

Electrical Conductivity and Optical Properties of Poly(*p*-phenylene sulfide) Doped with Some Organic Acceptors

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ABSTRACT: Poly(*p*-phenylene sulfide) films were doped with four organic acceptors (tetracyanoethylene (TCNE), dicyanodichlorobenzoquinone (DDQ), *p*-chloranil, and trinitrofluorenone (TNF)). The sample films remained flexible and tough after doping. The optical and electrical properties of the doped PPS have been measured and discussed in terms of electron affinity of the acceptor molecule. The systematic variation of optical transmission spectra of PPS by doping indicated that a charge-transfer complex was formed between PPS chains and acceptor molecules. Doping with TCNE and DDQ gave a 10 order increase of the conductivity, while chloranil and TNF possessed little effect to enhance the conductivity. The chemical reaction accompanied by doping was found to also give the effect to increase the conductivity of doped PPS. A good correlation between the conductivities and activation energies obtained from the temperature dependences of conductivity was found in all doped PPS samples. It was pointed out that the electronic conduction in PPS/dopant systems must be governed by the mechanism which was independent of dopant content and dopant species.

KEY WORDS Poly(*p*-phenylene sulfide) / Organic Acceptor / Electrical Conductivity / Optical Property / Electron Affinity / Charge Transfer Complex /

Recently, active studies on conductive polymers have been performed. In particular, the polymers with π -conjugated structures in their skeletal chains have attracted much attention, because they exhibited metallic properties by doping with strong electron acceptors or donors. Poly(*p*-phenylene sulfide) (PPS) has no π -conjugation along the skeletal chains, and X-ray crystal structure analysis shows that neighboring phenyl rings are inclined by alternating $+45^\circ$ and -45° with respect to the planar zig-zag chain of the sulfur atoms.¹ In spite of disadvantage in the chemical structure for the delocalization of π -electrons, the conductivity of PPS increases up to about 1 S cm^{-1} by AsF_5 doping. Therefore, one expects that PPS may have the electronic con-

duction mechanism different from the conventional polymers with π -conjugation in their skeletons.

Several reports on the electrical conductivity of PPS doped with AsF_5 are available.²⁻⁴ Because doped PPSs are brittle and unstable in air,² the report which discussed their electronic conduction on the basis of detailed experimental results is poor. Virgin PPS has the conductivity of $10^{-20} \text{ S cm}^{-1}$, which belongs to an excellent insulator. The conductivity of PPS increases by about 2 orders of magnitude due to a trace of oxygen incorporated from air, when it is measured in air.⁵ It has been reported that PPS doped with tetracyanoquinodimethane (TCNQ) exhibited the conductivity as large as $10^{-8} \text{ S cm}^{-1}$.^{6,7}

As we have reported previously, PPS films can be doped with some organic acceptors in the vapor phase.⁸ PPS doped with tetracyanoethylene (TCNE) possesses the conductivity of $10^{-9} \text{ S cm}^{-1}$. Although this value is much lower compared with that of PPS doped with AsF_5 , the sample films continued to be flexible and tough after the doping with TCNE. The electrical properties show no feature of degradation, even after the samples are exposed to the humid air. This fact gives us the expectation that PPS doped with organic acceptors is adequate for detailed electrical measurements.

In this paper, we will report the optical and electrical properties of PPSs doped with four organic acceptors, TCNE, dicyanodichlorobenzoquinone (DDQ), *p*-chloranil, and trinitrofluorenone (TNF). First, we present the optical properties and conductivities of the doped PPSs and discuss them from the standpoint of differences in electron affinity of the organic acceptors. Secondly, the dependence of the conductivities of the doped PPS on dopant content is examined. We will also show that the chemical reaction accompanied by doping increases the conductivity of doped PPSs. Thirdly, the temperature dependence of the conductivities of the doped PPSs is examined, and the effect of acceptor species on the conductivities is discussed from a viewpoint of apparent activation energy of conduction. Lastly, we summarize the temperature dependence of the conductivities of all the doped PPS samples and give phenomenological discussion on the electronic conduction mechanism in PPS/dopant systems.

