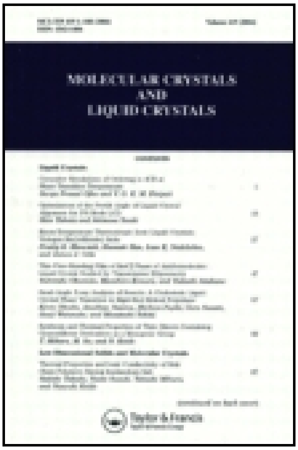

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STRUCTURE AND ELECTRICAL PROPERTIES OF THIN FILMS OF LINEAR ACENE COMPOUNDS DOPED WITH IODINE

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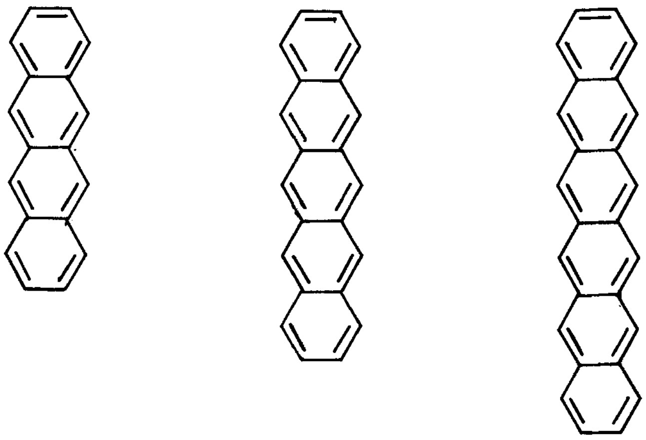
Abstract Structure and electrical conductivities of thin films of acene compounds doped with iodine were studied. In particular, doping of thin films of pentacene (PEN) with iodine caused characteristic changes in structure and electrical conductivity. The doped films exhibited high lateral conductivity above 10^2 S/cm with high anisotropy of 10^8 and well-defined layered structure in which iodine molecules intercalated between molecular layers of PEN. Metallic transport appeared in the highly ordered film at temperatures below 240 K. Transport behavior, lateral and perpendicular to the plane, was explained by two-dimensional (2D) variable range hopping (VRH) and by the tunneling mechanism, respectively. These electrical properties were strongly correlated with the degree of molecular orientation in the film.

INTRODUCTION

Conducting organic thin films have attracted significant attention because of their wide range of application for electronic devices.[1] These thin films were fabricated by techniques such as the Langmuir-Blodgett method [2] and the sublimation method [3], and most of them exhibited low electrical conductivity and low carrier mobility due to structural imperfections. Therefore, it is necessary to obtain highly ordered conducting thin film for these applications. Linear acene compounds such as anthracene, tetracene (TET) and PEN are expected to be used for these applications since the bandgap is controllable by selecting the number of aromatic rings.[4] Infinite linear acene, polyacene, is predicted to behave as a metal or a superconductor.[5,6] Several attempts [7,8] were made to synthesize polyacene; however, they were unsuccessful. Among acenes, PEN has interesting properties; it shows high conductivity of 10 S/cm without doping under high pressure of 10 GPa although it was an insulator in ambient pressure.[9] Thin films of acene compounds were prepared by the sublimation method, but doping of these films with donors or acceptors has not been reported thus far. We first demonstrated iodine doping of thin films of acene compounds prepared by the sublimation method.[10] Structure and electrical properties of thin films of acene compounds doped with iodine were studied.



TET **PEN** **HEX**

FIGURE 1 Structure of linear acene molecules

EXPERIMENTAL

Thin films of acene compounds such as TET, PEN and hexacene (HEX) were prepared by the sublimation method.[11] Molecular structure of these linear acene molecules are shown in Figure 1. Commercially available powders of TET and PEN were used as source materials. HEX was synthesized according to the literature.[12] Glassy quartz plates were used as substrates. Iodine doping of the films was conducted by introducing iodine vapor to them at room temperature after evacuating the film at a pressure of 10^{-6} Torr. The lateral conductivity of the film was measured by the DC four-terminal method. The conductivity perpendicular to the plane was measured by the DC two-terminal method. The crystalline structure of the film was measured by X-ray and electron diffractometry. Absorption spectra of the film in the infrared region and UV-visible region were measured.

