANI and its derivatives, i.e. changes of the intensity of light reflected from the polymer film with the applied potential [17]. This phenomenon has been discussed in connection with a change in mobility of charge carriers in the PANI films and the drastic increase of mobility with oxidation level is found to be closely related to a conformational change of the polymer backbone leading to the formation of the polaron lattice structure [18,19]. The *in-situ* reflection technique with a He-Ne laser allows us to detect sensitively conformational changes without giving any mechanical stress to the polymer.

In the present study, a new method for investigating kinetics of chain conformations for the PANI film in acid solutions is proposed on the basis of the *in-situ* reflection technique. The rate constants for PANI and its derivaties are successfully measured as a function of the film thickness and pH of the solution.

**1. Experimental**

Aniline from Aldrich, and *o*-methylaniline and *o*-methoxyaniline both from TCI were of reagent grade. They were distilled under Ar atmosphere and stored in Schlenck tubes filled with Ar gas. Tetraethylammonium perchlorate (Et$_4$NClO$_4$) from Katayama Chemicals and acetonitrile (MeCN) from Tokyo Kasei Co. were purified as described elsewhere [20]. PANI films were prepared on Pt-coated glass plates by the potential-sweep method in 2.3 M perchloric acid (HClO$_4$) containing 1.3 M aniline. Poly(*o*-methylaniline) (PMA) and poly(*o*-methoxyaniline) (PMOA) films were also prepared by the potential-sweep method in a 2.3 M HClO$_4$ solution with 0.7 M of *o*-methylaniline and *o*-methoxyaniline, respectively. Electrode potentials were referred to Ag/AgCl/NaCl(satd.) in a HClO$_4$ solution. After polymerization, the polymer electrodes were rinsed thoroughly with distilled water, and dried in air. Thicknesses of the polymer films were

evaluated with the amounts of electricity during a potential-step doping at 0.5 V by assuming the oxidation levels of PANI, PMA, and PMOA films at 0.5 V as 45, 44, and 37%, respectively [21,22]. The oxidation level is defined as the number of unit charges per monomer unit and calculated from the polymer weight, a molecular weight of the monomer unit, and the doping charge. The optical arrangement used in *in-situ* reflection measurements with a He-Ne laser (Japan Laser JLH-PT10U) is schematically depicted in Fig. 1, where the PANI electrode is slightly tilted from the two parallel glass plates to avoid the 633-nm light reflected directly at the front glass surface. The main compartment of the electrolysis cell was connected to the auxiliary compartment for the reference electrode through a filter paper. The 633-nm light was modulated at a frequency of 200 Hz by using a light chopper. A current signal of a Si photodiode with a small photoactive area (3.1 mm$^2$) (Hamamatsu Photonics S1226-5BK) was converted to a voltage using a current/voltage amplifier (NF LI-76) and the voltage signal was fed to a lock-in amplifier (NF LI-5640). To make sure that the response of the measuring system is fast enough to follow a change of the light signal, direct measurements of the reflected light intensity with a digital storage oscilloscope (Iwatsu DS-4372, 500 MHz) were made and the time changes of the signals observed with the lock-in technique and the oscilloscope were compared in some experimental runs. Before starting measurements, the potential of the polymer electrode was kept at a sufficiently negative potential so as to obtain its reduced form, i.e. leucoemeraldine. Reflection measurements were made with PANI, PMA, and PMOA films grafted on Pt/Cr-coated glasses in HClO$_4$ solutions. In the galvanostatic mode of the reflection study, a constant anodic current was applied to the electrode and a time course of the intensity of a reflected light was measured till the electrode potential reaches 0.5 V. The electrode potential was rested at -0.2 V till the cathodic current density fell down to -0.2 μA cm$^{-2}$ or below. Then the next current pulse was applied to the polymer-coated electrode. Electrochemical measurements were made with a potentio/galvanostat (Hokuto Denko HAB-151). All the measurements were made at room temperature.

## 2.   Results and discussion

Fig. 2 represents images of a 633-nm light reflected from the PANI-coated electrode biased at -0.2 V to 0.4 V in HClO$_4$(pH 1), which are projected on a tracing paper in place of a slit of Fig. 1. When the PANI film is completely reduced at -0.2 V, a hazy red light spreads over the projection plane without any clear spot, suggesting that the incident laser beam is considerably scattered by the neutral PANI film. The light spot appears at 0 V and becomes obvious with an increase in potential up to 0.2 V. This implies that the degree of light scattering is reduced by oxidation of the PANI. As the applied potential is made more positive, however, the red spot starts to reduce its intensity. At potentials beyond 0.4V, neither light spot nor hazy red light is seen on the projection plane. Such a pronounced change in the projected image with the applied potential was reproducible and similar observations were also made with PMA and PMOA films as well as PANI films. In order to detect a change of the reflected light sensitively, we will measure the intensity of the reflected light passing through a slit with a photodetector placed at a right position

where a specular reflection occurs, as shown in Fig. 1. As an example, the reflected light intensity observed with a PANI-coated Pt electrode in $HClO_4$(pH 1) during a potential scanning at 10 mV $s^{-1}$ from -0.2 V to 0.5 V and back is shown in Fig. 3, together with a corresponding cyclic voltammogram. When the potential is below 0 V, the reflected light intensity is almost zero, in agreement with no obvious light spot on the projection plane in Fig. 1. A sharp increase in the light intensity signal occurs at 0.1 V and the light intensity shows a peak at 0.2 V. When the potential is made more positive than 0.3 V, the signal strength becomes negligibly small concomitant with a change in color of the PANI film into bluish black. Like measurements of spin densities [23,24], volumes [25], optical absorbances [26] and conductivities [27] in the potential-sweep mode, a hysteresis effect is prominent for the potential change of reflectance as shown in Fig. 3. It tended to be reduced by lowering a potential-sweep rate, but even at a sweep rate as low as 0.2 mV $s^{-1}$ the hysteresis was observed, indicative of the presence of an extremely slow kinetic process. Fig. 4 depicts a reflected light intensity at its peak ($I_p$) and that at dedoped state ($I_d$) measured with PANI films of varying thicknesses during a forward potential scanning at 10 mV $s^{-1}$ in $HClO_4$ (pH 1). As the film thickness increases beyond 0.5 μm, the $I_d$ value decreases drastically. Four-fold increase of the film thickness from ca. 0.5 to 2 μm leads to almost four order-of-magnitude decrease of the reflected light intensity at the dedoped state of the PANI film. The peak light intensity $I_p$ is slightly higher than the $I_d$ value even at 0.6 μm and the difference between the two light intensities is enhanced by the increase in the film thickness. This feature is clearly shown in the inset of Fig. 4, where the ratio of $I_p$ to $I_d$ is plotted against the film thickness. The light intensity ratio $I_p/I_d$ increases with the film thickness and reaches one hundred when the PANI film is 2 μm thick. The semilogarithmic plot of $I_p/I_d$ against the film thickness does not pass the origin and the plot appears to fit a straight line passing through 0.6 μm at $I_p/I_d=0$. In general, the density and morphology of an electrosynthesized conducting polymer film are not uniform and a relatively dense layer tends to form at the beginning. This inhomogeneous film structure may be related to the observed delay of the increase of $I_p/I_d$.