EXPERIMENTAL

Biaxially oriented PPS films prepared from high molecular weight PPS, which were supplied from Toray Industries Inc. were used. Thickness of the films was about $30 \mu\text{m}$. Organic acceptors were commercial reagents and used without further purification. The

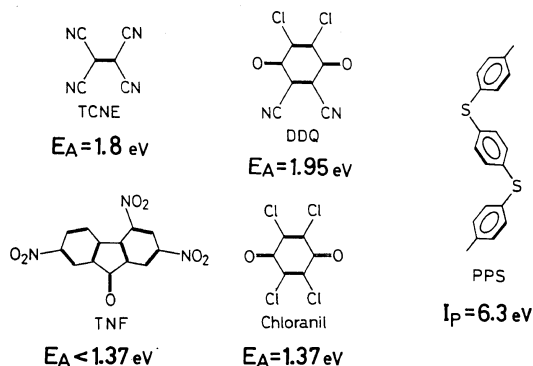


Figure 1. The molecular structures of the organic acceptors and PPS. E_A is the electron affinity and I_p is the ionization potential.¹²

molecular structures of the four acceptors are shown in Figure 1 with their electron affinities.⁹ For comparison, the molecular structure of PPS is also shown in the same figure.

Doping of the acceptor into PPS films was carried out by the following procedure. The surfaces of a PPS film ($25 \text{ mm} \times 25 \text{ mm}$) were cleaned with acetone, and the film was dried *in vacuo*. The PPS film and 1 g of the dopant powder were put in a glass tube avoiding a direct contact between the PPS and the dopant. Then, the glass tube was evacuated for 30 min and sealed. Doping of the acceptor into a PPS film was attained by keeping the glass tube at a constant temperature for 0.5 to 160 h. The amount of dopant incorporated into the PPS film was determined from a weight increase. We will express the dopant content in the form of mole dopant/mole PPS repeat unit. The rate of doping which was estimated qualitatively from the relation between doping conditions and the resulted dopant contents was in the order of $\text{DDQ} > \text{TCNE} > \text{chloranil} > \text{TNF}$. All the doped samples gave homogeneous outlook.

The conductivity measurements were carried out by using a power supply (Fluke 415B) and an electrometer (Keithley 614). Gold electrodes with a diameter of 10 mm were vacuum evaporated on both surfaces of the samples, and a guard electrode was vacuum evaporated

on one side to eliminate the contribution of surface current. The voltage dependence of current was linear up to about 100 V. The conductivities were measured under an electric field below $3.3 \times 10^4 \text{ V cm}^{-1}$. The sample was set in the measuring cell of stainless steel, and the cell was evacuated under a vacuum of 10^{-2} Torr. The temperature of the samples was controlled by a PID temperature controller. The conductivity did not change as long as the cell was kept at a vacuum of 10^{-2} Torr. Even after the sample was exposed to the air, its conductivity was reproduced within about 10% variation, when it was measured under the vacuum again.

Optical transmission or absorption spectra of the doped PPSs was measured by a spectrophotometer (Hitachi 330) in the wavelength region of 300–2000 nm.

RESULTS AND DISCUSSION

1. Effects of Acceptors on Conductivity and Optical Properties

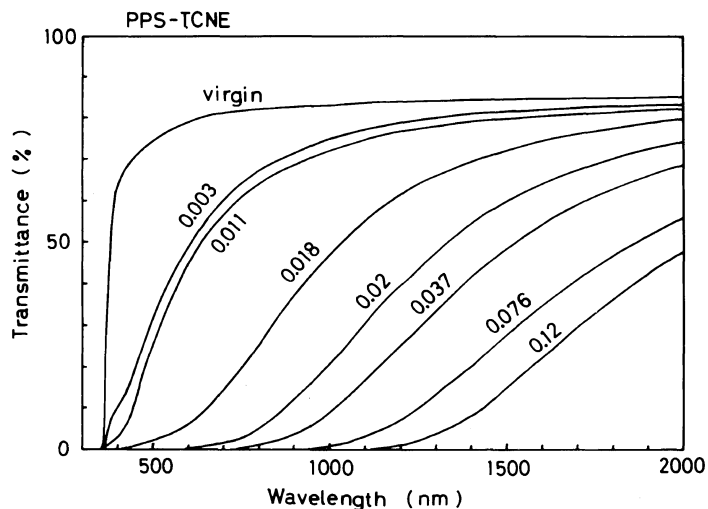
Dopants, doping conditions, and dopant contents together with sample colors and con-

