

Influence of film structure on mobilities of charge carriers in conducting polymers

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Abstract

Two sorts of poly(3-hexylthiophene) (PHT) films with the same chemical compositions were prepared, and their electrochemical, spectroscopic, and transport properties were studied with a special interest in a possible influence of film structure on mobilities of charge carriers. One of the PHT films was electrochemically synthesized using 3-hexylthiophene as a monomer (as-grown film) and the other was obtained by dissolving the as-grown film in chloroform and then casting the polymer solution (cast film). A clear difference was observed in the mobility vs. doping level plot between the two sorts of PHT films, demonstrating that the difference is caused only by a distinction in film structure. An initial decreasing feature of the mobility plot observed for the cast films was accounted for in terms of swelling of the films at an early stage of doping.

Keywords: Poly(3-hexylthiophene); Electrosynthesis; Doping; Mobility; Swelling

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Introduction

A simple electrochemical technique to evaluate mobilities of charge carriers in π -conjugated polymers with doping level as a parameter has been developed with a view of clarifying charge-transport mechanisms in conducting polymers [1-8]. Unless the kind of charge carriers or the conduction mechanism varies with a change in doping level, the mobility will be almost independent of doping level as in case of inorganic semiconductors. In reality, however, the mobilities determined by this technique were not constant, but varied greatly with doping level. A sharp rise of mobilities starting at 0.1 to 1% doping level has suggested the evolution of metallic conduction in the conducting polymer films. In the low doping region, on the other hand, the mobility plots exhibited different features. As for electrosynthesized films of polythiophene (PT) and poly(3-methylthiophene) (PMT), mobilities were almost constant, or not decreased at least, in the low doping region [1,4]. In contrast, cast films of regioregular poly(3-octylthiophene) (POT) showed an gradual decrease of mobilities, followed by a drastic mobility increase at higher doping levels [5]. The initial mobility decrease was tentatively explained in terms of an increased fraction of immobile diamagnetic species with doping level as well as scattering of charge carriers by bulky anions incorporated by doping into the film [5]. However, a later and more elaborate study made with cast and spun films of a series of chemically synthesized poly(3-hexylthiophene)s (PHTs) has revealed that this explanation is unlikely because no diamagnetic species are detected by *in-situ* ESR measurements at doping levels below 0.2%, where a significant mobility decrease occurs already [8]. In this mobility study with PHTs with different regioregularities, a strong influence of regioregularity of PHT upon the mobility plot was another salient feature to be noted. An analytic model based on the effective transport energy concept was proposed by Bässler et al. to formulate the hopping mobility in a disordered organic semiconductor at different charge carrier densities [9]. The theoretical model was demonstrated to fit the mobility plots for PHTs experimentally obtained by us. More recently, a general feature of these mobility plots, including the mobility decrease in the low doping region, was well reproduced by the model based on the concept of a strong Coulomb interaction between charge carriers and ionized dopants [10-12]. Oxidation of a conducting polymer increases the density of charge carriers in the polymer film, but also creates deep Coulomb traps due to the presence of dopants. The increase of the number of deep traps with doping is shown to be responsible for the mobility decrease observed with cast films of PHTs. We should recall here again that the mobility decrease has not been observed for electrosynthesized films of PT and PMT [1,4].

In the present study, two kinds of PHT films were prepared by electropolymerization of 3-hexylthiophene (as-grown film) and casting of a solution dissolving the as-grown films (cast film). The two kinds of PHT films with the same chemical structure and composition, but different film structures were subjected to electrochemical, spectroscopic, and mobility measurements to discuss a possible influence of film structure on the conduction mechanisms in conducting polymers.

Experimental

3-Hexylthiophene was purchased from Tokyo Kasei Co. and used after distillation. PHTs of 97% and 54% regioregularities used for a comparison purpose were purchased from Aldrich. Tetrabutylammonium perchlorate (Bu_4NClO_4) and tetraethylammonium perchlorate (Et_4NClO_4) from Tokyo Kasei Co. were purified by recrystallization from ethanol. Acetonitrile (AN) from Sigma-Aldrich Co. was refluxed over P_2O_5 for a couple of hours under Ar atmosphere and then distilled before use. Nitrobenzene (NB) from Katayama Chemicals was distilled before use. An air-tight glass cell with two subsidiary compartments was used for electrochemistry: one of the compartment was for the reference Ag/AgClO₄(0.1 M) electrode and the other for the Pt wire counter electrode. PHT films were grown by oxidizing 0.2 M monomer in Bu_4NClO_4 (0.02 M)/NB solution at 5°C at a constant potential of +1.0 V. It was found that the electrosynthesized PHT films were completely soluble in chloroform so long as the electropolymerization time was shorter than 10 minutes. When the time is longer than 10 minutes, however, a slight amount of an insoluble film started to remain on the electrode surface. In order to prevent any unexpected complexity, the PHT polymers prepared within 10 minutes were used for subsequent mobility experiments. The resulting PHT film was rinsed with a dry AN and dedoped in Bu_4NClO_4 (0.1 M)/AN solution for over 1 hour until a current density reduced to 0.1 $\mu\text{A cm}^{-2}$ or below. Then the as-grown film was rinsed with AN, dried under vacuum, and was subjected to mobility measurements. Under the same preparation conditions, i.e. solvent, electrolyte, applied potential, temperature, and polymerization time, PHT films were grafted on a Pt plate of ca. 2 cm^2 in surface area. The films were dissolved in chloroform and a concentrated polymer solution was prepared to yield cast films of PHT. Thicknesses of PHT films were roughly estimated from weights of the films with a round value of 1 g cm^{-3} for a density of the PHT film.

The electrochemical technique to determine mobilities of charge carriers in π -conjugated polymer films has been described earlier [1,7]. An essence of the technique lies in the use of the relation $\mu = \sigma / ne$ for a single carrier model, where n is the density of total charges, e the electronic charge, and σ denotes the conductivity. Another point is *in situ* and simultaneous determinations of conductivities and the amount of doped/dedoped charges at various potentials, made by the two-probe method and potential-step chronocoulometry, respectively. The amount of charges gives the charge density, n , if the weight of the polymer film and its density are known. Doping levels, defined as the number of unit charges per monomer unit, are obtainable from the charge density and used in this work as a measure of the extent of oxidation of the polymer film. The experimental set-up for simultaneous measurements of conductivities and charge densities (doping levels) is illustrated in Fig. 2 of Ref. [7]. Two-probe conductivity measurements were carried out using two kinds of electrodes. One was a conventional two-band electrode made of an insulating mica film and two Pt sheets of 0.1 mm thickness [13], and used in the high doping region. In the low doping region, where the film resistance was extremely high, a Pt microarray electrode (100 lines, 20 μm spacing, 50 cm in total width) was used. Resistance versus potential plots obtained with the two electrodes were compared and a unified conductivity versus potential plot was obtained by

combining the two sets of resistance data. *In situ* ESR measurements were carried out as described [2]. The PHT film was grown on a Pt wire of 0.5 mm diameter with the similar procedures as mentioned above. ESR spectra were recorded on an ESR spectrometer (JEOL JES-RE1X) operating in x-band mode. Microwave power used throughout this work was as low as 1 mW in order to avoid saturation of ESR signals. The field modulation amplitude was changed from 0.2 to 1 G, depending on the linewidth and the signal strength. *g*-Factors were determined from the microwave frequency and the resonance of magnetic field. DPPH (1,1-diphenyl-2-picrylhydrazil) was used as the *g*-factor standard ($g=2.0037\pm 0.0002$) for calibration. The number of spins (N_s) was evaluated by a double integration of the first-derivative ESR spectra. The absolute values of N_s were determined from ESR experiments by referring to a DPPH(10^{-4} M)/benzene solution and Mn^{2+} in MgO as an external standard. Optical absorption spectra of PHT films were taken on a Shimadzu UV-3101 spectrophotometer. The regioregularity (head-to-tail percentage) of the PHT was determined by comparing intensities of 1H NMR signals at 2.80 and 2.58 ppm. Weight- and number-average molecular weights (M_w and M_n) were measured by a gel permeation chromatography relative to polystyrene standards.

