Influence of extended π-conjugation units on carrier mobilities in conducting polymers

Y. Harima,[a,*] D-H. Kim,[a] Y. Tsutitori,[a] X. Jiang,[b] R. Patil,[c] Y. Ooyama,[a] J. Ohshita,[a] and A. Kunai[a]

[a]*Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan*
[b]*College of Chemistry and Environment Science, Nanjing Normal University, 122 Ninghai Road, Nanjing 210097, P R China*
[c]*Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India*

Abstract

Carrier mobilities in thin films of copolymers with repeat units consisting of oligothiophenes bridged by Si atoms are measured over a range of doping level, where the numbers of thienylenes in the repeat unit are 7, 8, 10, 12, and 14. The mobilities for these polymer films increased with the increase in doping level and the mobility enhancement followed an increasing order of the π-conjugation length. The magnitude of the mobility increase for the Si polymer comprising 14 thiophene units reached ca. 10^4, implying that this π-conjugation length is almost sufficient to reproduce transport properties of polythiophenes.

*Corresponding author. Fax: +81-82-424-5494.

E-mail address: harima@mls.ias.Hiroshima-u.ac.jp (Y. Harima).

1. Introduction

Clarification of charge transport mechanisms is one of the most intriguing topics on conducting polymers. Their conductivities change drastically by chemical or electrochemical doping, and conductivities of some polymers reach 100 S cm^{-1} or above when doped heavily. Many works have been focused on this topic from theoretical as well as experimental viewpoints [1-5].

In recent years, we have proposed a novel electrochemical technique to evaluate mobilities in conducting polymers and have discussed conduction mechanisms in terms of mobilities measured as a function of doping level [6-10]. Here, the mobility is an intensive physical property which characterizes transport of charge carriers and thus conduction mechanisms can be discussed reasonably using mobilities in place of conductivities that are products of mobility and carrier density (doping level). The technique was applied to a series of monosilanylene-oligothienylene copolymers that are abbreviated as PS*n*T, where *n* denotes the number of thienylene units in the repeat unit [11,12]. Oligothienylenes in the PS*n*Ts are bridged by monosilanylenes and thus a charge transport through the polymer chain are highly restricted by the presence of Si atoms acting as a barrier against a charge hopping. With this series of polymers, consequently, one can clarify a possible role of an intrachain hopping of charge carriers in the overall charge transport process. When PS*n*Ts with n=5 to 9 were examined [12], mobilities in the low doping levels below 1% had almost a common value of 3×10^{-6} cm^{2} V^{-1} s^{-1} irrespective of the π-conjugation length. Mobilities increased with the increase in doping level. However, the magnitude of the mobility increase was 3 to 30 for PS5T to PS9T, compared with ca. 10^{4} for polythiophene (PT) and poly(3-methylthiophene) (PMT) [6,9]. This clearly demonstrated that the π-conjugation unit in PS9T used as a model compound of PT is too short to reproduce conduction properties of PT or PMT.

The present study is an extension of our previous work, using PS7T, PS8T, PS10T, PS12T, and PS14T whose chemical structures are shown in Fig. 1.

2. Experimental

A series of monosilanylene-oligothienylene copolymers (PS*n*Ts: *n*=7, 8, 10, 12, and 14)) were synthesized, and details of their synthesis and characterization except for PS7T are described elsewhere [13]. M_w, M_w/M_n, and melting point of PS7T were 5,900, 1.23, and 82-86℃, respectively. Tetraethylammonium perchlorate (TEAP) from Katayama Chemicals and acetonitrile (MeCN) from Tokyo Kasei were purified as described previously [6]. Cyclic voltammetry was made with a three-electrode system using a potentiostat equipped with a function generator (Hokuto Denko HAB-151). The reference electrode used in electrochemical studies was $Ag/AgClO_4$(0.1 M). Thin films of PS*n*Ts were prepared by spin-coating with a chloroform solution of each polymer on the microarray or two-band electrode. The film thicknesses of the polymers for mobility measurements were evaluated as 0.1-0.2 μm by measuring the absorption spectra of their chloroform solutions with an assumption of the film densities being 1.0 g cm^{-3}. Simultaneous determinations of doping levels and conductivities were made in MeCN solutions as a function of potential with a microarray electrode in the low doping region and a two-band electrode in the high doping region. Mobilities were determined over a wide range of doping level by combining doping levels and conductivities. Details of the mobility measurements are described elsewhere [6,12]. All the measurements were made at room temperature.