Summarizing the above findings, it is reasonable to have the following image for the changes of the reflected light with oxidation states of PANI films. In the reduced state of the PANI film where polymer chains have a coiled structure [28,29], a light scattering or a diffuse reflection takes place in the polymer layer and thus a negligible intensity of light reaches the photodiode. By increasing the potential, polymer chains stretch and the coiled structure relaxes as has been demonstrated by MacDiarmid and Epstein [28,29]. Consequently, Rayleigh or Mie scattering is attenuated in the polymer film and the incident light can go deep into the polymer layer to reach a highly reflective Pt surface. Then, specular reflection at the Pt surface occurs effectively and the reflected light gains its intensity. In accord with this view, it has been reported that PANI particles of 4 to 5 μm in average diameter large enough to scatter a visible light are found in its reduced state and they disappear in the oxidized state [30]. When the potential is raised further, the PANI film turns a blue-black color. At the higher potentials, therefore, the PANI film starts to absorb the incident 633-nm light and the intensity of light reaching the Pt surface reduces. Absorption of the 633-nm light due to the heavily oxidized PANI layer is responsible for fadeaway of the light spot

at potentials beyond 0.3 V. For clarification, the events that occur in the polymer film at three different oxidation stages, i.e., a) completely reduced, b) oxidized, and c) heavily oxidized states, are schematically depicted in Fig. 5. Of course, when we measure the intensity of transmitted light in place of reflected light, the potential-dependent scattering of the PANI film will have an undesirable influence on precise determinations of its absorption spectrum. Fig. 6 denotes *in-situ* absorption spectra of a PANI film at varying potentials. In general, a precise determination of spectroscopic properties of films is difficult compared with that for solutions because reflection at the film surface is not easily compensated for the films. In the case of the PANI film, a pronounced change of light scattering in addition to a normal reflection problem adds further difficulty to measurements of absorption spectra of the films. As shown in Fig. 6 for the PANI film in $MeCN/Et_4NClO_4$(0.1 M), a significant drop of absorbance in the wavelength region close to 600 nm is clearly seen when the potential is 0 V and higher. This absorbance drop can be understood if we remember that the neutral PANI film scatters light in that wavelength region significantly and oxidation of the polymer film results in a reduction of scattering. In this way, by measuring the light intensity reflected from the polymer film, one can sensitively detect expansion or shrinking of polymer chains resulting from a conformational change.

Fig. 7 depicts a set of light intensity *vs*. charge curves for a PANI film in $HClO_4$(pH 1) obtained in the galvanostatic mode with varying applied currents. The state of a chain conformation should be controlled by the amount of charges or more explicitly the oxidation level. Therefore, the same charge will give the same light intensity irrespective of the applied current or the rate of polymer oxidation, if the response of a chain conformation to the electrochemical stimulus is sufficiently fast. This implies coincidence of the curves obtained at different applied currents for the fast limit of chain conformation. It is clearly seen, however, that the rising portions of the curves shift to the right as the currents applied to the PANI film are increased. The observed shift of these curves demonstrates a delay in response of chain conformation to an electrochemical oxidation of the PANI film, demonstrating that the rate of a conformational change of polymer chain is within an accessible limit of the proposed *in-situ* reflection technique. On the other hand, the descending portions of the curves merge into a single curve. The coincidence of the descending portions is a matter of course in view of the fact that coloration of the PANI film responsible for absorption of the incident light and thus attenuation of the reflected light intensity should occur much faster than the time scale of the current experiments. Analysis of the light intensity data of Fig. 7 is performed in the following way. A given intensity of reflected light corresponds to a certain state of chain conformation. We will draw a straight line parallel to the abscissa axis and read the charges at which the straight line intersects with the respective curves. Thus obtained charges are plotted against the currents corresponding to the curves of Fig. 7. Charge *vs*. current plots evaluated at different light intensities are shown in Fig. 8. The slope of the plot represents a time constant characteristic of the rate of a conformational change in the PANI film and its inverse gives a rate constant for this process ($k_c$). All the plots fit straight lines with almost the same slope values except for in the high current region. The slopes yield 2.4 s$^{-1}$ for the $k_c$ value of the PANI film in $HClO_4$ (pH 1). The rather small $k_c$ value suggests

that PANI chains in the electropolymerized film as thick as 2.3 μm are folded and intertwisted, so that loosening of their conformations upon oxidation may not be readily attained. Fig. 9 depicts plots of $k_c$ *vs*. thickness of PANI film in $HClO_4$ solutions of pH 0.2, 1 and 2. It is seen that greater pH values leads to smaller $k_c$ values. On the other hand, by increasing the film thickness the $k_c$ values tend to decrease in common for the respective solutions. The decrease in $k_c$ with the film thickness is in accord with the view that the rate constant of the conformational change is primarily controlled by tangling of polymer chains.

Reflectance measurements were also made with PMA and PMOA films in $HClO_4$(pH 1). Time responses of the reflected light intensity for the PMA and PMOA films in the galvanostatic mode had features similar with the one for the PANI films as shown in Fig. 7, except that in some experimental runs the plot exhibited a slight decrease in the low oxidation region up to a few percents. Similarly with the case of PANI films, furthermore, plots of charge *vs*. applied current fitted straight lines with almost the same slopes for the respective oxidation levels. The observed rate constants are represented in Fig. 10, together with the plot of PANI films obtained in $HClO_4$(pH 1). It appears that all the three plots fit straight lines with the same slope value, although the positions depend on the sort of the polymer films. The rate constants follow the order of PMOA≥PANI>PMA when compared at the same film thickness. It is worth noting here that the formation speed of PMA films was very slow compared with those for PANI and PMOA films. This hints that the slow kinetics of the PMA chain conformation is associated with a well tangled structure of the PMA film which would be attained by being prepared slowly. To demonstrate this possibility, reflectance measurements were made with PANI films prepared at different speeds by changing the anodic switching potential from 0.8 to 1.0 V. Indeed, SEM pictures of Fig. 11 for the PANI films obtained indicate that a drastic change of morphology takes place by changing the preparation rate of the PANI films. The rate constants determined from the reflectance measurements are summarized in Fig. 12. As expected, slower preparation speeds lead to lower rate constants for the conformational change.

## 3.  Conclusions

Kinetics of a polymer chain conformation for polyaniline, poly(*o*-methylaniline), and poly(*o*-methoxyaniline) in acid solutions is studied by measuring the light intensity reflected at the polymer surface during application of constant currents. The rate constants evaluated by this *in-situ* reflectance technique are in the range of 0.05-8 s$^{-1}$, depending on the film thickness and pH of the solution as well as the sort of the polymers. They are found to be enhanced by the decrease of the film thickness and the solution pH. In addition, preparation conditions of the polymer films affect the rate constants considerably.