Results and discussion

The regioregularity of the electrosynthesized PHT was evaluated as 77% and the M_w value was around 93000, corresponding to approximately 560 monomer units in a typical PHT chain. The polydispersity (M_w/M_n) was ca. 3.16. The chemical analysis of the electrogenerated polymer used here shows that it has a high molecular weight, relatively high solubility, moderate polydispersity and moderate regioregularity.

A difference in color was observed between dedoped as-grown and cast films of PHT: the former films appeared to be dark-violet, while the latter ones were yellow-brown. Typical absorption spectra of as-grown and cast films are depicted in Fig. 1, together with those for cast films of chemically synthesized PHTs of 97% and 54% in regioregularity (denoted hereafter as PHT97% and PHT54%). Absorption spectra of PHT films are known to depend greatly on regioregularity of the polymer because a higher regioregularity leads to the formation of a film with a better self-assembled structure [14-19]. A difference in absorption spectrum between cast films of PHT54% and PHT97%, shown in Fig. 1, is a clear indication for the presence of a stacked structure in the PHT97% film due to an enhanced interchain interaction. On the other hand, the as-grown PHT film exhibits a broad absorption band with a peak at 2.50 eV. The peak position is close to the one for the PHT97% film, which also shows two clear shoulders at 2.08 and 2.27 eV. These side peaks observed commonly with regioregular PHT films have been ascribed to a coupling of the π - π^* transition with vibrational levels of the excited states [14,20]. Furthermore, the vibronic coupling is found to arise from a quasiplanar and rigid-rod conformation of polymer chains [21]. As for the as-grown film, one can also see two humps at ca. 2.1 and 2.3 eV, corresponding well to the positions of the two shoulders for the PHT97% film. This and the agreement of main absorption peaks suggest that the as-grown film forms a stacked and ordered structure in part. For the cast film

of PHT, on the other hand, the absorption spectrum is very broad centered at 2.88 eV and no shoulders are seen. The spectrum compares well with the one for the PHT54% film, although its shape is much broader than that of the PHT54% film. The different spectral features between the as-grown and cast films of PHT demonstrate that the as-grown film is more ordered and conjugated than the cast film prepared by dissolving of the as-grown film. When the film thickness was increased, however, the main absorption peak of the as-grown film slightly shifted to a high energy side and tended to approach that of the cast film.

Fig. 2 compares cyclic voltammograms (CVs) of as-grown and cast films of PHT. The as-grown film exhibits a main redox wave at around 0.5 V with a prepeak at about 0.2 V, whereas the cast PHT film shows one redox wave at around 0.6 V with a small hump at 0.45 V. According to our previous study with chemically synthesized PHTs of different regioregularities, the redox waves at ca. 0.2 and 0.5-0.6 V are ascribable to oxidation of polymer zones of well-ordered and amorphous phases, respectively [8]. The presence of the well-ordered phase in the as-grown film is consistent with the spectroscopic observations for the PHT films described above. When the film thickness was increased, the first oxidation peak corresponding to oxidation of the ordered phase was reduced in magnitude relative to the main oxidation peak and its peak position was shifted systematically to the anodic direction, as shown in Fig. 3. Skompska has reported that the anodic branch of CV for the electrosynthesized PMT film is a superposition of two overlapping oxidation peaks [22]. The less positive peak is ascribed to oxidation of long-chain polymer segments that are formed mainly at the beginning of the electropolymerization and the other peak to the oxidation of short-chain segments formed later. In view of this, it is likely that an electrochemical oxidation of 3-hexythiophene at an early stage leads to better conjugated and ordered segments than those in the bulk and near the polymer surface. The M_w/M_n value as large as 3.1 for the electrosynthesized PHT may be explained on this basis, although additional structural disorders might be introduced during the processes of dissolving, casting, and drying. By taking account of the above findings and for avoiding unnecessary complications, thick as-grown films similar in nature to cast films were employed for the mobility study described below.

Doping levels and conductivities measured simultaneously are plotted against potential in Figs. 4 and 5, respectively. In the intermediate potential range between 0.1 and 0.4 V, the doping levels for the as-grown film are slightly higher than those for the cast film, although they are in good agreement in the potential regions below 0.1 V and above 0.4 V. The maximum doping levels are ca. 30% for both the as-grown and cast films. This value compares well with the maximum doping levels reported earlier for spun and cast films of PHTs [8]. A striking difference between as-grown and cast films is seen in the conductivity plot of Fig. 5. The conductivity for the as-grown film increases steadily with potential and levels off at 0.6 V, while that for the cast film increases in two steps, i.e. an initial slow increase followed by a rapid rise at potentials beyond 0.25 V (ca. 1% doping level). For both the films, the conductivities are increased by ca. seven orders of magnitude in the potential range studied. The maximum conductivities are 1.0 and 0.6 S cm⁻¹ for as-grown and cast films, respectively. It has been reported that the conductivity of an as-grown film is higher than that of a doped solution-cast film [23].

Mobilities evaluated from the data of conductivity and doping level shown in Figs. 4 and 5 are plotted in Fig. 6 as a function of doping level. As is expected in the introduction, a clear difference is seen in the mobility plots between as-grown and cast films, in spite of the fact that the two kinds of PHT films comprise PHT polymers having identical chemical structure and composition. For both the as-grown and cast films, at the lowest doping level of ca. 0.01%, mobilities of charge carriers are close to each other at around $3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. As for the as-grown film, the mobility is almost constant in the low doping region between 0.01% and 0.2%. In contrast, the mobility plot for the cast film of PHT shows a gradual decrease in the low doping region up to 1%, although mobilities for both the films drastically increase at higher doping levels. The maximum mobilities are 0.8×10^{-2} and $0.4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, for the as-grown and cast films at a doping level of ca. 20%. The trend in the mobility change for the as-grown film of PHT resemble well those for electrochemically synthesized PT and PMT films reported earlier [1,4]. As shown in Fig. 7, the mobility plot for the electrosynthesized PT film is very similar to that of the as-grown PHT film, in particular, except for the polaron mobility for the former being three times lower than that for the latter. The slightly higher polaron mobility for the as-grown PHT film may be due to the well-ordered phase adjacent to the substrate surface. The ordered and stacked structure of polymer chains enhances an interchain hopping of polarons, leading to higher polaron mobilities. On the other hand, the mobility plot for the cast film has a close resemblance in feature with those for spun or cast films of chemically synthesized PHT or POT [5,8]. Mobility plots for cast films of both chemically and electrochemically synthesized PHTs are compared in Fig. 8. The plots for chemically synthesized PHTs shift upwards with the increase in regioregularity of PHT. The regioregularity of electrosynthesized PHT is found to be 77%. However, the plot for the cast film of electrosynthesized PHT is placed in a lower position than those for the cast films of PHT70% and PHT81%, or rather close to the mobility plot for a regiorandom PHT (PHT54%). Most likely, the evaluation of regioregularity for the electrosynthesized PHT is erroneous.