3. Results and discussion

Cyclic voltammograms of thin films of PS*n*Ts are depicted in Fig. 1. Each of the films gives a sharp oxidation peak and the corresponding broad reduction peak. The shapes of these voltammograms were stable during many potential cyclings within the potential range of -0.2 to

0.7 V, indicative of oxidized species being stable. The redox peaks, E_{pa}/E_{pc}, were 0.57/0.34, 0.40/0.23, 0.41/0.21, 0.35/0.18, and 0.37/0.14 V for PS7T, PS8T, PS10T, PS12T, and PS14T, respectively. Redox potentials determined from the E_{pa}/E_{pc} values were 0.46, 0.32, 0.31, 0.27, and 0.26 V correspondingly. They shift systematically to the cathodic direction with the increase in length of repeating oligothienylene unit. This trend is consistent with that observed earlier with end-capped oligothiophenes in solution [14-16].

Fig. 3 depicts plots of doping level vs. potential for the five sorts of PS*n*T films. Here, the doping level is defined as the number of unit charge per thiophene ring. For all the films, doping and dedoping charges in the potential-step chronocoulometry coincided well with each other in the potential ranges investigated, suggesting a reversible nature of the doping/dedoping process at the PS*n*T films. They exhibit a similar trend: an initial linear increase of log (doping level) with potential followed by a leveling off at higher potentials. As for the PS7T film, the log (doping level) vs. potential plot in the linear portion had a slope value of 65 mV/decade, in good agreement with 60 mV/decade for a common one-electron transfer process at room temperature. In contrast, the slope values for the other PS*n*T films were slightly smaller than that of PS7T. This may be accounted for in terms of involvement of dicationic (bipolaronic) species in early oxidation processes. The maximum doping levels attained in the potential ranges investigated were 16.3, 23.4, 23.8, 24.5, and 22.7% for PS7T, PS8T, PS10T, PS12T, and PS14T, respectively. Recalling the definition of the doping level, this implies that each oligothienylene unit in PS*n*Ts can admit about two polarons or one bipolaron at the maximum.

Conductivities of the PS*n*T films measured simultaneously with the doping levels are plotted in Fig. 4 as a function of potential. The conductivity at a given potential was determined by extrapolating the resistances of a polymer film measured at various scan rates to a zero scan rate as earlier [12]. They change drastically with the increase in potential and the plots depend greatly on the polymers. The conductivity plots for PS7T to PS10T films show a slight decrease in the high potential regions. Most likely, the conductivity decrease is caused by degradation of the polymer films at higher potentials. The maximum conductivities were 3.2×10^{-3}, 0.10, 0.28, 1.2, and 2.3 S cm^{-1} for PS7T to PS14T, respectively. It is to be noted that the maximum conductivity values for PS12T and PS14T are comparable with those of common conducting polymers at heavily doped states.