ductivities at room temperature are summarized in Table I. The ultimate conductivities of PPS doped with TCNE or DDQ were located between 10^{-9} and $10^{-11} \text{ S cm}^{-1}$, which were 10 orders of magnitude higher than that of virgin PPS and ranged in high resistive semiconductor. The conductivities of PPS doped with chloranil or TNF were lower than $10^{-16} \text{ S cm}^{-1}$ and remained as insulators. Referring to the electron affinities shown in Figure 1, one can recognize that only the dopants with large electron affinity, E_A , contribute to the increase of the conductivity of PPS. Specifically, the comparison between DDQ and chloranil will throw light on this matter: both dopants have very similar quinoide structure, and molecular sizes are not so different from each other, but the conductivities of PPS/DDQ and PPS/chloranil systems gave the difference of 6 orders of magnitude. This should be explained by the difference in E_A of about 0.5 eV.

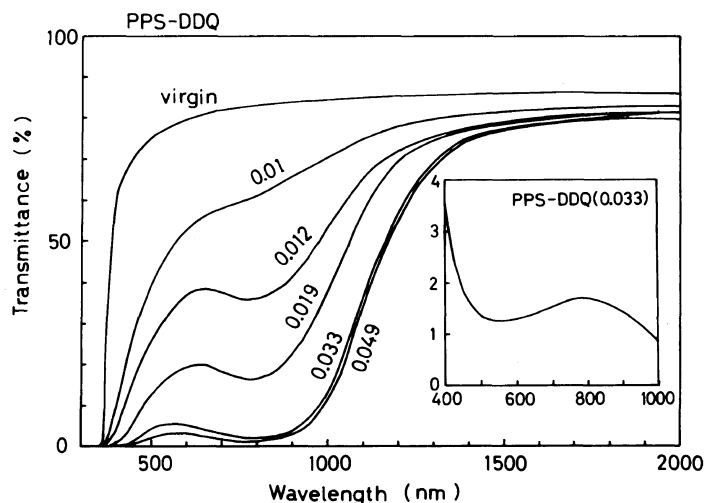
A transparent PPS film turned colored with the progress of doping, and the color became deeper with the increase of dopant content. The colors of the films were dependent on dopant species (Table I). These color changes

Table I. Dopants, doping conditions, and dopant contents together with colors and conductivities at room temperature of the resulted samples

Dopant	Doping condition		Dopant content (molar ratio)	Color	Conductivity S cm^{-1}
	Temp/ $^{\circ}\text{C}$	Time/h			
None	—	—	—	Colorless	$\sim 10^{-20}$
TCNE	180	2	0.011	Brown	1.4×10^{-16}
	180	3	0.018	Dark brown	3.4×10^{-13}
	180	30	0.04	Black	6×10^{-11}
	200	50	0.067	Black	6.8×10^{-10}
	200	96	0.145	Black	2×10^{-9}
DDQ	180	0.5	0.012	Green	$\sim 10^{-17}$
	180	1	0.023	Dark green	1.3×10^{-11}
	180	1.5	0.049	Dark green	2.8×10^{-11}
	180	2	0.067	Dark green	6.5×10^{-11}
	180	5	0.081	Dark green	7.6×10^{-12}
Chloranil	180	32	0.037	Red brown	1.4×10^{-18}
	200	30	0.046	Brown	4×10^{-17}
	200	120	0.067	Black	5×10^{-17}
TNF	180	72	0.027	Yellow brown	$\sim 10^{-19}$
	200	120	0.042	Red brown	$\sim 10^{-18}$



(a)



(b)

Figure 2. Optical transmission spectra of (a) PPS/TCNE system and (b) PPS/DDQ system. Numerals in the figure express the dopant content (molar ratio). Inserted figure is optical absorption spectrum of PPS/DDQ (0.033).