An *in situ* ESR study was carried out with as-grown and cast films of PHT. Fig. 9 summarizes the results. The ESR signals for the as-grown PHT film could be decomposed into one Lorentzian and two Gaussian components with different g -values, while the cast PHT film gave one Lorentzian and one Gaussian components. The Gaussian components shown by filled circles in Figs. 9a)-d) were ascribable to defects because their spin numbers (N_s) and linewidths (ΔH_{pp}) are independent of the number of electrons (N_q) removed from the PHT films upon oxidation and they are observed even for almost completely reduced films. Such a Gaussian component has not been observed for cast and spun films of chemically synthesized PHTs [8], implying that defects are introduced in the PHT films during electrochemical synthesis of polymers. It is to be noted here that, if the ESR signals due to defects being neglected, Figs. 9a) and b) resemble the $\log N_s$ versus $\log N_q$ plots for the PHT97% and PHT54% films, respectively, with respect to the number of ESR components and the trend of the change [8]. CV and spectroscopic studies have already demonstrated that the as-grown film consists of well-ordered and amorphous phases, and the cast film has only an amorphous phase. In view of this, it is reasonable to presume that the Lorentzian signals observed with both as-grown and cast films originate from polarons in an amorphous phase

and the Gaussian ones from polarons in an crystalline phase. Irregular couplings of thiophene rings which are likely to generate defects having unpaired electrons may be related to the wrong evaluation of regioregularity for the electrosynthesized PHT.

In what follows, we will discuss features of the mobility plots for as-grown and cast PHT films with an emphasis on a possible cause for the initial decrease of mobility observed commonly for cast or spun films of conducting polymers [5,8]. It is now clear that decreasing or constant mobilities in the low doping regime are not related to a chemical structure of conducting polymers, but to a difference in the film structure arising from separate film preparation methods. We will abandon our previous interpretation for the gradual decrease of mobility for the cast films [5] and propose an alternative one based on *swelling* of the polymer films during doping as described below.

Intensive studies have been performed so far on volume changes of π -conjugated polymers such as polyacetylene, polypyrrole, polyaniline, and poly(alkylthiophene)s during electrochemical doping or dedoping [24-27]. The small volume change is sensitively detected by the bending beam method and the phenomenon is applied to building of artificial muscles or soft actuators. It is presumed that the mechanical deformation arises from doping/dedoping of anions, repulsive force due to like charges on polymer chains, and conformational changes of polymer chains. Chen and Inganäs have studied doping-induced volume changes for cast films of chemically synthesized POT and electrosynthesized POT films by using the bending beam method with AN as solvent [28]. They have found that the maximum volume change for the former film is 1.08% at 1.2 V, much greater than 0.14% for the latter film. The large difference in the volume change was ascribed to a highly cross-linked structure of the electropolymerized film which increases hardness of the film. Obviously, this reasoning is quite reasonable. In addition to this, however, one can imagine another cause for smaller volume change for the electropolymerized films than the cast films, as described below. During an electropolymerization process, a PHT film is obtained automatically as a film heavily doped with anions. Consequently, the as-grown film may take a polymer chain structure so as to incorporate anions at its production stage. It is likely that even after anions are removed by electrochemical reduction of the film (dedoping), the chain structure is kept almost unchanged and an interstitial region to accept anions remains. Therefore, when the as-grown film is doped again, no considerable change in chain structure may not occur. This is not the case for cast or spun films. When cast or spun films were prepared on the substrate, they were at a neutral state and no dopant ions were included in the film. It is known that CV curves of a pristine cast or spun film are different in shape between the very initial scan and subsequent scans. These pristine films are substantially dense and may not allow dopant anions to easily enter into the films. A considerable change in the CV curve after an electrochemical stimulus is ascribed to expansion of the polymer film for enabling anions to enter smoothly. Once the film is relaxed and experiences incorporation of anions, expansion/contraction of the polymer film will take place reversibly upon electrochemical oxidation/reduction. When the doping level is increased, the cast or spun films swells and the film expansion results in weakening of interchain interaction. Thus, the polaron mobility, which would be observed in the low doping region, will be reduced because swelling of

the film leads to a lower rate of a hopping transport of polarons between adjacent polymer chains [7,8]. This results in the observed decrease of mobility in the low doping region, as shown in Fig. 6. As the doping level is increased beyond 1% doping level, on the other hand, mobilities for both as-grown and cast films start to increase drastically and the difference in mobility between both of the films becomes smaller. It has been demonstrated that mobilities in the high doping region are controlled by an intrachain hopping of charge carriers rather than an interchain route [7,8]. In this doping region, therefore, mobilities of charge carriers may not be affected much by swelling of the PHT film.

Conclusion

Two kinds of PHT films were prepared by electropolymerization of monomer (as-grown film) and by casting of PHT solution recovered from as-grown PHT films (cast film). It was found that both films include structural defects giving rise to ESR signals with a Gaussian component and leading to a wrong evaluation for regioregularity of the PHT polymer. CV and absorption measurements suggested that the as-grown films consisted of both crystalline and amorphous phases like a regioregular PHT film, whereas the cast films comprised a single amorphous phase similarly to a regiorandom film. This finding was supported further by *in-situ* ESR measurements. Mobility measurements were made with the two kinds of PHT films with the same chemical structure and composition, but with different film structures. Cast films of PHT showed mobility plots with an initial decreasing trend, whereas no mobility decrease was observed for as-grown PHT films. The difference in the mobility plot was explained in terms of a doping-induced swelling that is more likely for the cast films.

References

- [1] Y. Harima, T. Eguchi, K. Yamashita, *Synth. Met.* 95 (1998) 69.
- [2] Y. Harima, T. Eguchi, K. Yamashita, K. Kojima, M. Shiotani, *Synth. Met.* 105 (1999) 121.
- [3] Y. Harima, Y. Kunugi, H. Tang, K. Yamashita, M. Shiotani, J. Ohshita, A. Kunai, *Synth. Met.* 113 (2000) 173.
- [4] Y. Harima, Y. Kunugi, K. Yamashita, M. Shiotani, *Chem. Phys. Lett.* 317 (2000) 310.
- [5] Y. Kunugi, Y. Harima, K. Yamashita, N. Ohta, S. Ito, *J. Mater. Chem.* 10 (2000) 2673.
- [6] R. Patil, Y. Harima, K. Yamashita, K. Komaguchi, Y. Itagaki, M. Shiotani, *J. Electroanal. Chem.* 518 (2002) 13.
- [7] Y. Harima, X. Jiang, Y. Kunugi, K. Yamashita, A. Naka, K.K. Lee, M. Ishikawa, *J. Mater. Chem.* 13 (2003) 1298.
- [8] X. Jiang, R. Patil, Y. Harima, J. Ohshita, A. Kunai, *J. Phys. Chem. B* 109 (2005) 221.
- [9] V.I. Arkhipov, P. Heremans, E.V. Emelianova, G.J. Adriaenssens, H. Bässler, *Appl. Phys. Lett.*, 82 (2003) 3245.
- [10] V.I. Arkhipov, P. Heremans, E.V. Emelianova, H. Bässler, *Phys. Rev. B* 71 (2005) 045214.
- [11] V.I. Arkhipov, E.V. Emelianova, P. Heremans, H. Bässler, *Phys. Rev. B* 72 (2005) 235202.
- [12] I.I. Fishchuk, A.K. Kadashchuk, A. Vakhnin, Yu. Korosko, H. Bässler, B. Souharce, U. Scherf, *Phys. Rev. B* 73 (2006) 115210.
- [13] G. Shiavon, S. Sitran, G. Zotti, *Synth. Met.* 32 (1989) 209.
- [14] R.D. McCullough, R.D. Lowe, M. Jayaraman, D.I. Anderson, *J. Org. Chem.* 58 (1993) 904.
- [15] R.D. McCullough, *Adv. Mater.* 10 (1998) 93.
- [16] T. Kaniowski, W. Luzny, S. Nizioł, J. Sanetra, M. Trznadel, *Synth. Met.* 92 (1998) 7.
- [17] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J. H. Spiering, R.A.J. Janssen, E.W. Meijer, *Synth. Met.* 111-112 (2000) 129.
- [18] K.E. Aasmundtveit, E.J. Samuelsen, M. Guldstein, C. Steinsland, O. Flornes, C. Fagermo, T.M. Seeberg, L.A.A. Pettersson, O. Inganäs, R. Feidenhans'l, S. Ferrer, *Macromolecules* 33 (2000) 3120.
- [19] H.J. Fell, E.J. Samuelsen, J. Als-Nielsen, G. Grübel, J. Mardalen, *Solid State Commun.* 94 (1995) 843.
- [20] S.D.D.V. Rughooputh, S. Hotta, A.J. Heeger, F. Wudl, *J. Polym. Sci., Polym. Phys. Ed.* 25 (1987) 1071.
- [21] D. Fichou, J.M. Nunzi, F. Charra, N. Pfeffer, *Adv. Mater.* 6 (1994) 64.
- [22] M. Skompska, *Electrochim. Acta* 44 (1998) 357.
- [23] J. Roncali, *Chem. Rev.* 92 (1992) 711.
- [24] E.W.H. Jager, E. Smela, O. Inganäs, *Science* 290 (2000) 1540.
- [25] T.F. Otero, M.T. Cortés, *Adv. Mater.* 15 (2003) 279.
- [26] E. Smela, *Adv. Mater.* 15 (2003) 481.
- [27] S. Hara, T. Zama, W. Takashima, K. Kaneto, *Synth. Met.* 149 (2005) 199.
- [28] X. Chen, O. Inganäs, *Synth. Met.*, 74 (1995) 159.