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**Figure captions**

Fig. 1. Schematic illustration of an optical arrangement for measuring the reflected light intensity at a polymer-coated Pt electrode.

Fig. 2. Projection images of a He-Ne laser beam reflected from a PANI-coated Pt electrode biased at different potentials in $HClO_4$(pH 1).

Fig. 3. Change of the reflected light intensity at the PANI-coated Pt electrode with potential during scanning of the potential at 10 mV s$^{-1}$ from -0.2 V to 0.5 V and back in $HClO_4$(pH 1). The CV curve simultaneously measured is included.

Fig. 4. Dependences of PANI film thickness on light intensities reflected from PANI-coated Pt electrodes (□) at its peak, $I_p$, and (●) at the dedoped state, $I_d$, during a forward scanning of potential at 10 mV s$^{-1}$ in $HClO_4$(pH 1). The inset shows the ratio of $I_p$ to $I_d$ as a function of film thickness.

Fig. 5. Proposed mechanisms for light reflection at PANI film in a) reduced, b) oxidized, and c) heavily oxidized states.

Fig. 6. *In-situ* absorption spectra of PANI-coated ITO electrode at various potentials in $MeCN/Et_4NClO_4$(0.1 M).

Fig. 7. Changes of intensities of 633-nm light reflected at PANI film of 2.3 μm thickness in $HClO_4$ (pH 1) with the amount of charges in galvanostatic experiments with different currents. For clarification of the figure, only the curves obtained with the applied currents of 0.5 to 8.0 mA with a current interval of 0.5 mA are illustrated.

Fig. 8. Plots of charge *vs*. applied current obtained from Fig. 7 to evaluate the rate constant of the conformational change. Numerals near the respective plots denote oxidation levels of the PANI film.

Fig. 9. Dependences of $k_c$ value on thickness of PANI film measured in $HClO_4$ solutions with pH values of (○) 0.2, (□) 1, and (  ) 2.

Fig. 10. Dependences of $k_c$ value on thickness of (○) PANI, (□) PMA, and (  ) PMOA films in $HClO_4$(pH 1). All these polymer films were prepared by cycling the potential at 50 mV s$^{-1}$ in a 2.3 M $HClO_4$ solution with 0.7 M of the corresponding monomers. Potential-sweep ranges were -0.1 to 0.9 V for PANI, -0.1 to 0.9 V for PMA, and -0.1 to 0.85 V for PMOA.

Fig. 11. SEM images of PANI films prepared in $HClO_4$(pH 1) by cycling the potential at 50 mV s$^{-1}$ from -0.2 V to a) 0.8 V, b) 0.9 V, and c) 1.0 V.

Fig. 12. Dependence of $k_c$ value on the film formation rate. PANI films were prepared in $HClO_4$(pH 1) by cycling the potential at 50 mV s$^{-1}$ from -0.2 V to (○) 0.8 V, (□) 0.9 V, and ( ) 1.0 V.
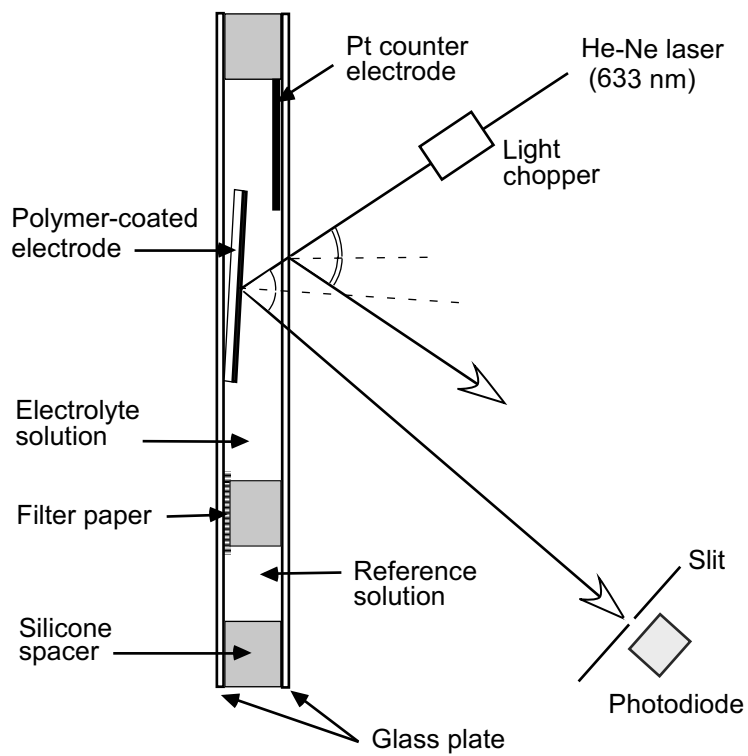
Pt counter electrode

He-Ne laser (633 nm)