implied the formation of charge transfer complex between PPS and dopants, which was confirmed by the measurement of optical transmission spectra. Optical transmission spectra of doped PPSs are shown in Figures 2 and 3. Numerals in Figures 2 and 3 express the dopant content. Variation of the optical trans-

mission spectra with doping was very much dependent on dopant species and could not be explained simply by the use of E_A values. In PPS/TCNE system, the wavelength at which optical transmission is almost zero, which we call an "absorption edge," shifted to a longer wavelength with the increase of TCNE con-

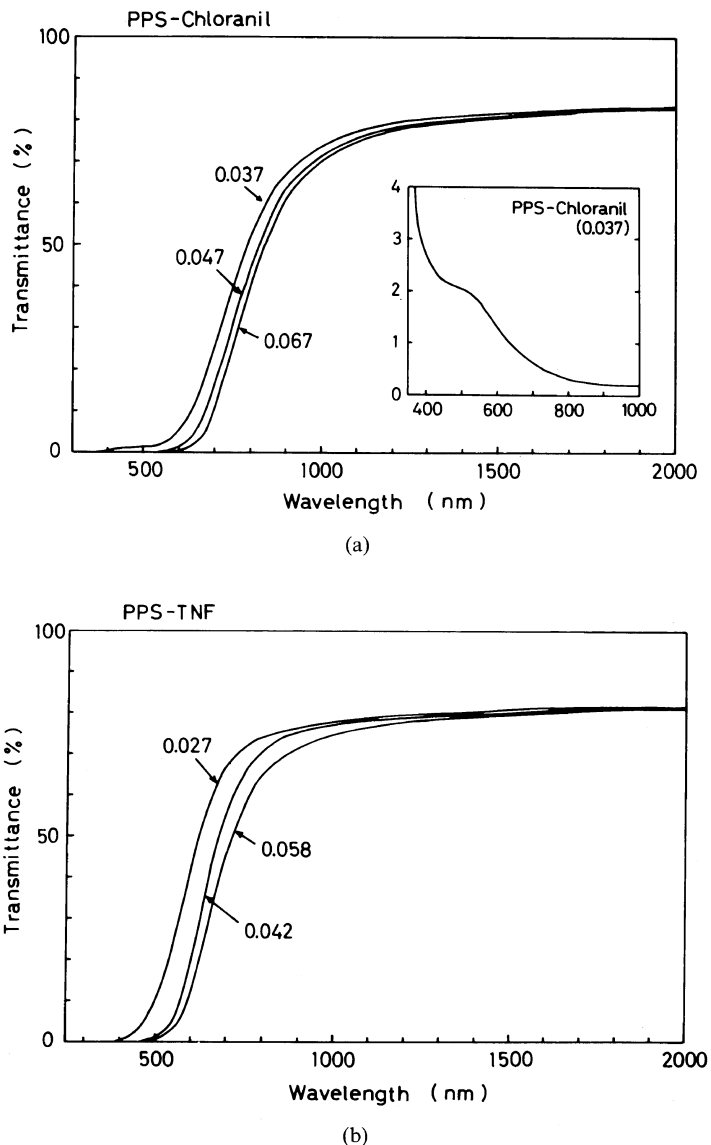


Figure 3. Optical transmission spectra of (a) PPS/chloranil system and (b) PPS/TNF system. Inserted figure is optical absorption spectrum of PPS/chloranil (0.037).

tent, reaching to entire absorption in the whole visible spectral region at about 4 mol% doping. In PPS/DDQ system, a transmission minimum appeared at around 800 nm, which corresponded to a peak in absorption spectra. This optical absorption peak shifted to longer wavelength with the increase of DDQ content.

PPS/chloranil and PPS/TNF systems possessed the absorption edges at around 700 and 600 nm, respectively. The shift of the edges was very small compared with that of the case of TCNE. These observations suggest that the larger the shifts of the absorption edges to lower energy (longer wavelength) are, the high-

er the conductivities of the doped samples are. However, we cannot offer a generalized relationship between the absorption edge and the conductivity, since the shapes of the transmission spectra of these four systems significantly differ from each other.