Figure Captions

Fig. 1. Absorption spectra of (1) as-grown and (2) cast films of PHT, and cast films of (3) PHT97% and (4) PHT54% in their neutral states.

Fig. 2. Cyclic voltammograms of as-grown and cast films of PHT at 10 mV s^{-1} in $\text{Et}_4\text{NClO}_4(0.1 \text{ M})/\text{AN}$.

Fig. 3. Cyclic voltammograms of as-grown films of PHT at 10 mV s^{-1} in $\text{Et}_4\text{NClO}_4(0.1 \text{ M})/\text{AN}$. Thicknesses of PHT films are (a) 0.30, (b) 0.80, (c) 1.2, and (d) 3.3 μm .

Fig. 4. Doping levels of (\circ) as-grown and (\square) cast films of PHT as a function of potential.

Fig. 5. *In situ* conductivities of (\circ) as-grown and (\square) cast films of PHT as a function of potential.

Fig. 6. Mobilities of charge carriers in (\circ) as-grown and (\square) cast films of PHT at different doping levels.

Fig. 7. Comparison of mobility plots between as-grown films of (\circ) PHT and (\bullet) PT films. The mobility plot for the PT film is cited from Ref. [4].

Fig. 8. Mobility plots for the cast film of (\square) PHT in the present study and (\blacktriangledown) PHT97%, (\blacklozenge) PHT81%, (\blacktriangle) PHT70%, and (\blacksquare) PHT54%. The mobility plots for PHT97% to PHT54% films are cited from Ref. [8].

Fig. 9. (a) and (b) Double logarithmic plots of N_s versus N_q , and (c) and (d) plots of ESR linewidth versus logarithm of doping level for (a) and (c) as-grown, and (b) and (d) cast films of PHT. Symbols (\bullet) and (\square) denote Gaussian components with different g -values, and (\circ) represents a Lorentzian component.