Light chopper

Polymer-coated electrode

Electrolyte solution

Filter paper

Reference solution

Silicone spacer

Slit

Photodiode

Glass plate
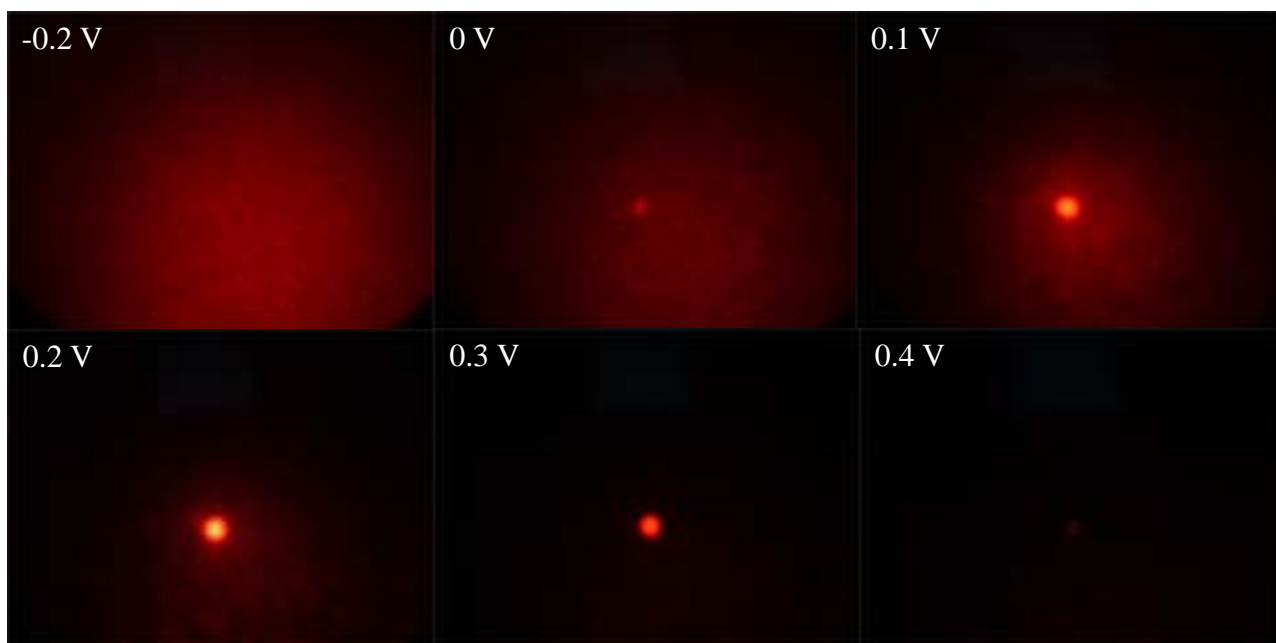
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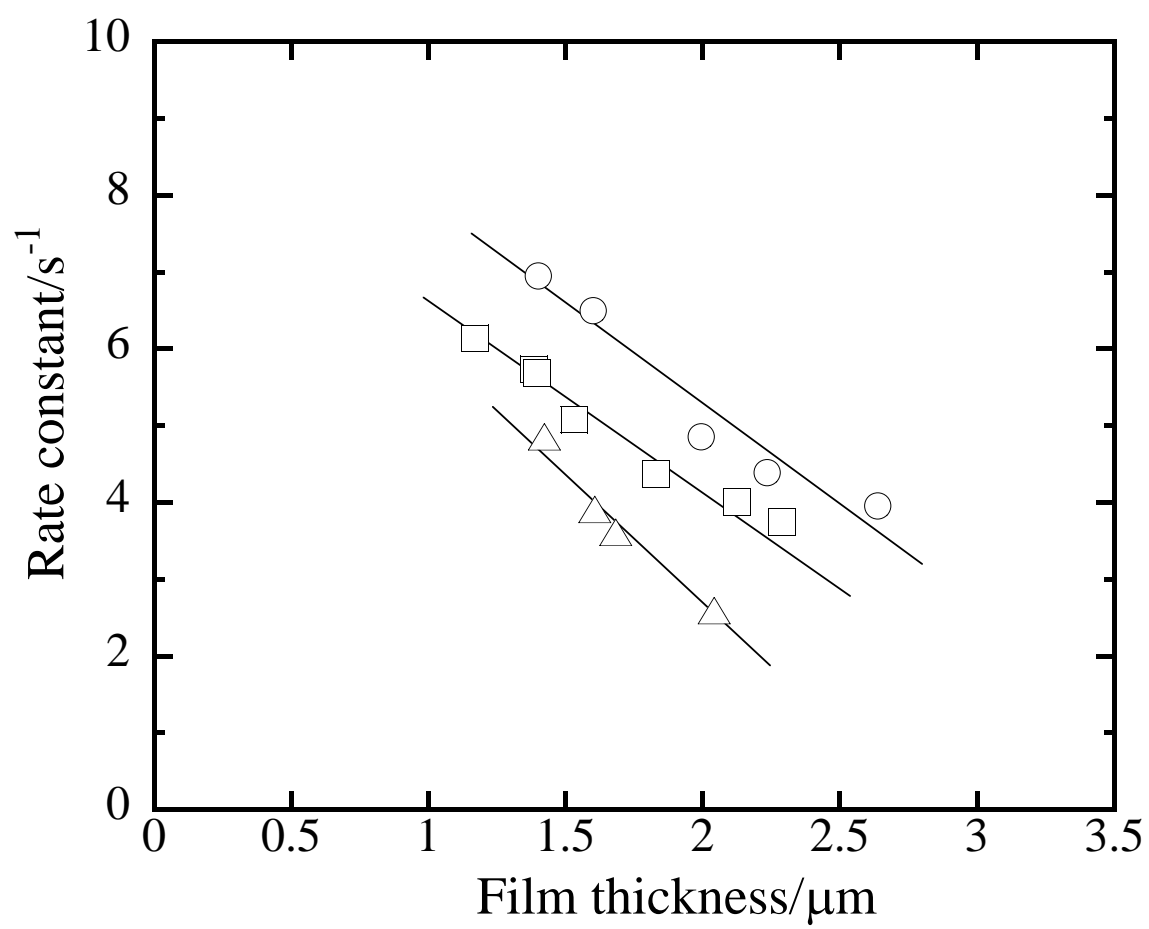
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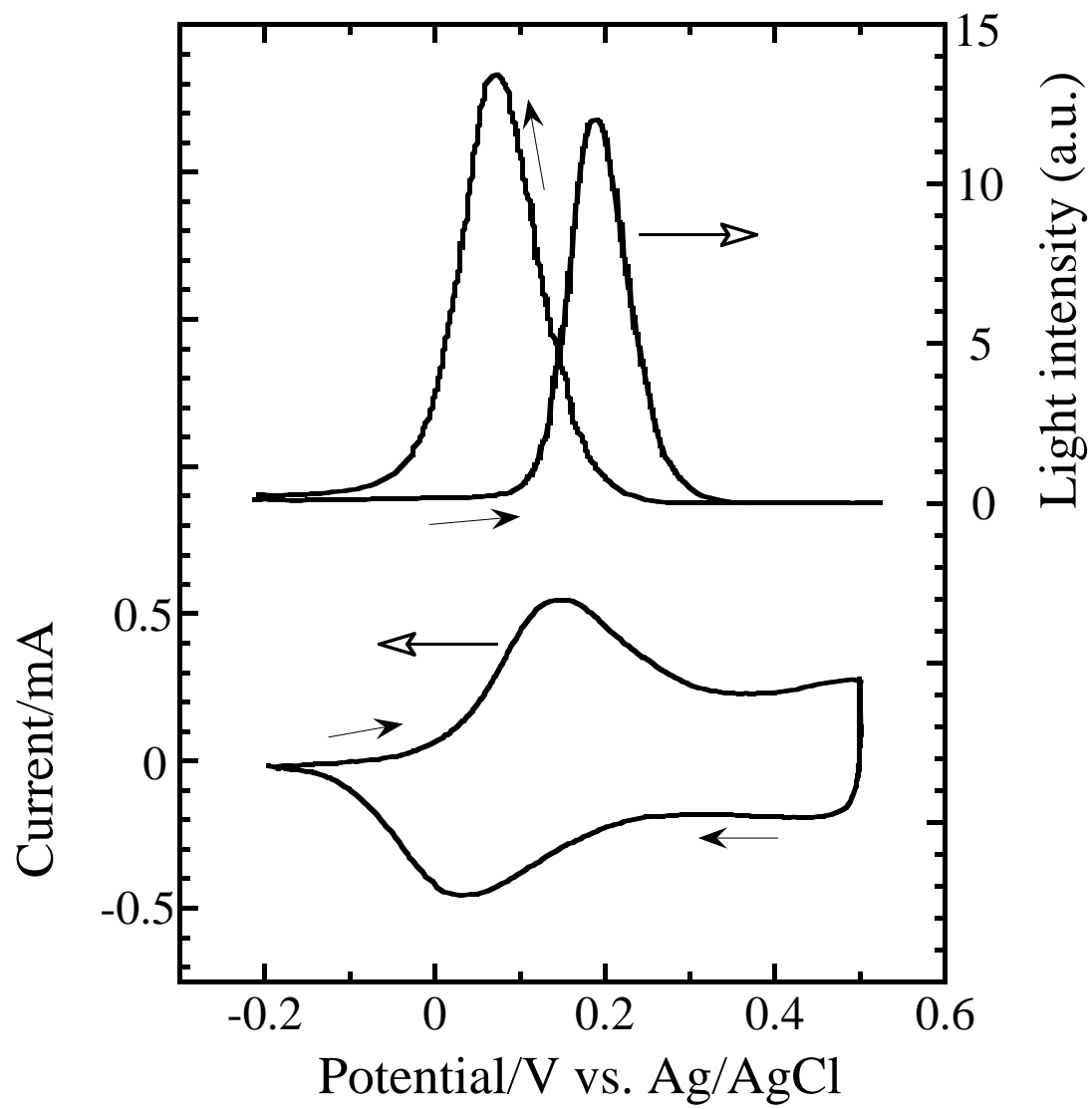
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Fig. 4. Y. Harima et al.

