Title	Dependence of DC-Resistivity on Morphology in Polypyrroles (Commemoration Issue Dedicated to Professor Tetsuya HANAI On the Occasion of His Retirement)
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1991), 69(4): 331-341
Issue Date	1991-12-30
URL	http://hdl.handle.net/2433/77410
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Dependence of DC-Resistivity on Morphology in Polypyrroles

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DC-resistivity was measured for several polypyrroles, which have irregular powdery, regular spherical or rod-like morphology. The conduction seems to follow Mott's variable range hopping process, in spite of their different morphologies. T_0 in Mott's equation was found to depend on the morphology and the dependence can be explained by size effect. The bigger polymer particles give weaker temperature dependence in resistivity.

INTRODUCTION

Many investigations have been carried out to understand conduction mechanism in electrically conducting polymers. However, polymers in examination were not always well characterized from the standpoint of structure and morphology. Since macroscopic electrical properties should be deeply related to the structure and morphology of polymers, it is of essential importance to investigate the electical properties of polymers whose structure and/or morphology are well controlled and well known. In this paper, the electrical properties of polypyrrole, whose morphology is well characterized by electron microscopy, are discussed. Bulk DC-resistivity was measured for several polypyrroles, which have irregular powdery, regular spherical[1] or rod-like morphology, and the relationship between the DC-resistivity and the morphology is discussed from the viewpoint of size effect.

EXPERIMENTAL

Polypyrroles were polymerized chemically in aqueous solution of pyrrole using $FeCl_3$ and sodium cellulose sulfate (SCS) as oxidizing agents (Table I). When SCS is used, spherical particles of polypyrroles are known to be obtained[1]. The diameters of spherical particles are surprisingly constant in a solution and change depending on the concentrations of SCS. Pyrrole and water were used after distillation. $FeCl_3$ and SCS

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Table I. Concentrations of pyrrole, FeCl₃, SCS, TMV and IMO in water solvent. d is the diameter of the particles of polypyrroles observed with electron microscope (see Figs. 1-3 and Figs. 7-8).

	Pyrrole (mol/l)	FeCl₃ (mol/l)	SCS, TMV, IMO (g/l)	morphology (d)
PPy	0.1	0.2	—	irregular powder (about 100nm)
PPySCS1	0.1	0.2	0.19 (SCS)	regular sphere (100nm)
PPySCS2	0.1	0.2	0.57 (SCS)	regular sphere (40nm)
PPyTMV	0.1	0.03	0.02 (TMV)	irregular powder (about 300 nm)
PPyIMO	0.1	0.03	0.33 (IMO)	irregular powder (about 100 nm) rod-like (about 500 nm)

were obtained from Aldrich-Chemie and used without further purification.

After polymerization, polypyrroles were washed with water and ethyl alcohol, dried in vacuum and pressed in the form of a disk. Bulk DC-resistivity was obtained by measuring a current through the disk specimen with guard electrode under application of a DC-potential in nitrogen atmosphere.

Morphological investigation was carried out with transmission electron microscopes (Phillips EM-300 operated at 80 kV and JEOL 200CX at 200 kV). A droplet of the solution containing produced polypyrroles was taken on an electron microscopic grid covered with a carbon thin film, carefully washed with water and ethyl alcohol, dried in vacuum and served for electron microscopic observation.

For comparison, other polypyrroles were also polymerized with FeCl₃ as an oxidizing agent in aqueous solutions containing imogolite (IMO) or tobacco mosaic virus (TMV) (see Table I). These molecules themselves are known to take rod-like forms in solution. In these cases, the polymerization was carried out in a lower concentration of FeCl₃ (0.03 mol/l), because gel (or aggregation of IMO or TMV molecules) is formed above the concentration of 0.2 mol/l. Their morphology and the resistivity were measured with the same procedure as mentioned above.