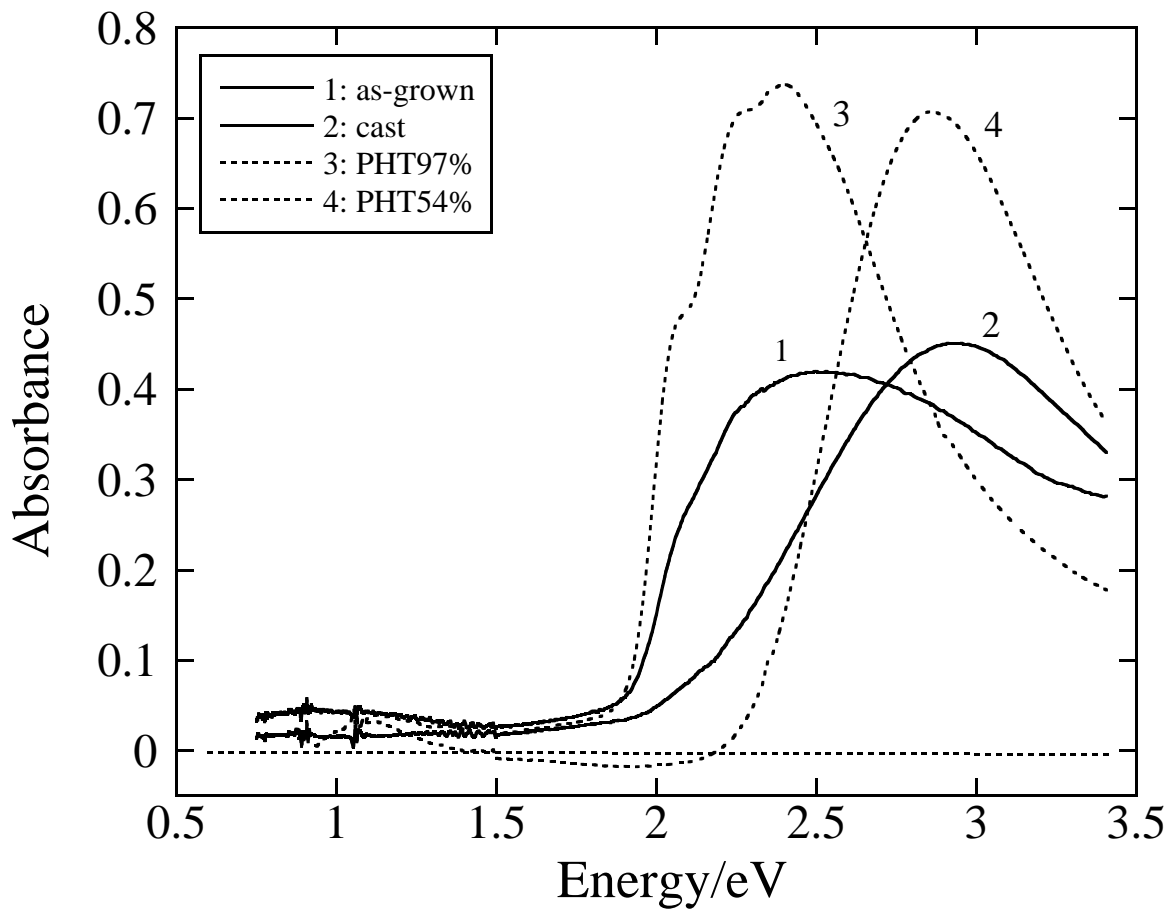


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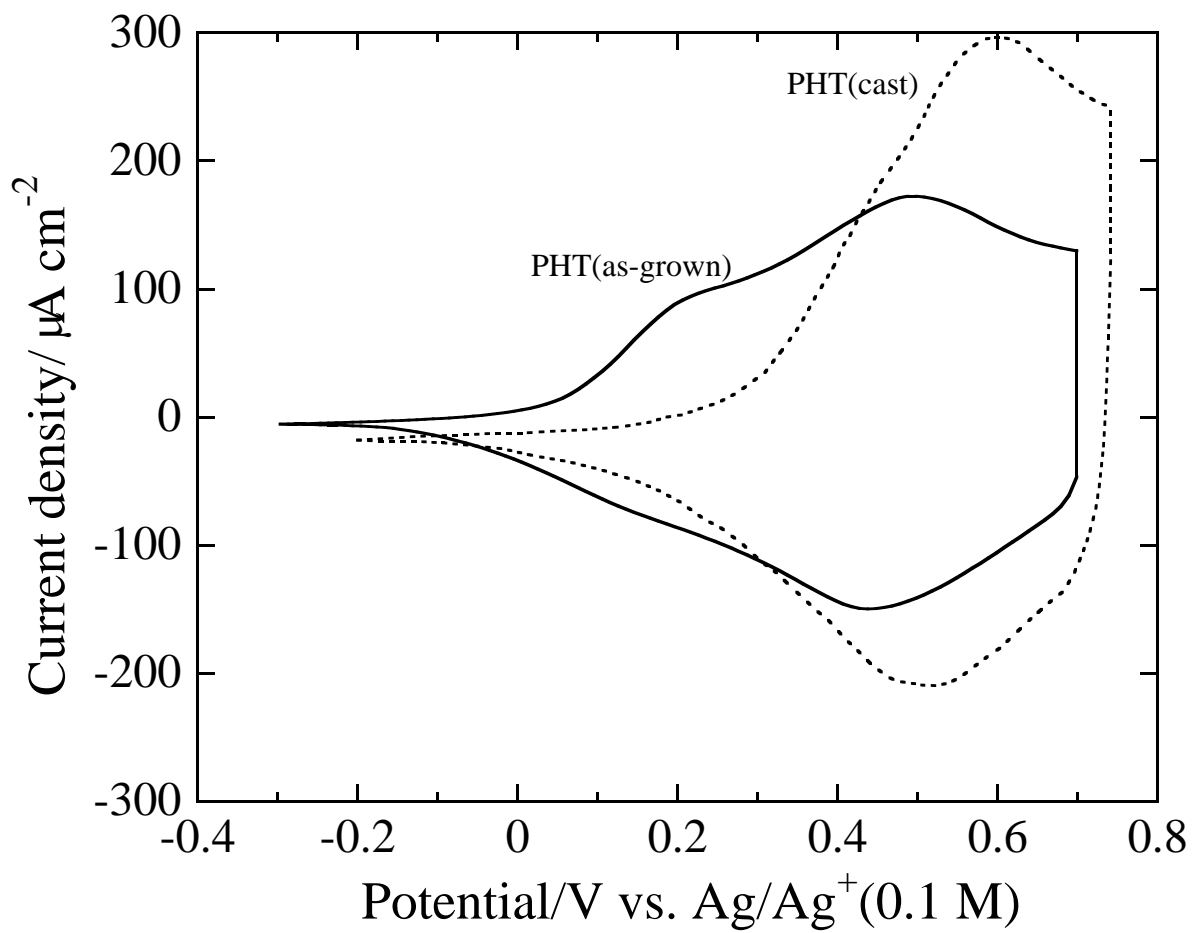


Fig. 2. Harima et al.

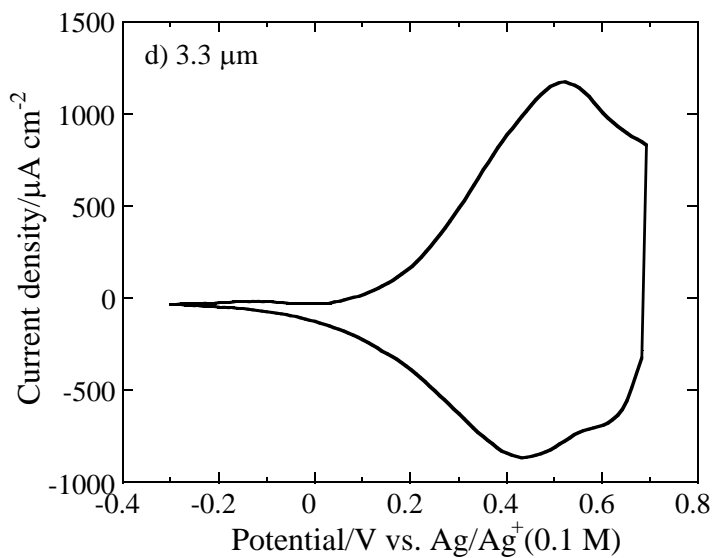
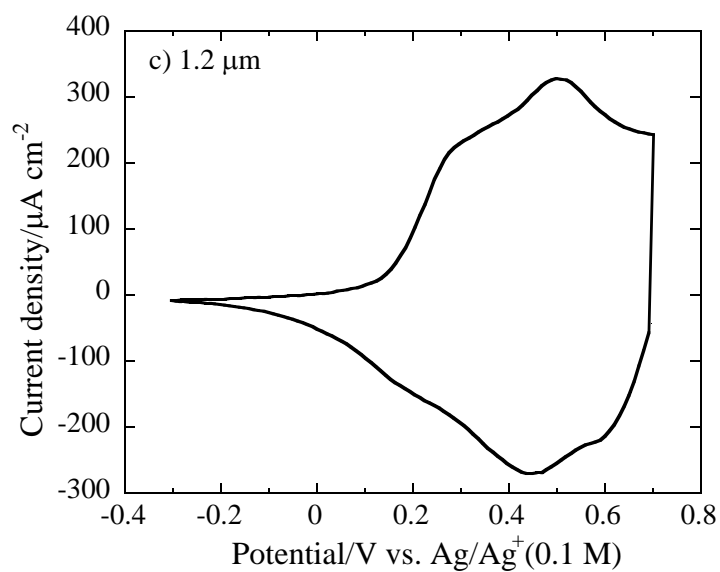
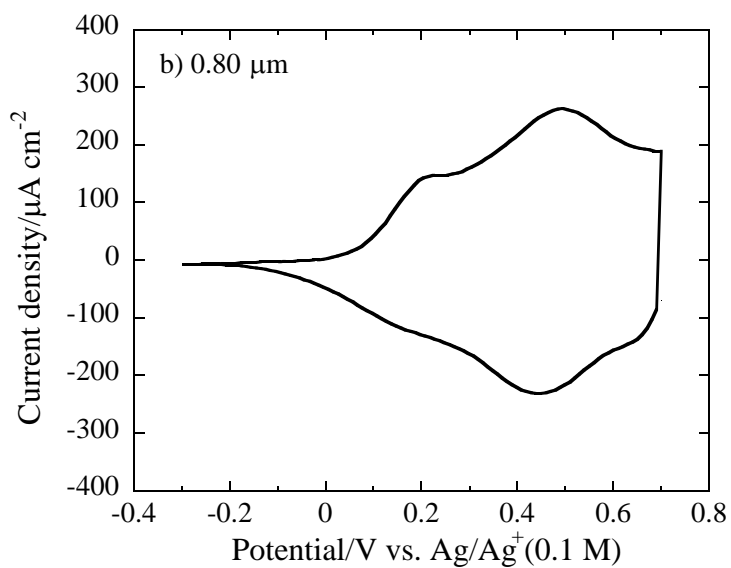
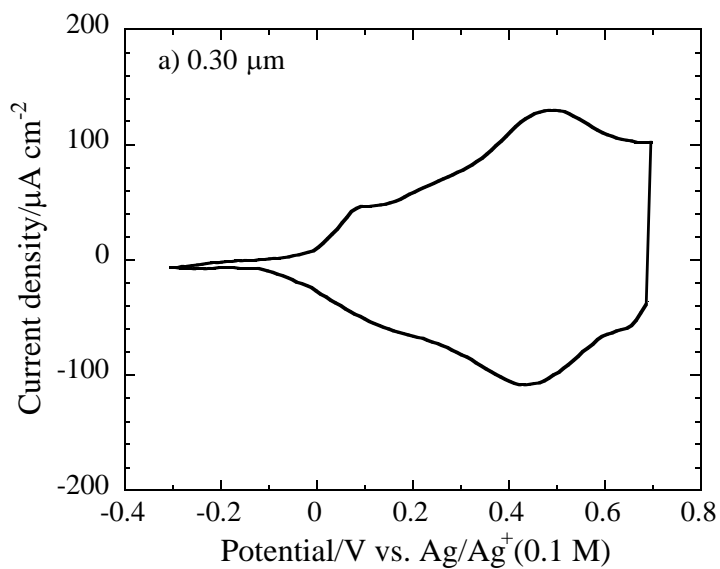