Again, the comparison between PPS/DDQ and PPS/chloranil systems will give an important clue (Figures 2(b) and 3(a)). In both systems, broad absorption peaks could be found near 780 and 520 nm, respectively. This suggests the formation of charge-transfer complex structures. In the cases of the molecular complexes, the energy of charge-transfer absorption band, $h\nu_{CT}$, is approximately expressed by a following equation.¹⁰

$$h\nu_{CT} = I_p - E_A - W \quad (1)$$

where I_p is the ionization potential of a donor molecule, E_A the electron affinity of an acceptor molecule, and W the dissociation energy of the charge transfer excited state. Referring to this equation, the difference of wavelengths of absorption peaks in PPS/DDQ and PPS/chloranil systems (260 nm) can be understood. The absorption peak of PPS/DDQ system is very broad, differing from the well-known cases of molecular complexes. This suggests that the charge transfer interaction between PPS chains and DDQ molecules is rather weak, and not a unique interaction but a variety of interactions exist in the system.

In the case of PPS/TCNE system, an absorption peak due to a charge-transfer complex could not be found; a main feature was a monotonous decrease of transmittance. A specific variation of transmission spectrum at 380–400 nm at the early stage of TCNE doping was observed, which was very similar to the spectral change reported in the case of AsF_5 doping.¹¹ It follows that chemical modification of PPS chains occurred in PPS/TCNE system. Therefore, the transmission spectra in Figure 2(a) would be composed of the charge-transfer absorption and the absorption due to the crosslinked structure at intra-³ or inter-PPS

chains.

2. Dependence of Conductivity on Dopant Content

In Figure 4, the relations between the conductivity at 300 K and dopant content in PPSs doped with four acceptors are shown. The conductivity drastically increased by doping of *ca.* 2 mol% of TCNE or DDQ. Similar results have been reported on many polymer/dopant systems, such as polyacetylene/ I_2 , polyacetylene/ AsF_5 ,¹² and polythiophene/ AsF_5 .¹³ On the other hand, chloranil and TNF gave small effect on conductivity.

Hereafter, we will concentrate our discussion on PPS/TCNE and PPS/DDQ systems. The conductivity of PPS/TCNE system increased gradually with the increase of dopant content over 2 mol%, while that of PPS/DDQ system took a maximum at 6–7 mol% and began to decrease with the further increase of DDQ content. Although E_A of DDQ is a little larger than that of TCNE, the conductivity of PPS with high DDQ content is lower than that with high TCNE content. Thus, one should not conclude that the conductivity of heavily doped PPS can simply be

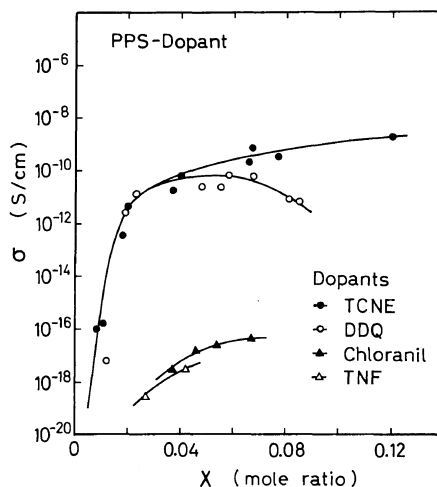


Figure 4. The relation between the conductivity at 300 K (σ) and dopant content (x) in PPSs doped with four acceptors.

explained in terms of the electron affinities of acceptors.

The difference in the conductivity of PPS/TCNE and PPS/DDQ systems should be attributed to the difference in chemical reactivity during doping. There are several signs of the occurrence of chemical crosslinking during TCNE doping. First, the variation of transmission spectrum at 380–400 nm region with TCNE doping suggests the formation of crosslinks as mentioned before. Secondly, tough and flexible appearance of heavily doped PPS with TCNE indirectly indicates the presence of dense crosslinking. Thirdly, dynamic viscoelasticity measurements as well as a solubility test of doped PPSs also implied the presence of crosslinks as described in another paper.¹⁴ Probably, intra or inter-molecular cross-links similar to the case of PPS/AsF₅ system are formed in the PPS/TCNE system. Judging from the systematic shifts of the optical edge, as shown in Fig. 2(a), the growth of π -conjugated structures which might also contribute to the increase of the conductivity, is expected in PPS/TCNE system.