RESULTS AND DISCUSSION

Figures 1-3 show the morphologies of PPy (polymerized only with FeCl₃), PPySCS1 (polymerized with FeCl₃ and a smaller amount of SCS) and PPySCS2 (polymerized with FeCl₃ and a larger amount of SCS). PPy is obtained as irregular powdery polymer particles as shown in Fig. 1. PPySCS1 and PPySCS2 consist of spherical particles with regular diameter. The diameter decreases with increasing the concentration of SCS. In Table II, the atomic compositions obtained by elementary
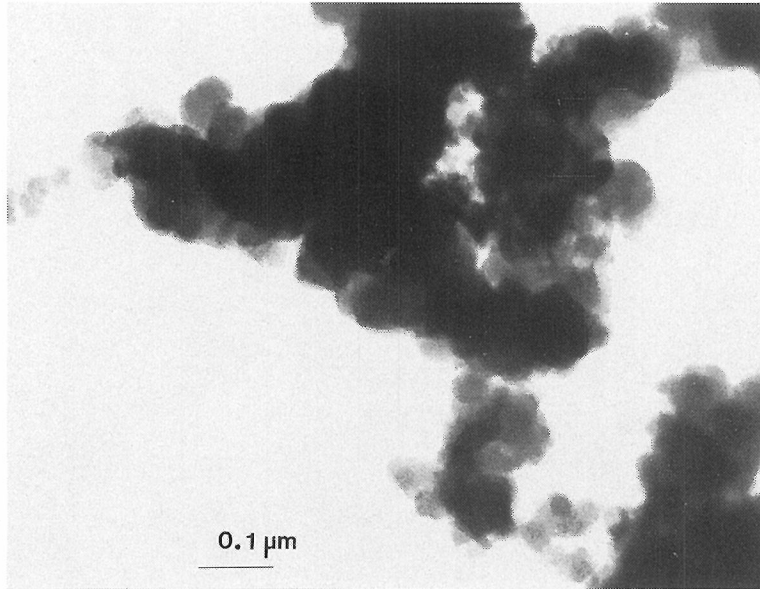
Fig. 1.　Morphology of irregular powdery PPy polymerized only with FeCl₃. The shape and the dimension are widely varied from particle to particle and the mean diameter of the particles is about 100nm.
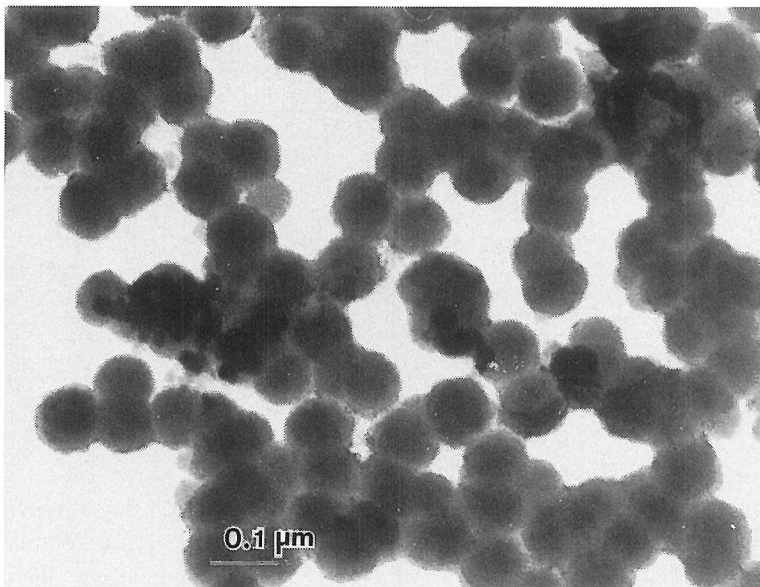

Fig. 2.　Spherical polypyrrole particles obtained by polymerization with FeCl₃ and SCS (PPySCS1). The dimension of the particles is the same for all particles of 100 nm in diameter.

analysis for the specimens with SCS are shown. The polypyrroles are co-doped with FeCl₃ and simultaneously with SCS, where about 20–25 % of monomeric units are oxidized.