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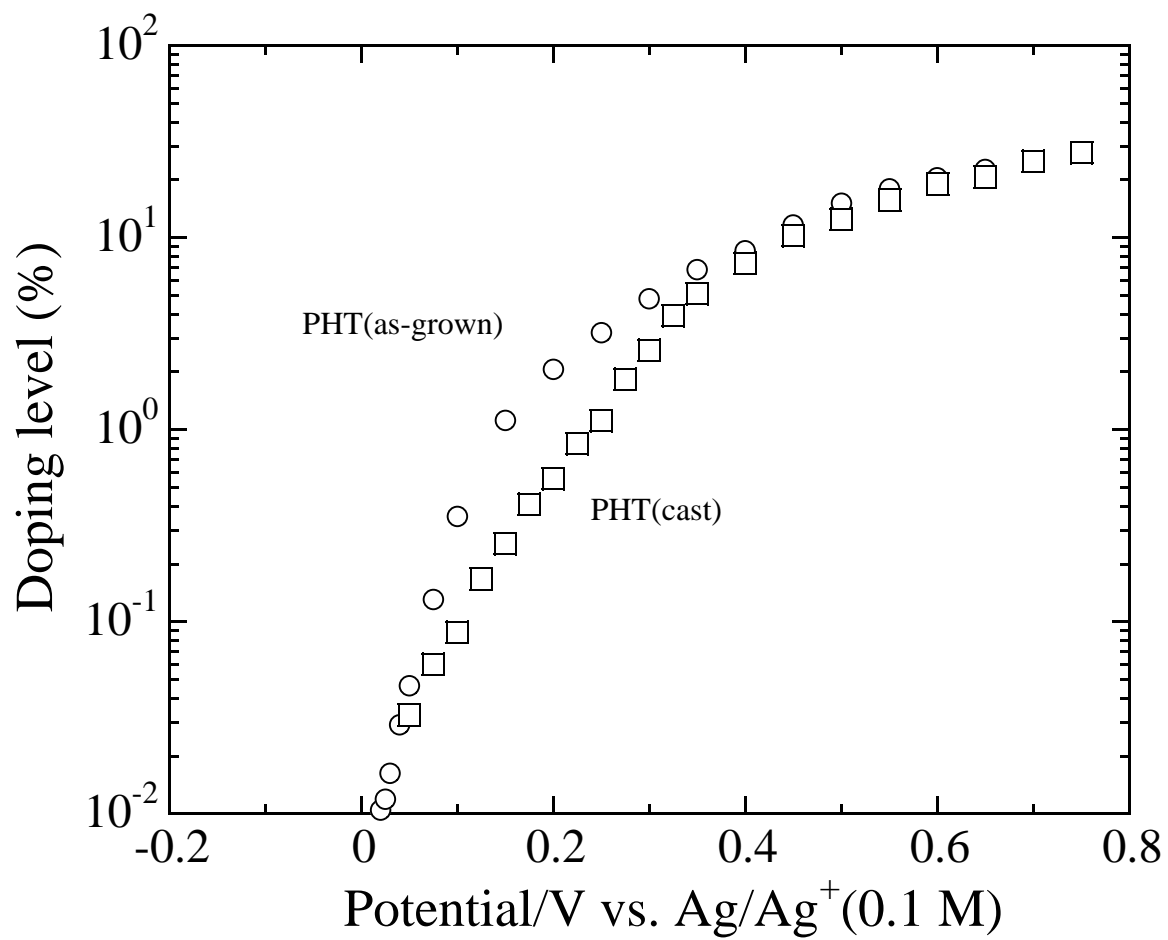


Fig. 4. Harima et al.

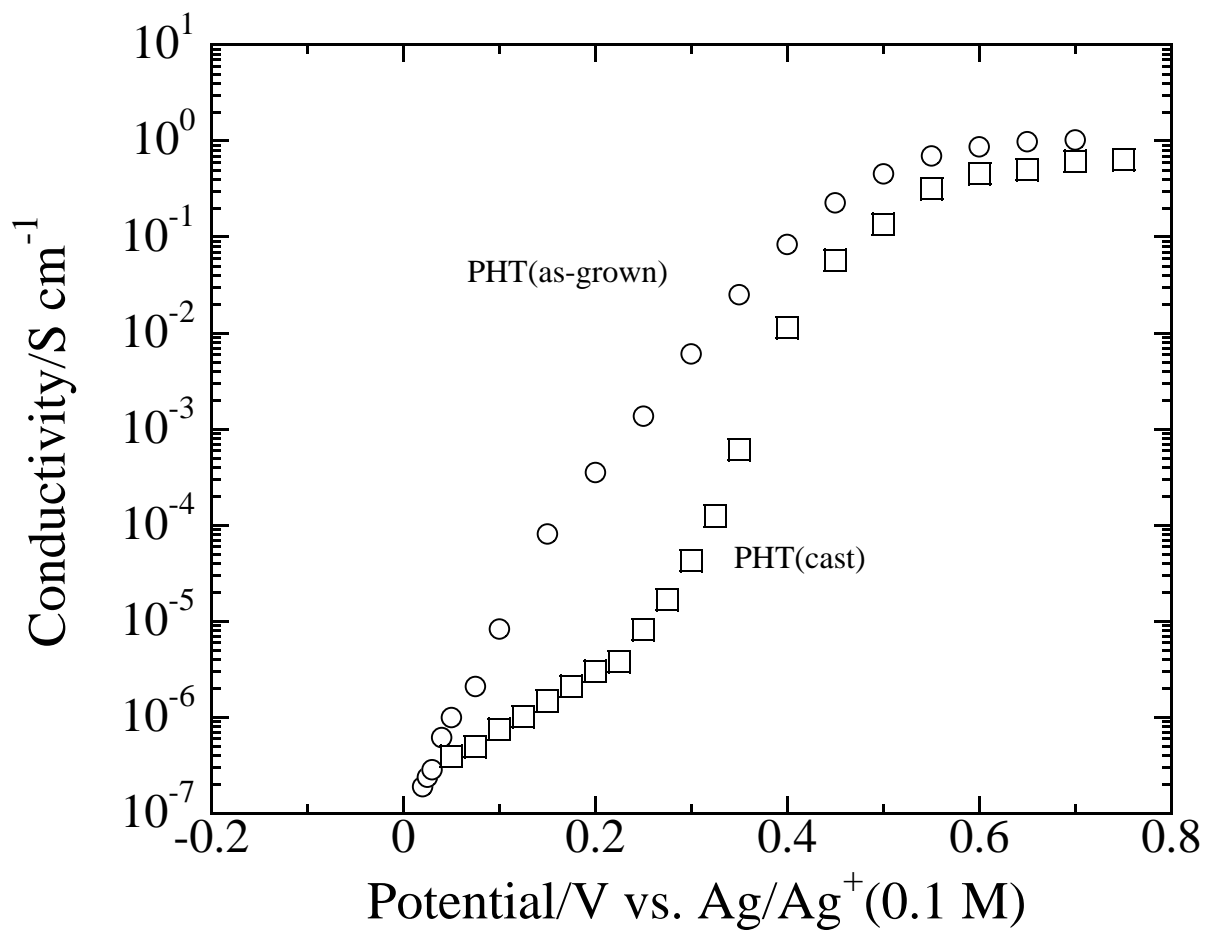


Fig. 5. Harima et al.