a) Reduced state     b) Oxidized state     c) Heavily oxidized state
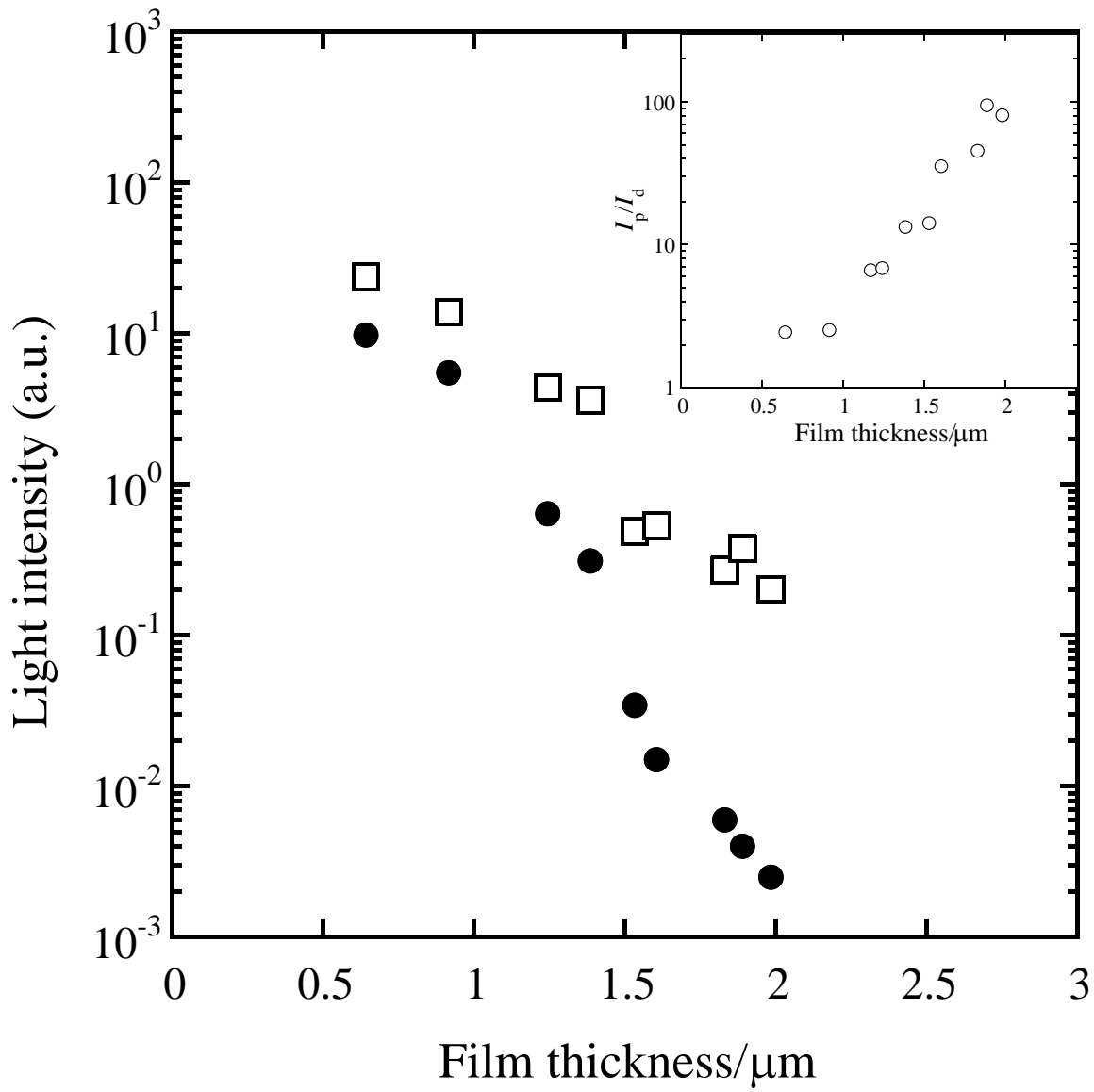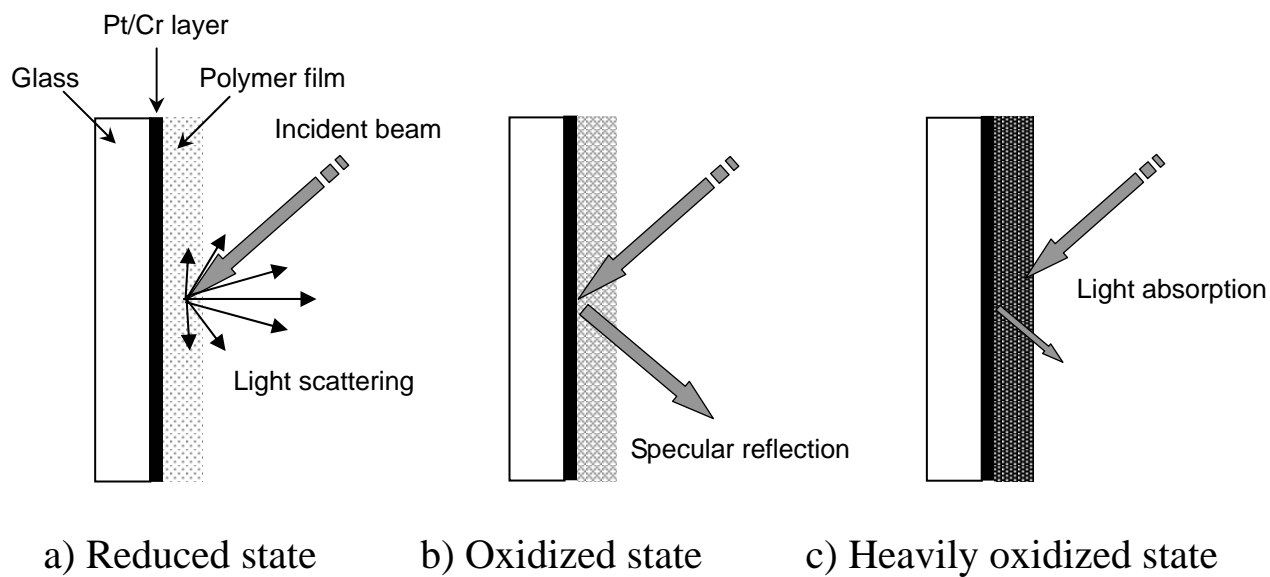