　　Let consider the conduction mechanism in the polypyrrole in terms of the conduc-

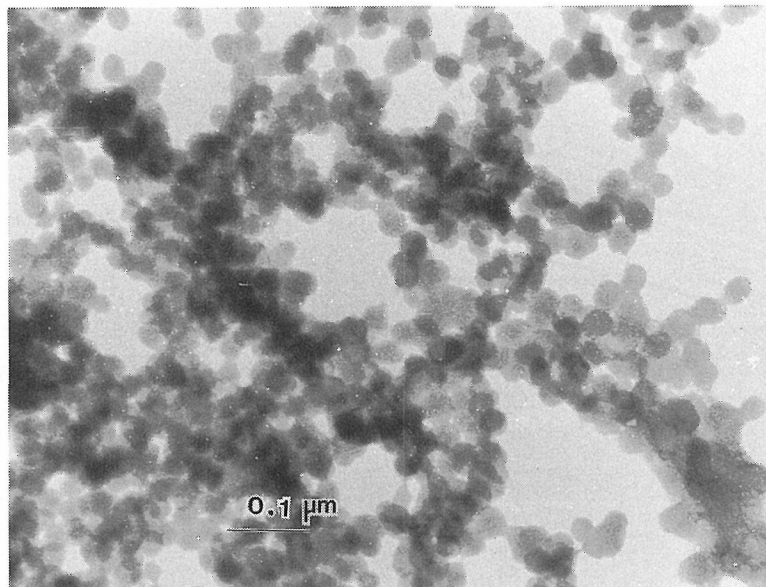S. Isoda, Y. Kita, N. Donkai, Y. Sano and G. Wegner

Fig. 3. Spherical polypyrrole particles obtained in the higher concentration of SCS (PPySCS2). The diameter is 40 nm.

Table II. Atomic compositions in polypyrroles prepared. The ratios are normalized to 1 for nitrogen atom. From this table the degrees of oxidation are almost the same for the samples, that is, 20~25% of pyrrole units are seemed to be oxidized by Cl and/or SCS ions.

	C	N	H	Cl	S
PPy	3.88	1	2.90	0.18	0.00
PPySCS1	3.98	1	3.02	0.21	0.04
PPySCS2	3.94	1	3.06	0.21	0.02
PPyTMV	4.04	1	3.23	0.26	—
PPyIMO	4.04	1	3.13	0.25	—

tion models proposed so far.

1. Phonon Assisted Hopping Conduction

A phonon assisted hopping conduction of solitons in lightly doped polyacetylene[2] was proposed in Kivelson's model which described quantitatively the temperature and frequency dependence of the conductivity. However, for conducting polymers with non-degenerated ground state like as polypyrrole, polarons and bipolarons would be responsible, instead of soliton and antisoliton pairs. In such case, Kivelson's conduction model should be modified slightly to deal with this case[3], the modified model was found satisfactory to describe the temperature dependence of conduction in lightly doped polypyrrolle[4]. In this Kivelson's interpolaron model, the DC-resistivity (ρ_{DC}) is given as,

$$\rho_{DC} = \frac{kTR_0{}^2 \exp(2BR_0/\xi)}{Ae^2\xi\Gamma_0(T)},$$ (1)

where

$$\Gamma_0(T) = \frac{Y_p\,Y_{bp}}{(Y_p + Y_{bp})^2}\,(T/300)^{n+1}\gamma_{0'}$$ (2)

with T being the absolute temperature, e the electronic charge, k the Boltzmann constant, A and B the constants of 0.45 and 1.39, respectively, R_0 the mean distance between impurities, ξ the averaged decay length of polaron or bipolaron wave function, n the numerical constant of about 10, Y_p and Y_{bp} the concentrations of polarons and bipolarons, respectively, and γ_0 the transition rate of electrons between polaron and bipolaron states at 300 K. Equations (1) and (2) imply ρ_{DC} to be proportional to T^{-n}. Figure 4 shows the log (ρ_{DC}) vs. log(T) plot for three kinds of polypyrrole (PPy,
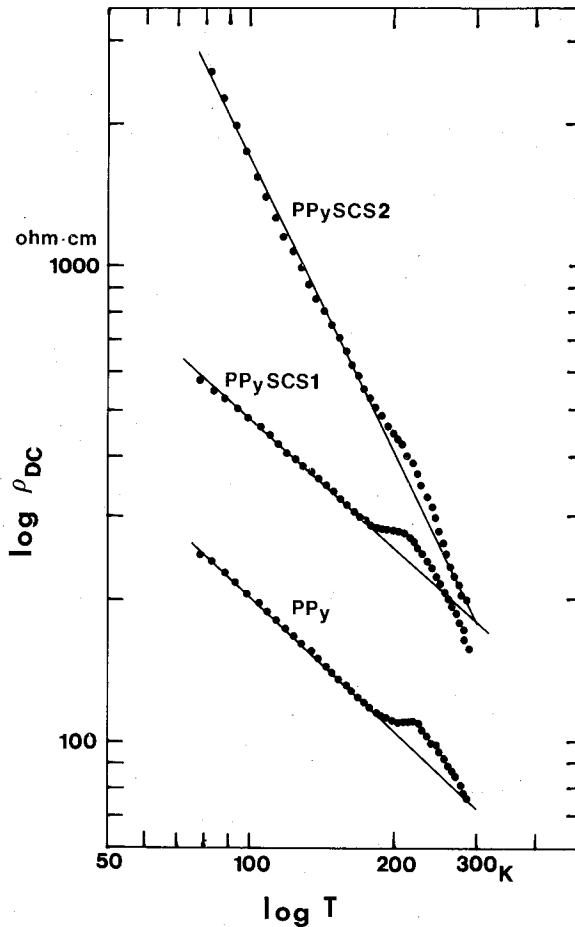