Mobilities calculated by combining the data of conductivities and doping levels shown in Figs. 3 and 4 are plotted in Fig. 5 as a function of doping level, together with a similar plot for PT [9]. In the low doping region well below 1%, mobilities for PS8T to PS14T are almost constant at 2×10^{-6} cm^2 V^{-1} s^{-1}, whereas the mobility plot for PS7T shows a slight decrease and the mobility value at 0.1% doping level is a little smaller than those for the others. It is quite reasonable to presume that the mobility values in such a low doping region reflect those of polarons that are only charge carriers in the lightly doped polymer films. The polaron mobilities for PS8T to PS14T films compare well with 3×10^{-6} cm^2 V^{-1} s^{-1} reported earlier for PS6T to PS9T [12], demonstrating that they are negligibly affected by the length of π-conjugated unit through which polarons can migrate. The mobility values are also similar with the one for PT which may consist of much more extended π-conjugation unit. The negligible influence of polaron mobilities on π-conjugation length provides a further confirmation that the transport process of polarons in π-conjugated polymers is governed primarily by an interchain hopping path instead of an intrachain path. The polaron mobility for PS7T is smaller than those for other polymers. A similar distinction in mobility is already found between the group of PS6T to PS9T and PS5T [12]. The reason for this was ascribed to the fact that PS5T has no butyl groups attached to quinquethienylene unit although the other polymers have two butyl groups on a repeating oligothienylene unit. PS7T used in this study has also no butyl groups on oligothienylene unit. Therefore, the smaller mobility for PS7T may be explained on the same basis. The slight mobility decrease for PS7T in the low doping region was typical of the mobility plots for spun films of regioregular and regiorandom poly(3-hexythiophene)s [17,18]. On the other hand, mobilities measured with the FET technique for PS8T to PS14T fell in a small range between 3.4×10^{-5} and 6.9×10^{-5} cm^2 V^{-1} s^{-1} [13], although they were by one order of magnitude higher than those determined here by electrochemistry. In view of difference in principle between the two techniques, however, the difference in mobility seems to be conceivable.

A remarkable and common feature in the mobility plots of Fig. 5 is a drastic increase of mobilities with doping level. The mobilities for PS*n*T with *n*=8 to 14 start to increase at doping levels beyond 0.2-0.5%, depending on the sort of the polymers. With PS7T, they start to increase at 3% doping level, which corresponds to the potential of 0.45 V. This onset potential for the mobility increase is too low for bipolarons to be formed in the film, suggesting that bipolarons are not responsible for the mobility increase. This conclusion is consistent with that obtained in our previous study, where the role of π-dimers in the conduction process is addressed [12]. Enhancement factors defined as the ratio of a maximum mobility to a mobility in the low doping regime increased systematically with π-conjugation length in repeating units of PS*n*Ts. They were 27, 540, 1,400, 3,300, and 6,500 for PS7T to PS14T, respectively. The enhancement factor for the PS14T film is close to those for thin films of electrochemically synthesized PT and PMT [6,9] and a feature of the mobility plot resembles those for these polymers. These findings strongly demonstrate that π-conjugation length corresponding to 14-thienylene units is almost enough to reproduce charge transport properties of common conducting polymers.

In a final remark, it is to be noted that the enhancement factors found in this study are relatively greater than those reported earlier [12]. For example, the enhancement factor for PS8T in the present study is 540, much greater than 23 for PS8T synthesized previously [11]. Even for PS9T [12], it was as small as 30 compared with 1,400 for PS10T in the present study. One possible reason for this tremendous difference in the enhancement factor might be found in the difference of M_w/M_n between PS*n*Ts synthesized in this and previous works. The M_w/M_n values were 1.23, 1.68, 1.40, 1.31, and 1.73 for PS7T to PS14T in this study, much smaller than 5.09, 3.11, 4.52, 5.67, and 2.93 for PS5T to PS9T in the previous one [12]. At present, we have no reasonable explanation for this issue. However, it is likely that the difference in distribution of chain lengths of a polymer results in different film structures and hence leads to different conduction mechanisms.

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Figure captions

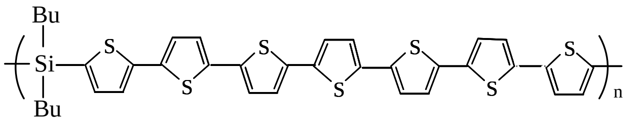
Fig. 1. Chemical structures of PS*n*Ts used in the present study.

Fig. 2. Cyclic voltammograms of thin films of PS*n*Ts in TEAP(0.1 M)/MeCN. Potential-scan rate is 100 mV s^{-1}.