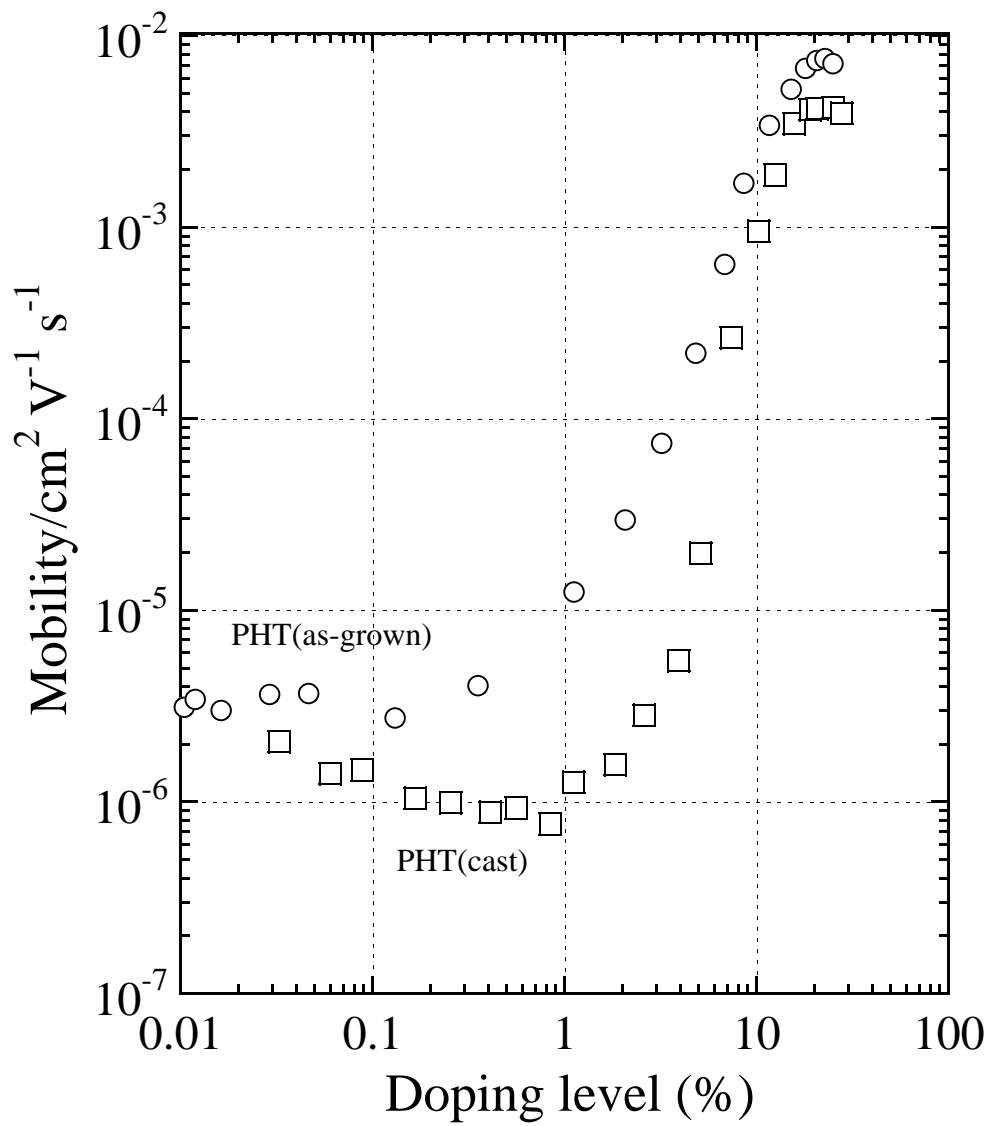


Fig. 6. Harima et al.

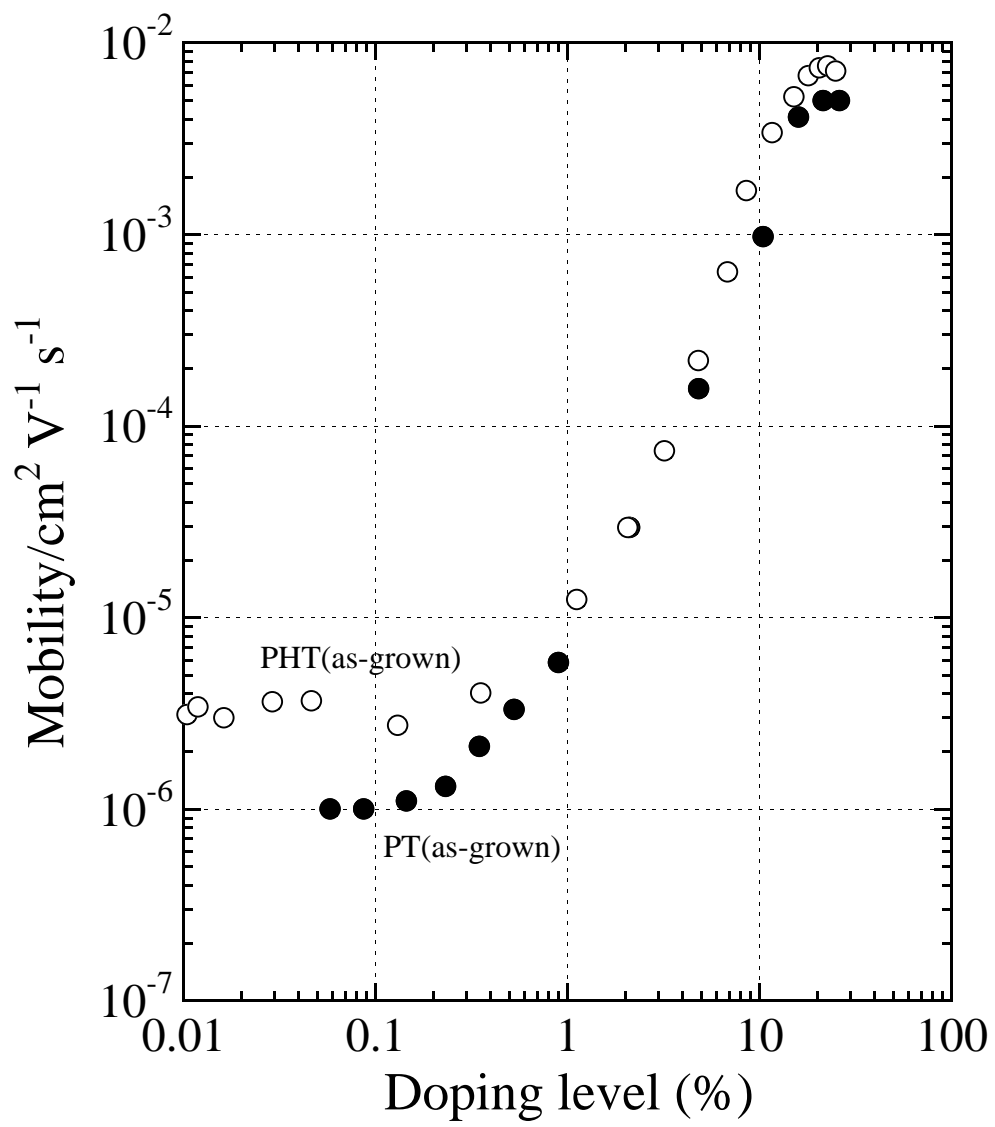


Fig. 7. Harima et al.