RESULTS AND DISCUSSION

Structure of the films

X-ray diffraction patterns of the films of TET and PEN before and after doping with iodine were measured. The diffraction patterns of the films of TET and PEN showed peaks corresponding to (00ℓ) (ℓ=1 to 4) lines with the spacings of 13 Å and 15 Å, respectively, which are shown in Figure 2. This indicated that molecules were aligned with the long molecular axis perpendicular to the plane because the spacing was very close to the molecular length, 14 Å for TET and 16 Å for PEN. After iodine doping, the diffraction pattern of TET film remained the same as that of as-deposited film,

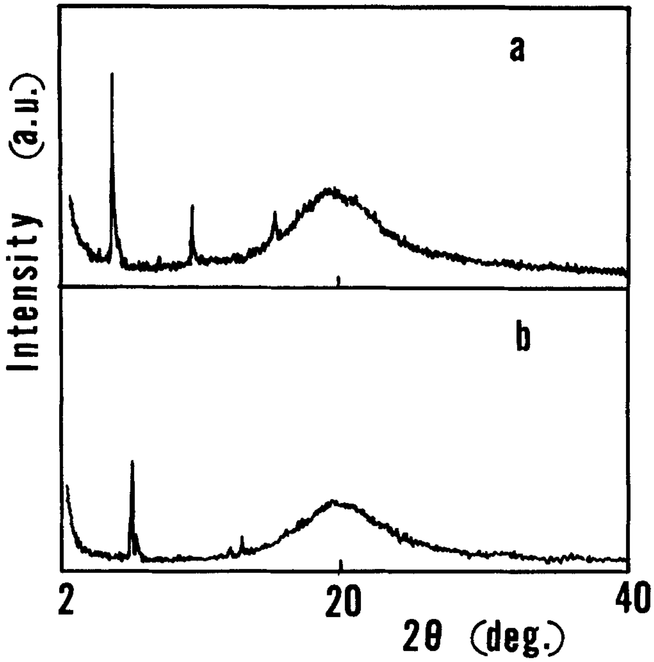
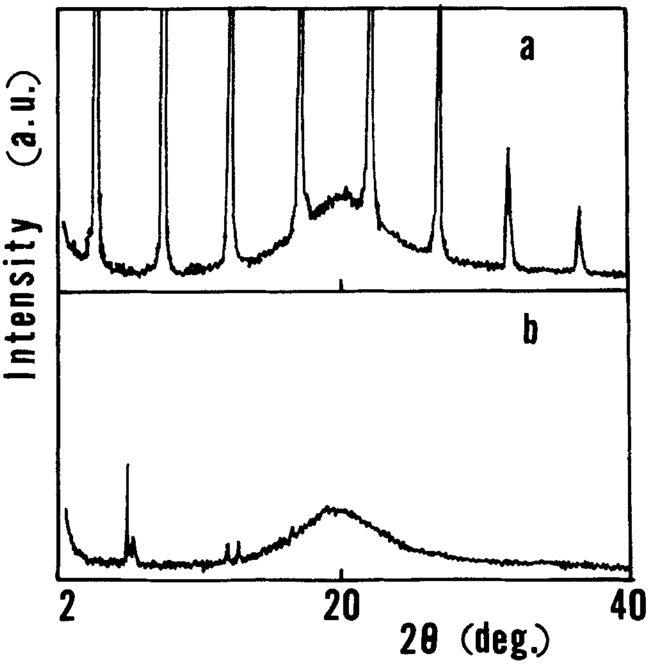


FIGURE 2 X-ray diffraction patterns of as-deposited films, (a) PEN, (b) TET.