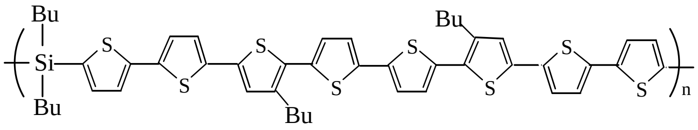
Fig. 3. Logarithmic plots of doping levels against potential for PS*n*T films in TEAP(0.1 M)/MeCN.

Fig. 4. Logarithmic plots of conductivities against potential for PS*n*T films in TEAP(0.1 M)/MeCN.

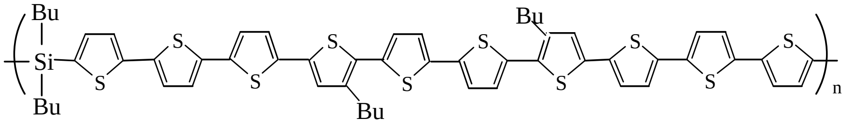
Fig. 5. Double logarithmic plots of mobility vs. doping level for PS*n*T films. For reference, a similar plot for PT is included [9].



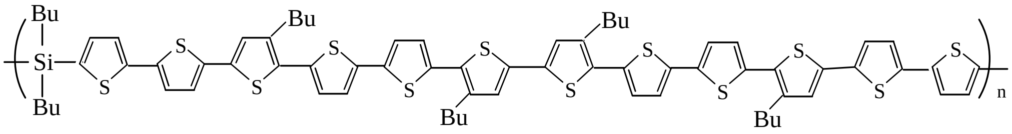
PS7T



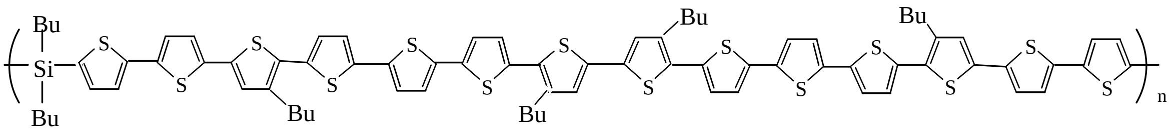
PS8T



PS10T

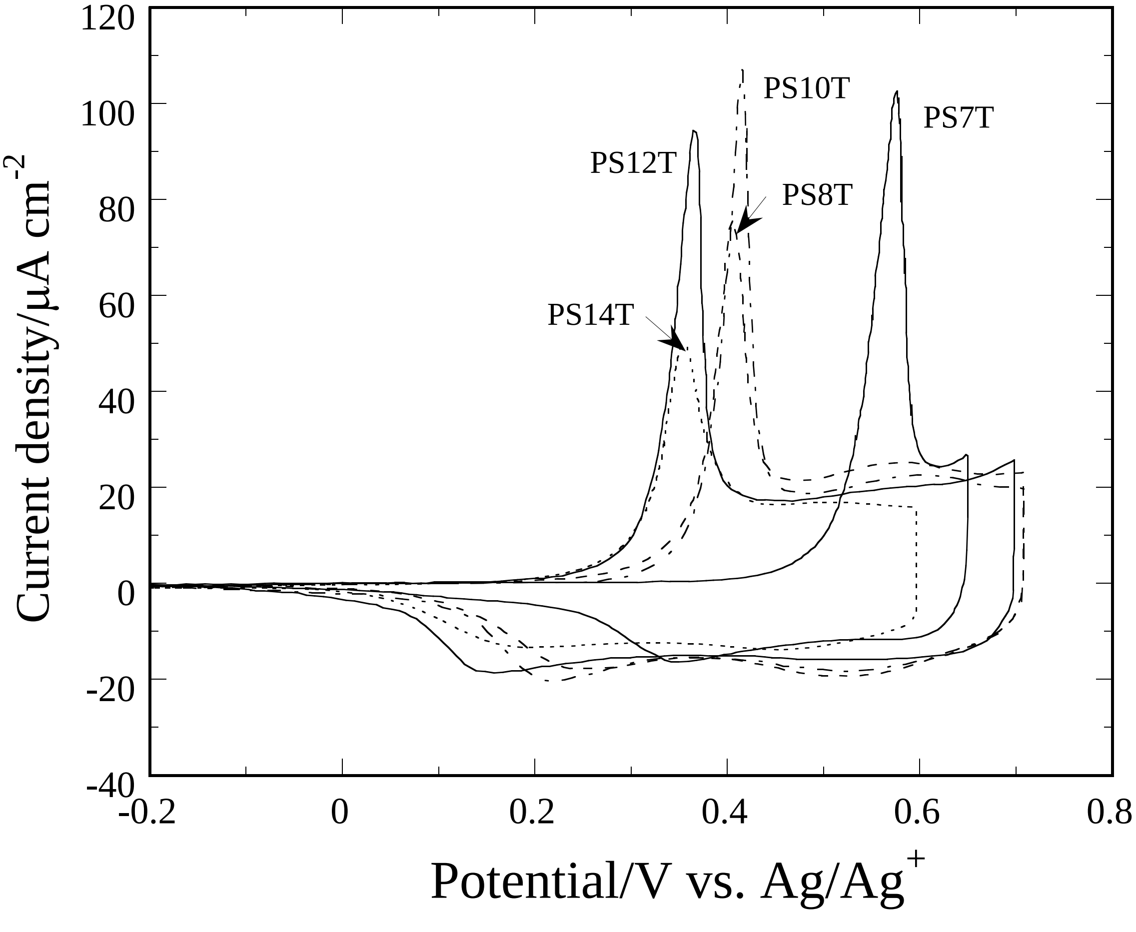


PS12T



PS14T

Fig. 1. Y. Harima et al.



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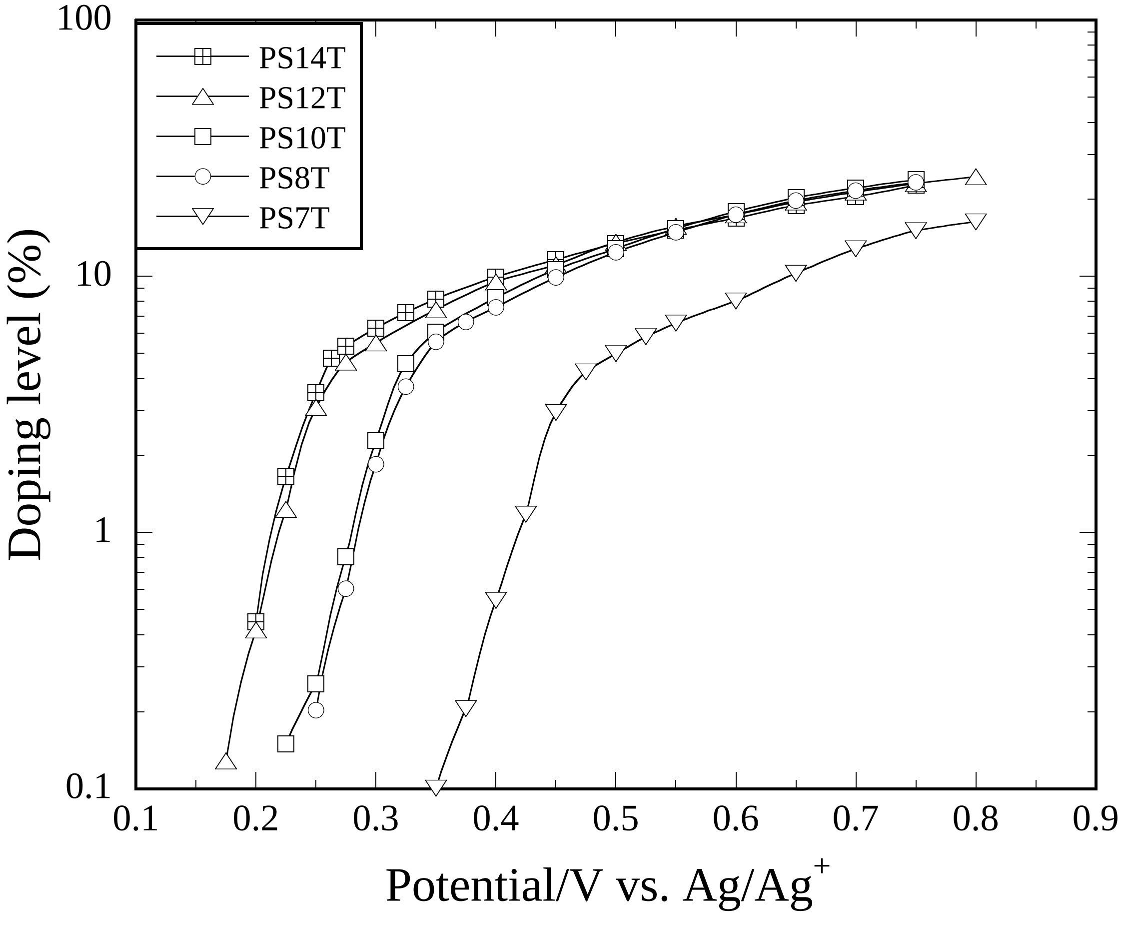