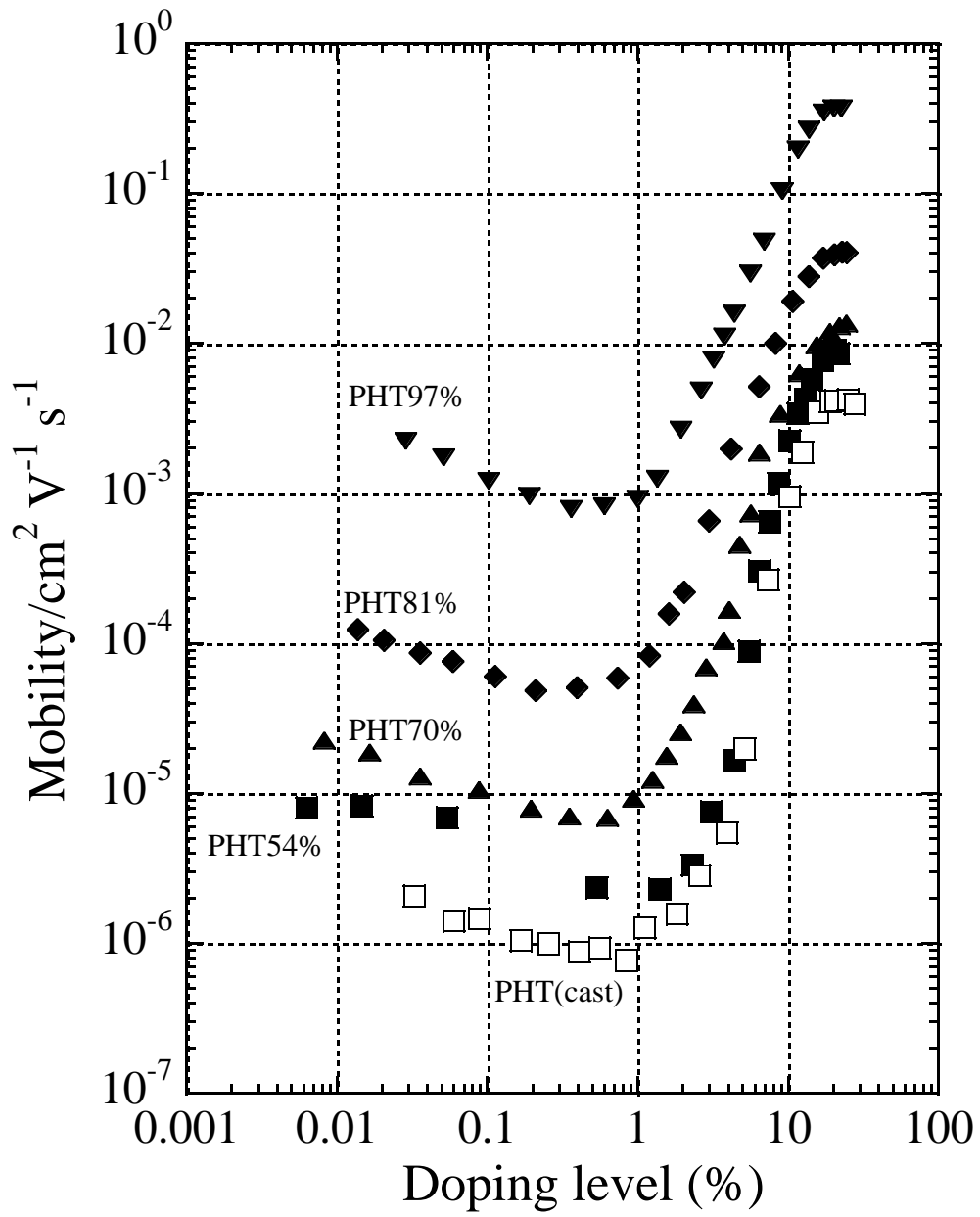


Fig. 8. Harima et al.

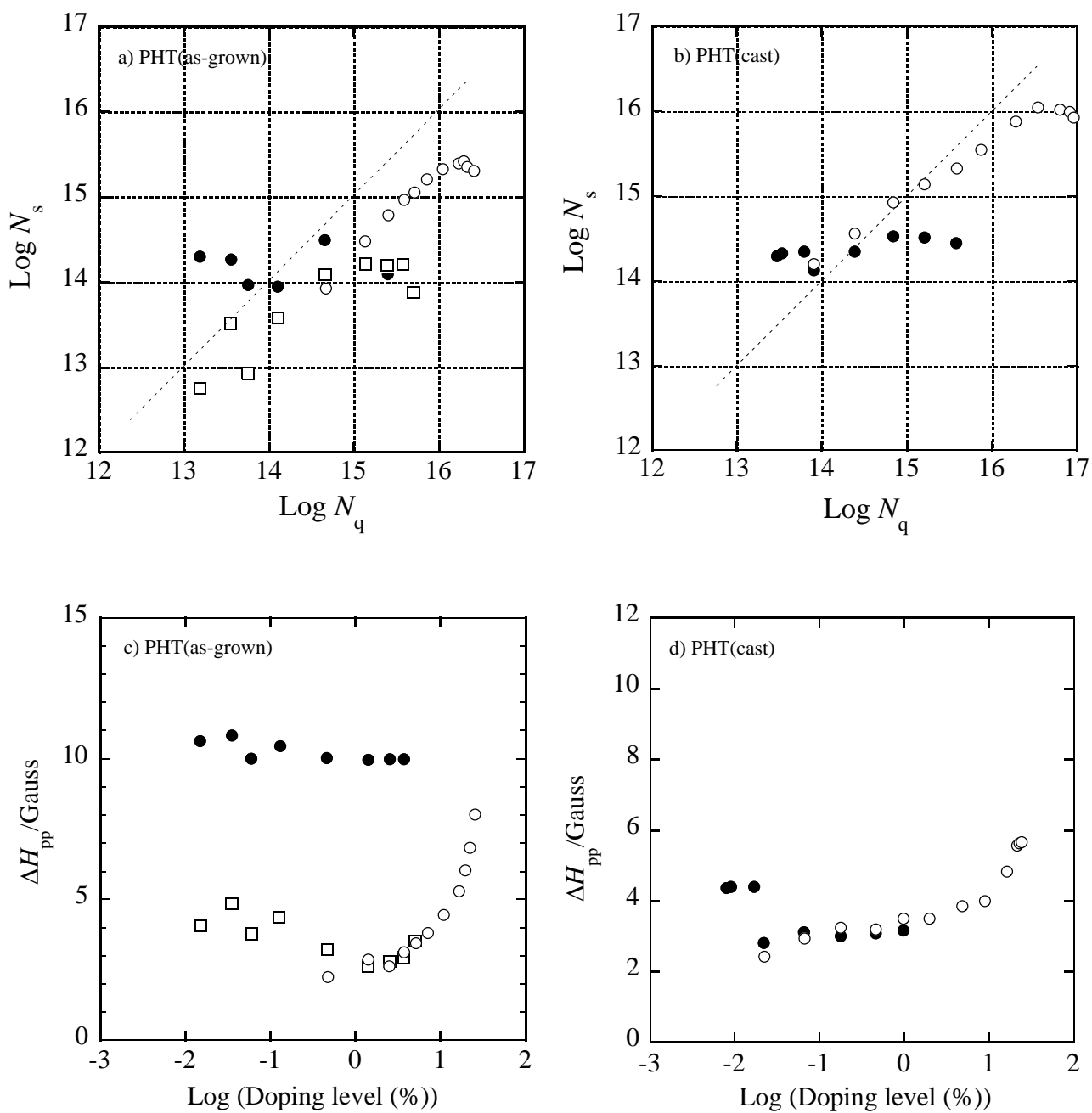


Fig. 9. Harima et al.