In the case of PPS/DDQ system, the films became brittle with DDQ content over 7 mol%, and the conductivity did not increase with further increase of DDQ content. Heavily doping of DDQ is considered to cause scission of PPS skeletal chains.

3. Temperature Dependence of Conductivity

In Figure 5, the temperature dependences of conductivity in PPS/TCNE system are shown. The relation between the conductivity and the reciprocal temperature in all the samples, including virgin PPS, obeyed the expression $\sigma \propto \exp(-\Delta E/kT)$. The activation energy of conduction of virgin PPS estimated from the $\log \sigma$ vs. T^{-1} plot was about 2 eV. Starting from this 2 eV, the activation energy of conduction in doped PPSs gradually decreased with the increase of TCNE content. Figures 6 and 7 show the $\log \sigma$ vs. T^{-1} plots in PPS/DDQ, PPS/TNF, and PPS/chloranil systems.

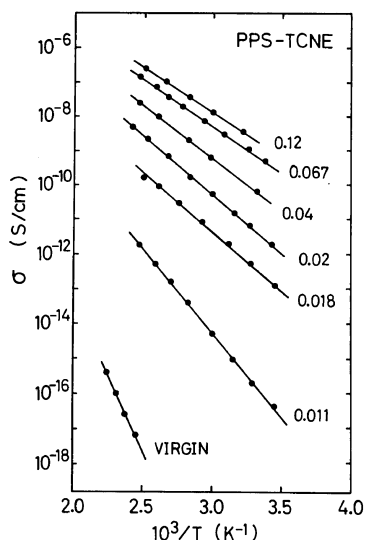


Figure 5. The temperature dependences of conductivity in PPS/TCNE system.

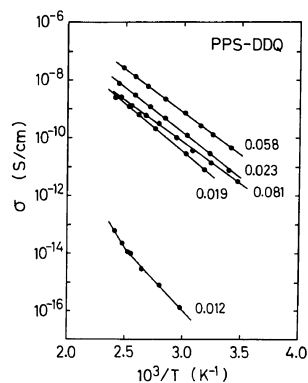


Figure 6. The temperature dependences of conductivity in PPS/DDQ system.

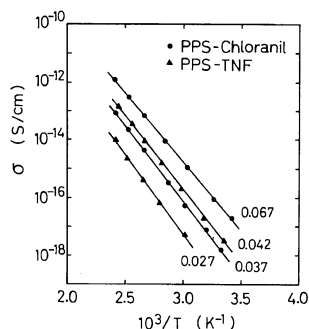


Figure 7. The temperature dependences of conductivity in PPS/chloranil and PPS/TNF systems.

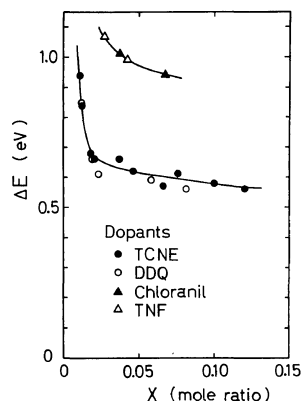


Figure 8. The apparent activation energies of conduction (ΔE) plotted against the dopant contents (x) in PPSs doped with four acceptors.

These plots also obeyed the expression $\sigma \propto \exp(-\Delta E/kT)$. The apparent activation energies ΔE obtained from Figures 5, 6, and 7 are plotted against the dopant contents in Figure 8. In PPS/TCNE and PPS/DDQ systems, ΔE values drastically decreased in the range of 0–2 mol% doping, and reached a constant value of *ca.* 0.5 eV at high dopant content. Whereas, in PPS/chloranil and PPS/TNF systems, ΔE values decreased by a small extent and ceased decreasing at around 0.9 eV. This results are reminiscent of the relation between the conductivity and dopant content shown in Figure 4.

Although no increase of the conductivity was observed in the PPS with the further increase of DDQ content (more than 7 mol%), ΔE continued to decrease. This is only one exceptional behavior in doped PPSs studied here and may be due to the degradation of PPS during doping at higher temperature.