Fig. 3. Y. Harima et al.

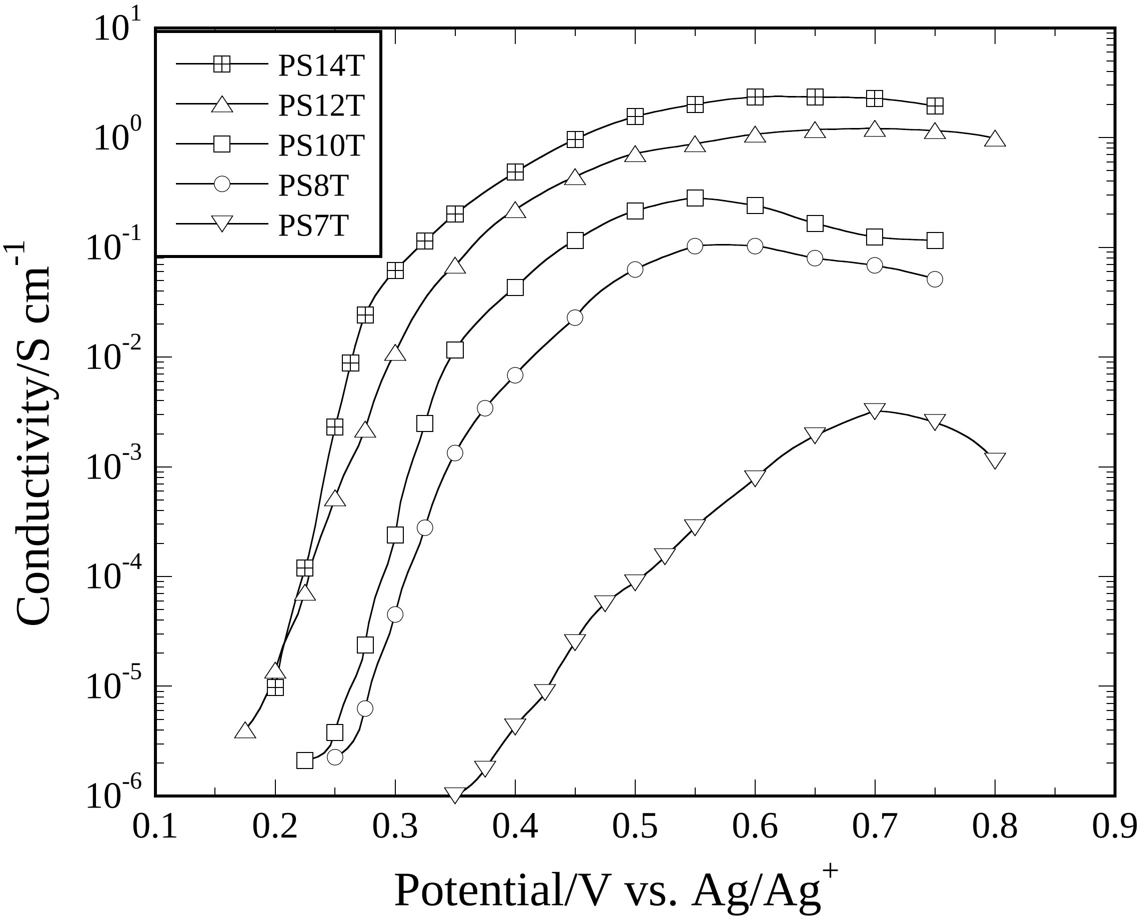