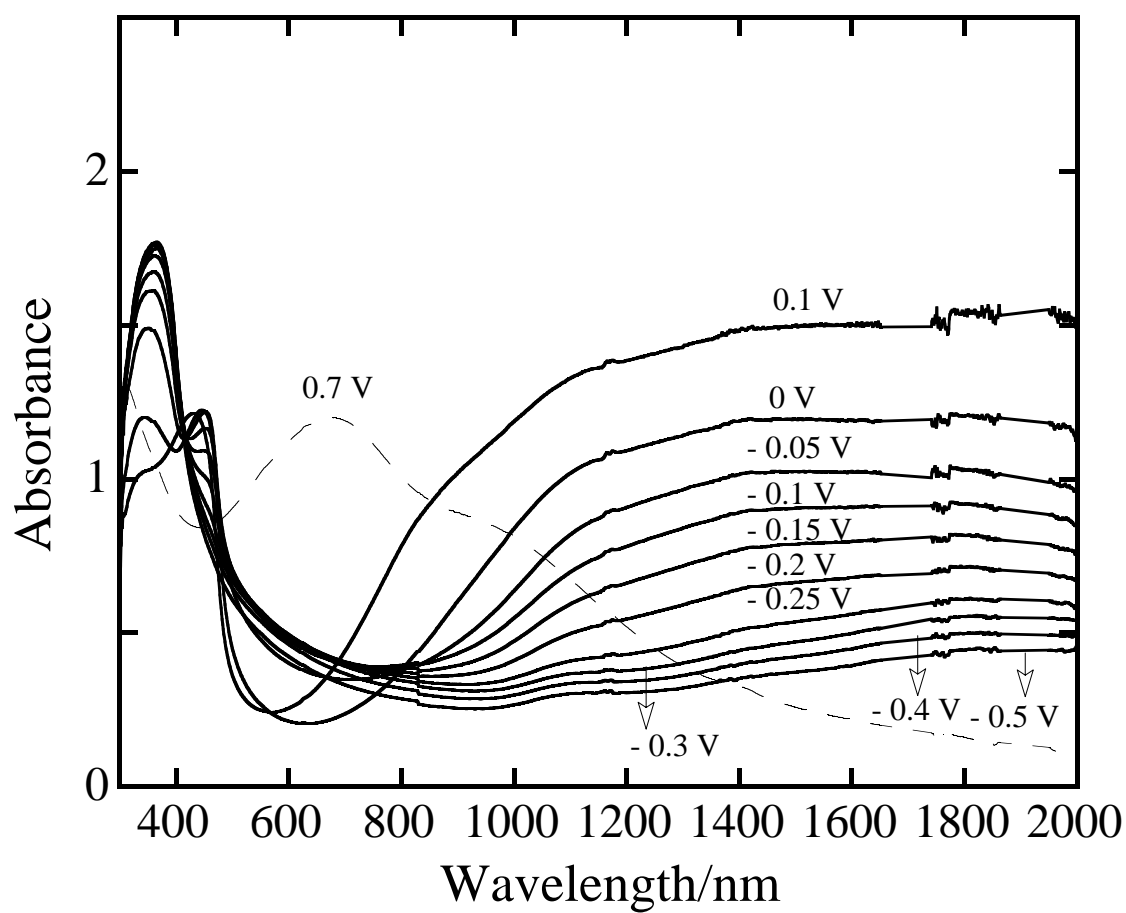
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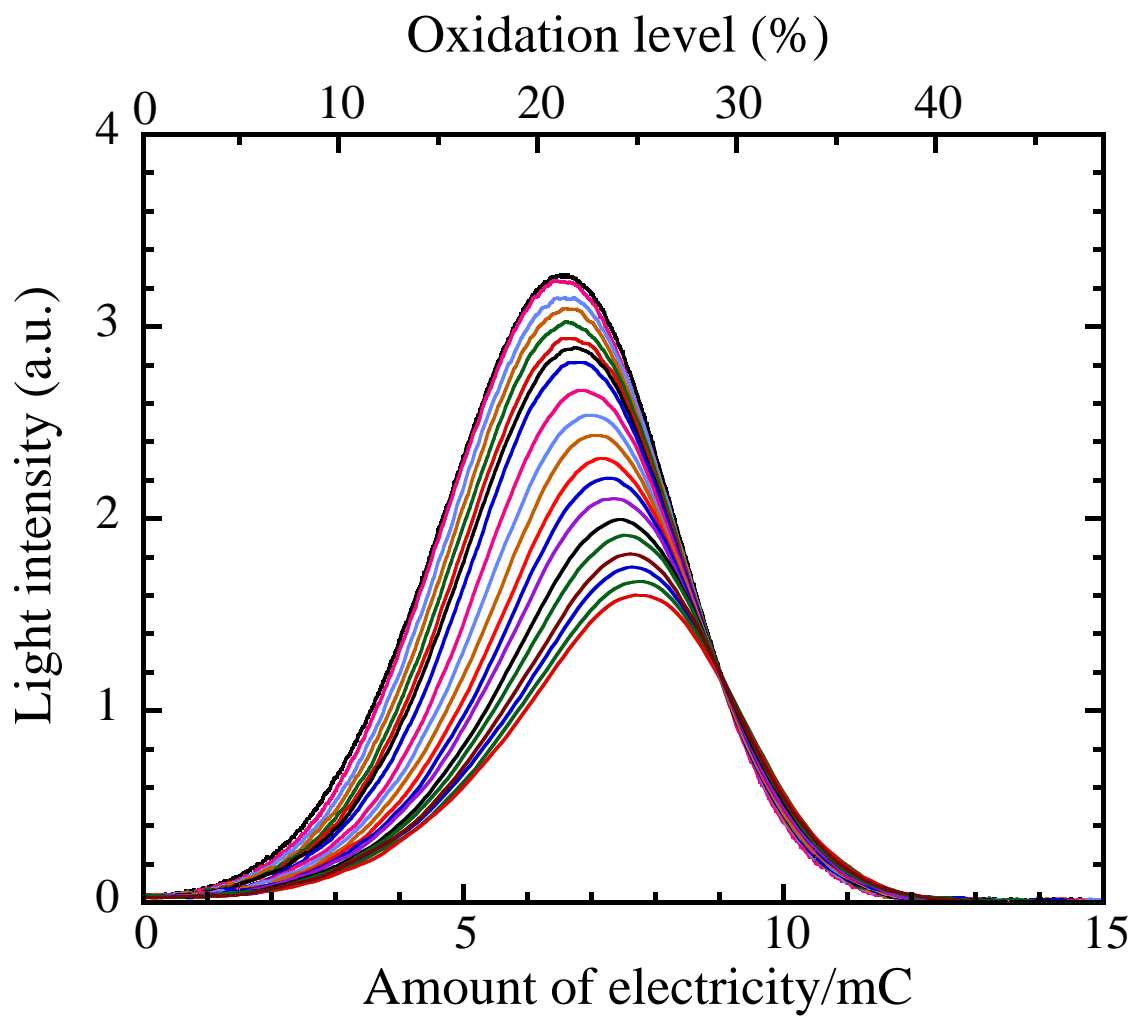