All the data of temperature dependence of conductivity showed above were limited to the temperature region above room temperature (20–130°C). For PPS/AsF₅ system, the conductivity in the temperature region between room temperature and –100°C was reported. The conductivity was found to obey the expression $\sigma \propto \exp(a/T^{1/2})$.² Then, we also measured the temperature dependence of the con-

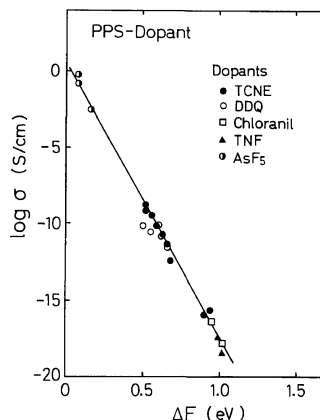


Figure 9. The relation between the conductivities at 300 K (σ) and the apparent activation energies (ΔE) in PPS doped with various dopants.

ductivity in PPS/TCNE and PPS/DDQ systems in the temperature region between 80 and –100°C. However, it was difficult to decide whether the conductivity obeyed the expression similar to the case of PPS/AsF₅ system or not. If one desires to discuss the conduction mechanism of doped PPSs in detail, the measurements at lower temperature are indispensable. We stress, however, that the Arrhenius plots at the temperature region above room temperature, in rough approximation, should give important clues for our understanding of the conduction behavior in doped PPSs.

4. Relation between Conductivity and Activation Energy of Conduction

As we observed very similar behavior between $\log \sigma$ and ΔE as a function of the dopant contents, we are interested in the relation between σ and ΔE . We thus examined the relation between σ and ΔE in PPS/dopant systems adding the literature data of PPS/AsF₅ system.¹⁰ Figure 9 shows the relation between the conductivity at room temperature and ΔE in PPSs doped with various dopants. The data of PPS heavily doped with DDQ (DDQ content > 7 mol%) were omitted. All the points of data locate on a single straight line, irrespec-

tive of dopant species and dopant content. The straight line can be expressed by eq 2, where K ($\approx 10^0 \text{ S cm}^{-1}$) and α are parameter which is independent of dopant species.

$$\sigma_{\text{RT}} = K \exp(-\alpha \Delta E) \quad (2)$$

This relation claims that the conductivity values are uniquely determined, if ΔE values are given.

The slope of this straight line is about 17.4. Surprisingly, this value is very close to the value of $(kT_{\text{RT}} \ln 10)^{-1}$. Therefore, a more specific equation between σ and ΔE can be derived.

$$\sigma \approx 10^0 \exp(-\Delta E/kT) \quad (3)$$

Once we have this expression, we easily recognize that the group of straight lines in Figure 5 obeys eq 3.

Generally, a good correlation between σ and ΔE , or carrier mobility and its activation energy, which can be expressed by an equation similar to eq 2, has been known empirically in some semiconducting polymers¹⁵ and amorphous silicon.¹⁶ However, no report is available that claims that eq 3 holds between σ and ΔE . Therefore, we reach the conclusion that PPS/dopant systems studied here are very specific, and that the electronic conduction in PPS/dopant systems is dominated by a certain common mechanism independent of dopant species.

One expects that the charge carriers move by hopping between localized states in the polymer which includes large portion of amorphous regions. In a subsequent paper, we will show that activation energy of charge transport is very close to that of dark conduction in doped PPS; the activation energy of charge transport can be represented by the activation energy of the conductivity. Then, eq 3 turns out to mean that the dopants act to lower the activation energy for carrier hopping.

PPS has no apparent π -conjugated structure along the skeletal chains. The highest occupied band obtained by the VEH technique, how-

ever, is fairly large (1.2 eV), which suggests that π -electrons on the phenyl rings are delocalized throughout several PPS repeating units.¹⁷⁻¹⁹ Therefore, the charge transport should occur *via* hopping among the delocalized segment regions of various lengths. The rate-determining step in the carrier transport must be an interchain hopping.

Recently, it has been demonstrated for poly(*p*-phenylene) and polypyrrole that the electronic conduction can be explained by the interchain charge hopping *via* charge defects such as bipolarons.¹⁹⁻²¹ The interchain hopping in PPS/dopant systems might be explained in terms of a similar concept, although the concept of bipolaron might not be directly applicable for this case.

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