Fig. 4. Y. Harima et al.

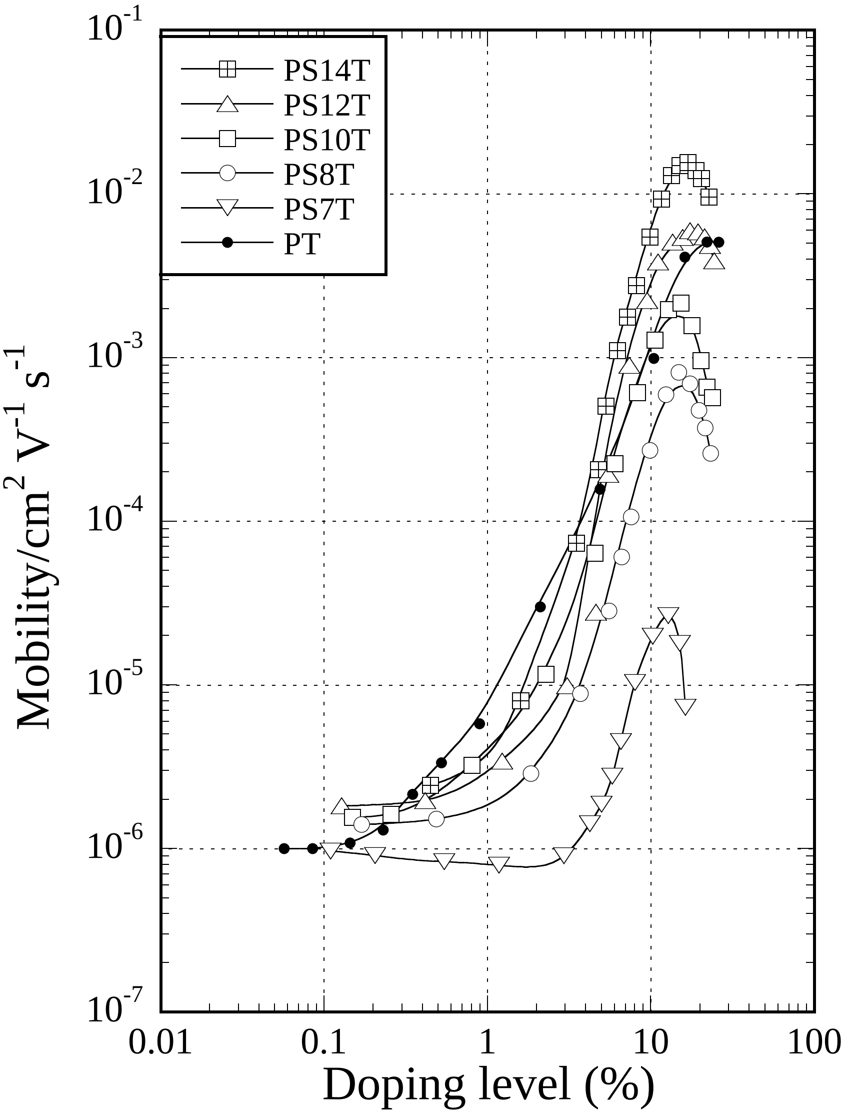

Fig. 5. Y. Harima et al.