FIRURE 3 X-ray diffraction patterns of doped films, (a) PEN, (b) TET.

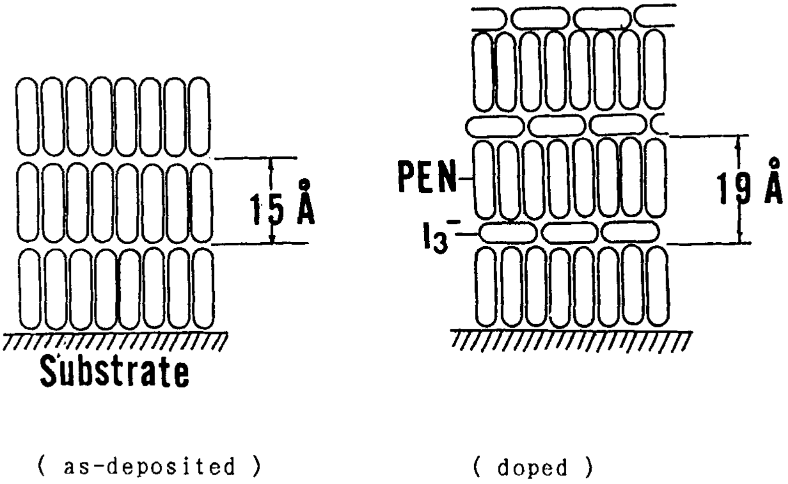
while that of PEN film significantly changed, as shown in Figure 3. Diffraction peaks of the doped film of PEN were shifted to lower angles which were assigned as $(00\ell')$ (ℓ=1 to 16) lines with the spacing of 19 Å. This indicates that iodine molecules were incorporated between molecular columns of PEN to form a layered structure since the increase of the spacing due to the doping, 4 Å, was in good agreement with the ionic diameter of iodine.[13]

In order to study the in-plane structure of PEN films, electron diffraction patterns of the PEN films before and after the doping were measured. Spot patterns were observed in the PEN films both before and after doping with iodine, while the direction of spots changed from part to part. This indicates that polycrystalline structure consisting with single crystalline domains was formed in the film. The change in these diffraction patterns due to iodine doping was small, which indicates that the in-plane structure of doped PEN film is almost the same as that of as-deposited film. The lattice parameters of PEN films were determined and are listed in Table I. The lattice constant of the c-axis in the PEN film was extended by 25 % due to doping with iodine, while those of the a-axis and b-axis in the doped film remained almost the same as those in the film before doping.[14] These results indicate that iodine molecules were selectively incorporated between molecular layers of PEN.

We conclude that the intercalation of iodine to PEN film occurred. This phenomenon is unique because the intercalation in organic materials has not been reported. The assumed structure of the PEN films before and after doping is schematicaly shown in Figure 4. The intercalation of PEN film was specific to the doping with iodine, and doping with other acceptors such as Br_2, SO_2, and NO_3 caused disorder in the molecular alignment.[10]

TABLE I Lattice parameters of PEN films before and after doping with iodine

	a (Å)	b (Å)	c (Å)	γ (deg.)
as-deposited film	7.41	5.76	15.3	90
doped film	7.64	5.85	19.3	90
powder	7.90	6.06	16.01	85.8



(as-deposited) (doped)

FIGURE 4 Structure of PEN film doped with iodine.

The formation of a charge transfer (CT) complex of PEN-I in the films was confirmed by the measurement of infrared and UV absorption spectra. The broad absorption peak around 2000 cm^{-1} appeared in the doped film after the doping, which was considered to be the CT band of PEN-I complex.[10] The UV absorption spectra of the PEN films showed that a new absorption peak at 310 nm appeared in the doped film, which was assumed to be I_3^-.[10] These results indicate that the CT complex of PEN^+-I_3^- was formed in the films. In contrast, the change in spectra of TET thin films by iodine doping did not appear, which indicates that the charge transfer complex was not formed in the doped film.