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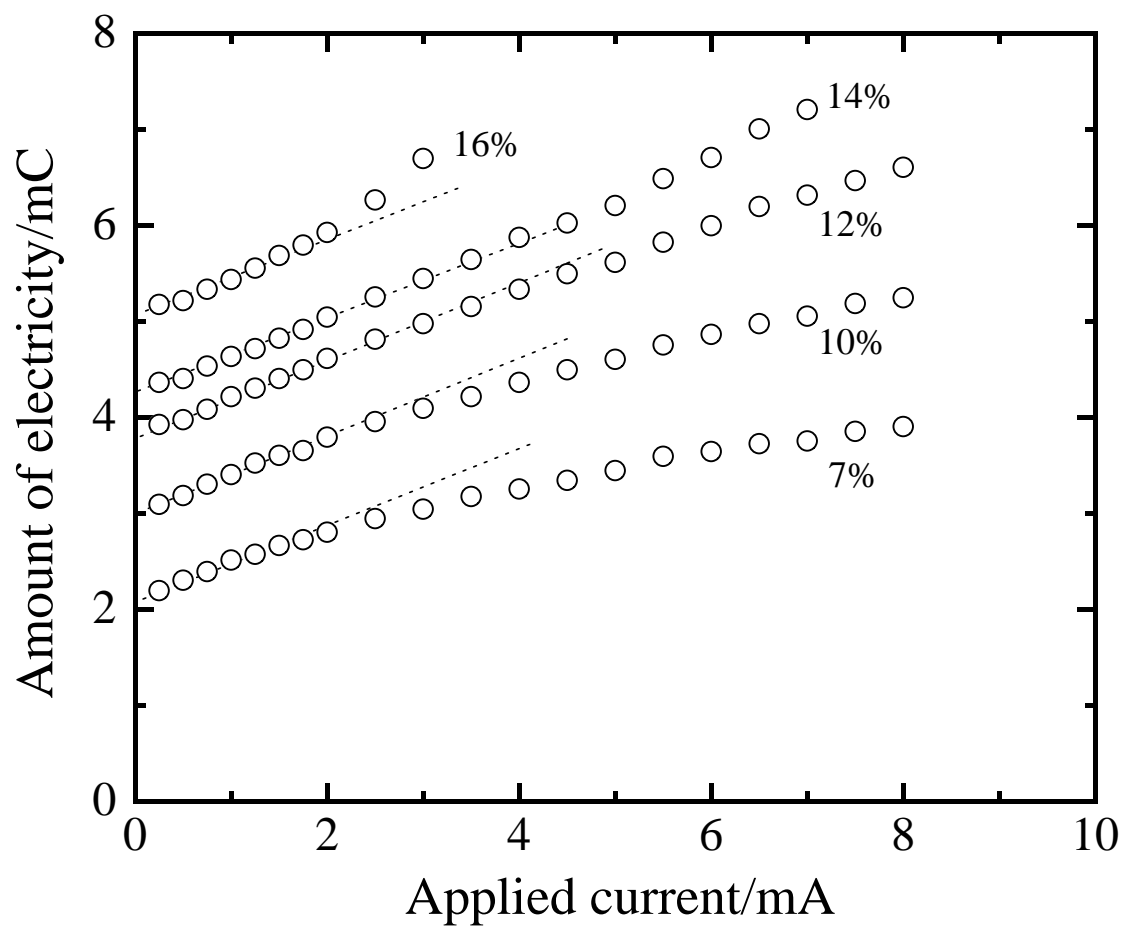
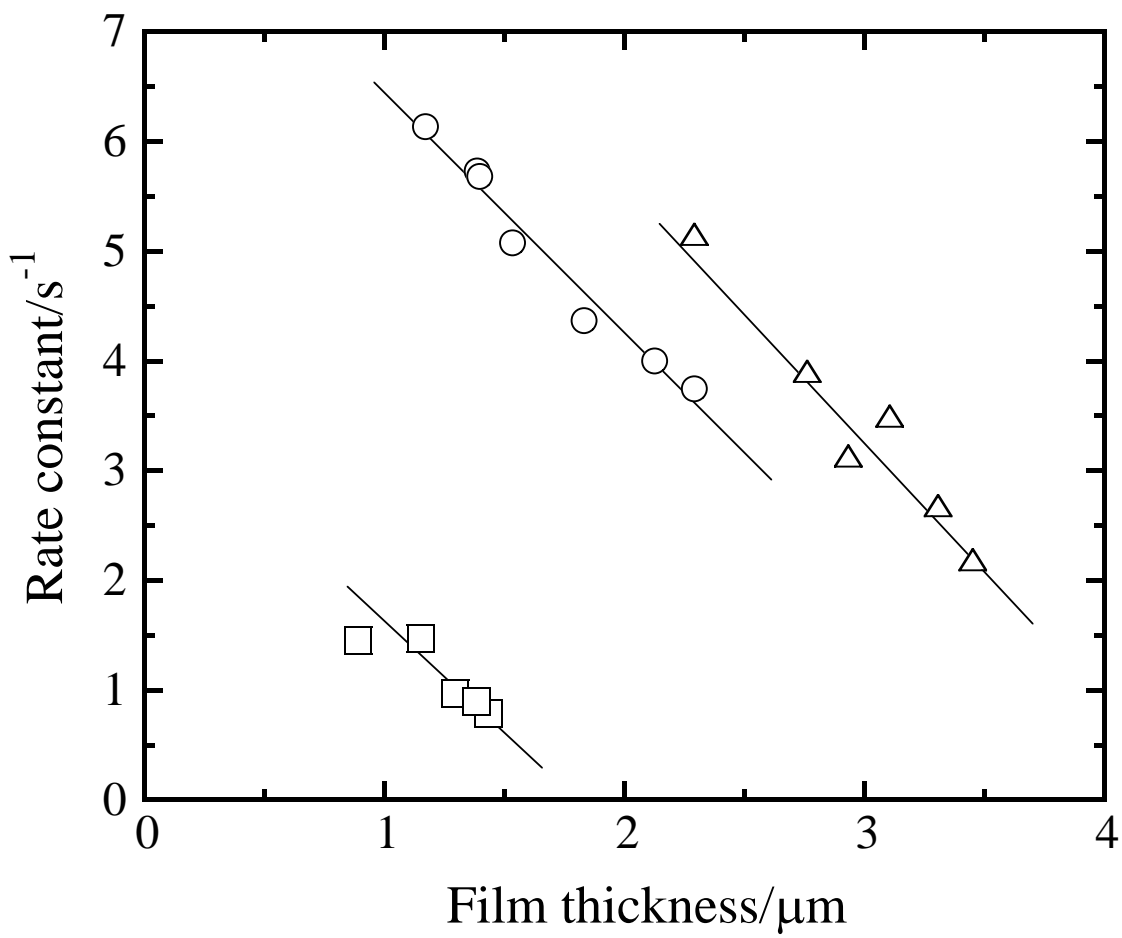Fig. 8. Y. Harima et al.