Thin film of HEX showed no peaks in X-ray diffraction patterns, which indicates that the structure of the film is amorphous. The absorption peak of I_3^- at 320 nm in the UV-visible absorption spectrum was observed.[15] This indicates the formation of HEX-iodine complex. However, the HEX film was less stable than PEN film since the deep green color of the as-deposited film rapidly disappeared upon exposure to air.

We conclude that thin films of acene molecules having more than five aromatic rings form a charge transfer complex with iodine. In particular, PEN film formed highly ordered structure in which iodine molecules intercalated between molecular layers of PEN.

Electrical properties of the films

The electrical conductivities (σ) of thin films of TET, PEN and HEX before and after doping with iodine were measured and are listed in Table II. The increase in σ of the films of PEN and HEX that was observed was due to the formation of CT complex. The σ change in the PEN film in relation to the doping time is shown in Figure 5. The σ, both lateral and perpendicular to the plane, were saturated for around 1 hour of doping, and large anisotropy ($\sigma_{/\!/}/\sigma_{\perp}$) of 10^8 was observed. The highly ordered PEN film exhibited the lateral conductivity ($\sigma_{/\!/}$) of 150 S/cm, which was 11 orders of magnitude larger than that of as-deposited film.[10]

The influence of molecular orientation of PEN thin film on the electrical properties was studied. The $\sigma_{/\!/}$ and anisotropy of the PEN film were drastically reduced with increasing the disorder of molecular alignment. This indicates that the $\sigma_{/\!/}$ and anisotropy of the doped PEN film with iodine can be controlled by the preparation conditions. The amount of iodine in the doped film was determined to be $PEN_1I_{2.2}$ by the weight gain after the doping. The carrier mobility (μ) of highly ordered PEN film was calculated to be 0.5 $cm^2 \cdot V^{-1} \cdot sec^{-1}$ from the σ and the amount of iodine, which was in good agreement with the measured μ of 0.2 to 1 $cm^2V^{-1}sec^{-1}$. The strong relation between the μ and the molecular orientation of PEN films was confirmed since the μ of amorphouslike PEN film was degraded by four orders.[11] The low σ of iodine-doped HEX film, 0.2 S/cm, was explained by the amorphous nature of the film.[15]

Temperature dependence of the lateral resistivity ($\rho_{/\!/}$) of the doped PEN films is shown in Figure 6. Highly ordered film showed metallic transport below 240 K, although semiconductive transport appeared around room temperature.[11] The metallic behavior disappea-

TABLE II Lateral conductivities of thin films of acene compounds before and after doping with iodine

Source Material	σ (before) (S/cm)	σ (after) (S/cm)
TET	$< 10^{-8}$	$< 10^{-8}$
PEN	$< 10^{-8}$	150
HEX	3×10^{-6}	3×10^{-2}

The conductivity of the doped film was measured after doping with iodine for two hours.

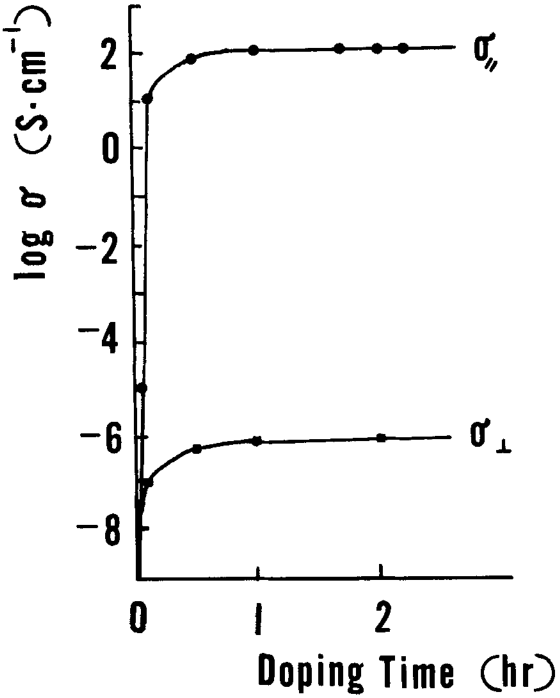


FIGURE 5 Conductivity of PEN film in relation with doping time, (a) lateral conductivity, (b) conductivity perpendicular to the plane.

red and the semiconductive part became predominant in amorphous-like film in comparison with highly ordered films. The semiconductive resistivities (log ρ) fitted the $T^{-1/3}$ dependence, which indicates that the lateral transport in the films is governed by 2D-VRH,[16] a finding which was supported by the layered structure formed in PEN films.[14] In contrast, perpendicular resistivity ($\rho_{\perp}$) of the film was almost independent of changing temperature. This indicates that the tunneling transport [18] is predominant perpendicular to the plane of the doped PEN film. The anisotropy was assumed to be induced from the conduction barrier formed in the perpendicular direction of the film. The width of the conduction barrier of highly ordered PEN film was calculated to be 13 to 19 Å on the

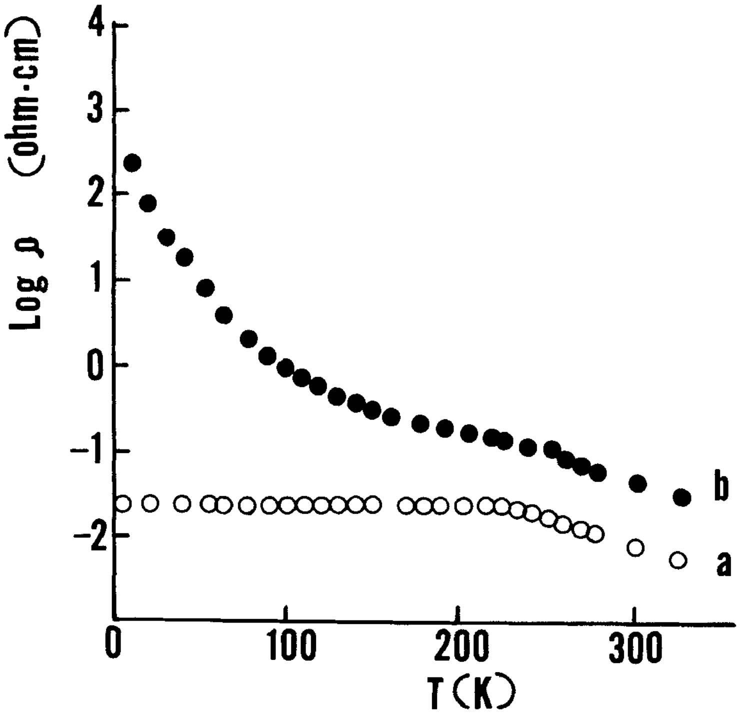


FIGURE 6 Temperature dependence of lateral resistivity of PEN film on quartz substrate, prepared with the substarate temperature at (a) 303 K and (b) 273 K.

basis of tunneling probability.[17] The large conduction barrier was assumed to be caused by the structure of PEN film where the carriers in PEN molecular layers were localized in the vicinity of the iodine layer.

Temperature dependence of HEX film doped with iodine showed semiconductive transport with the activation energy of 200 meV,[16] which was caused by the disorder of molecular orientation.[16]

In conclusion, the electrical properties such as σ, μ, and anisotropy of thin film of PEN and HEX are strongly correlated with the molecular orientation of the film. Highly ordered film of PEN exhibited metallic transport behavior from room temperature to 240 K, and high $\sigma_{//}$ of 150 S/cm with large anisotropy of 10^8. Transport behavior, parallel and perpendicular to the plane of PEN film, was explained by 2D-VRH and a tunneling mechanism, respectively. These findings are supported by the well-defined layered structure of the film. Applications of thin films of linear acene compounds for electrical devices are promising since these electrical properties can be controlled by the preparation conditions.

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