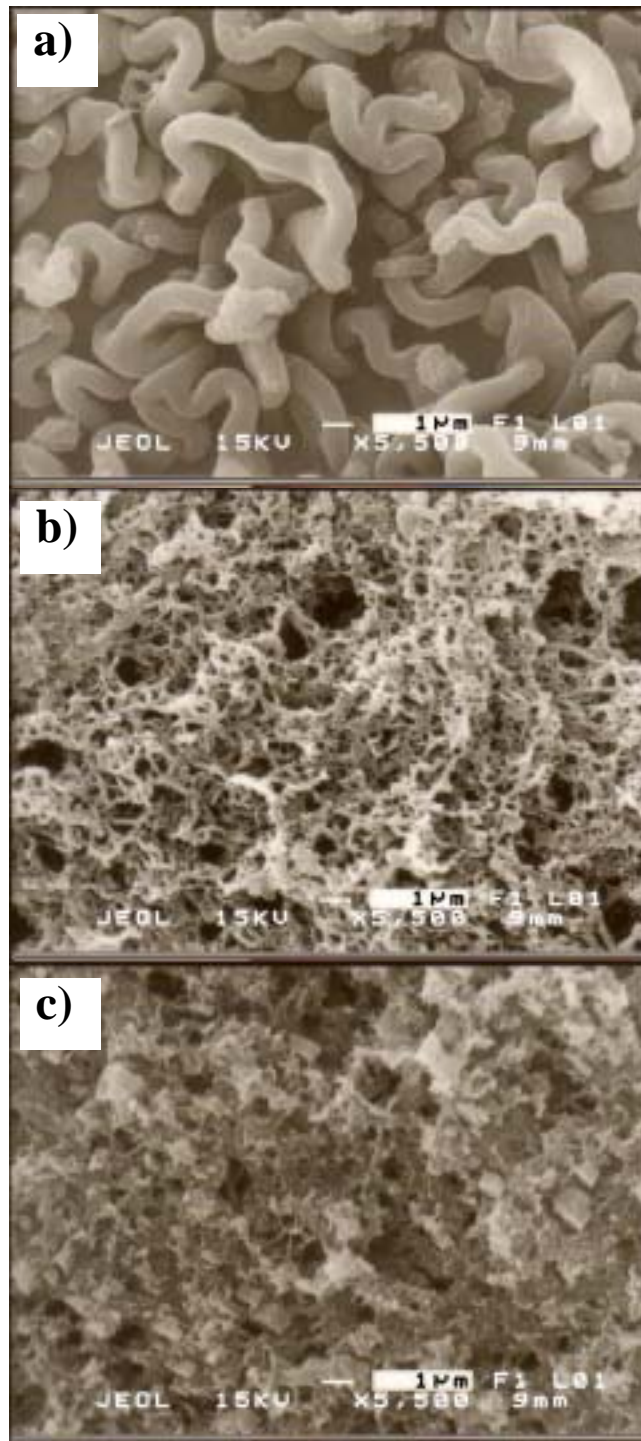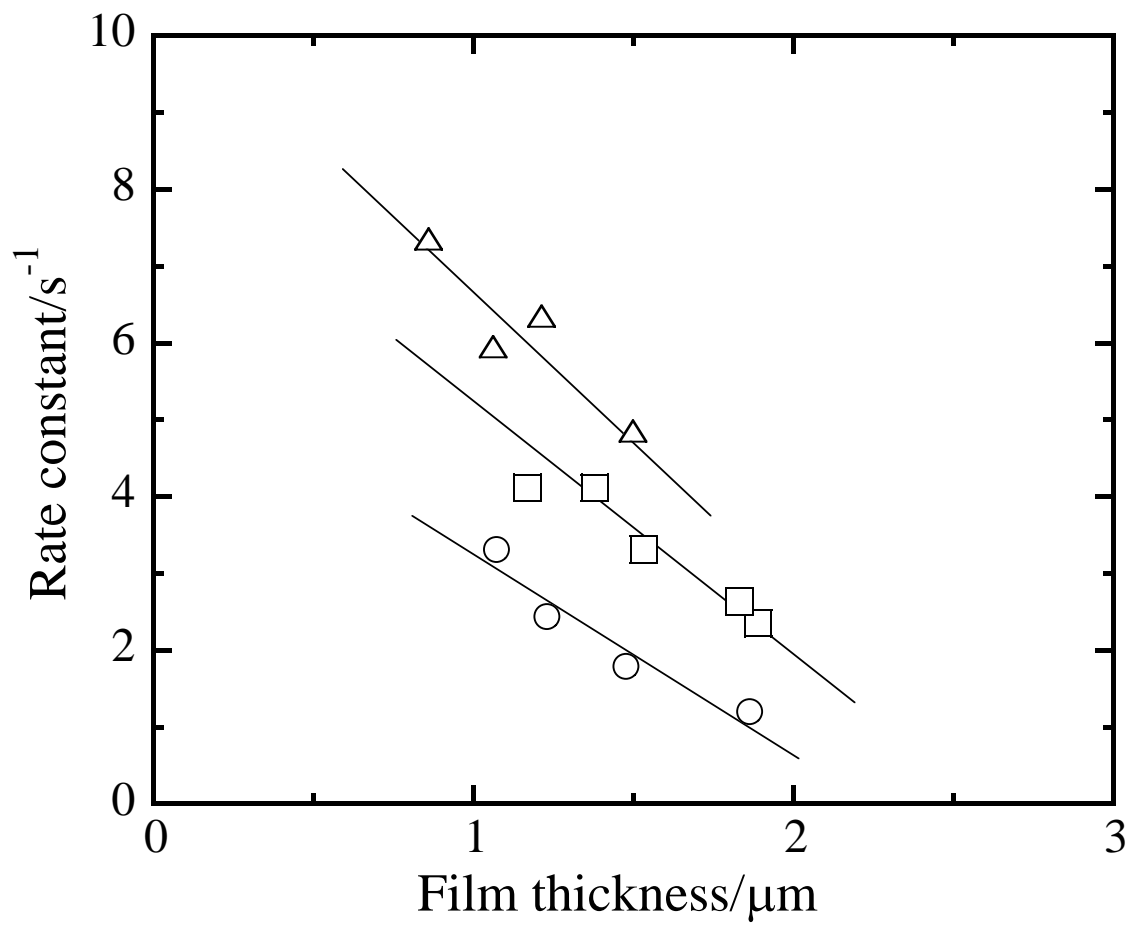
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Fig. 12. Y. Harima et al.