Fig. 4. Log(ρ_{DC}) vs. log(T) plot based on Kivelson's model. $n = 0.9$, 1.0 and 2.1 for PPy, PPySCS1 and PPySCS2, respectively.

PPySCS1 and PPySCS2), where linear relations are obtained in a lower temperature range (below 180 K). The slopes of these lines yield n as about 0.9, 1.0 and 2.1 for PPy, PPySCS1 and PPySCS2, respectively, though the values of n estimated above are much smaller than that expected from Kivelson's model. For example, Hirai et al. found $n=14.7$ for lightly doped polypyrrole[4]. Considering the degrees of oxidation derived from the elementary analysis, our polypyrroles are highly doped and would not follow the conduction mechanism of Kivelson's model.

2. Nearest Neighbor Hopping Conduction

The activation process due to nearest neighbor hopping may considered to be a conduction mechanism appropriated for amorphous semiconductor. The following expression can be considered for nearest neighbor hopping [5] as,

$$\rho_{DC} = C_0 T \exp(\varepsilon/kT) \tag{3}$$

where ε is the activation energy and C_0 the constant. The resistivity data are replotted in $\log(\rho_{DC})$ vs. T^{-1}, as shown in Fig.5. Linear relations are observed only in a lower temperature region (below 120 K) for the three samples. The fitting is not so good. The conduction of these polypyrroles do not follow the nearest neighbor hopping.

3. Variable Range Hopping Conduction

The same data is plotted in $\log(\rho_{DC})$ vs. $(1/T)^{1/4}$, where a linear relation is expected in Mott's variable range hopping in three-dimension[6]. A good linearity is
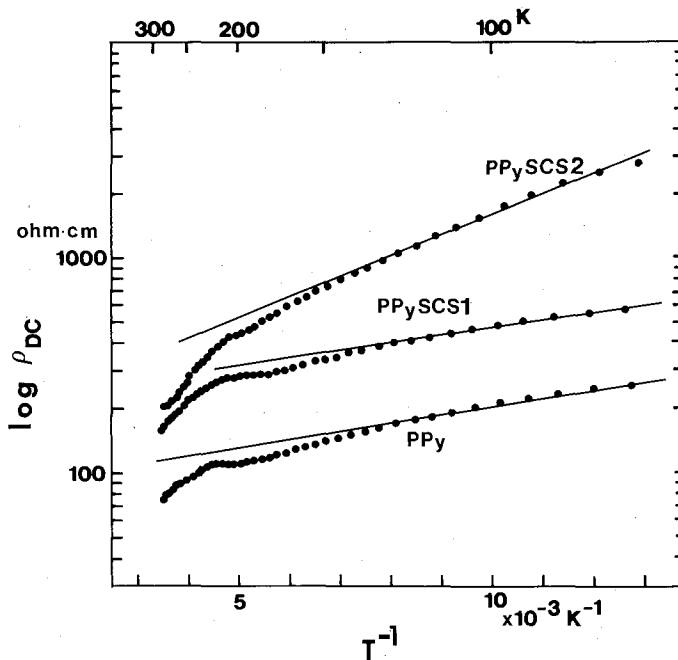

Fig. 5. Log(ρ_{DC}) vs. T^{-1} plot based on nearest neighbor hopping.
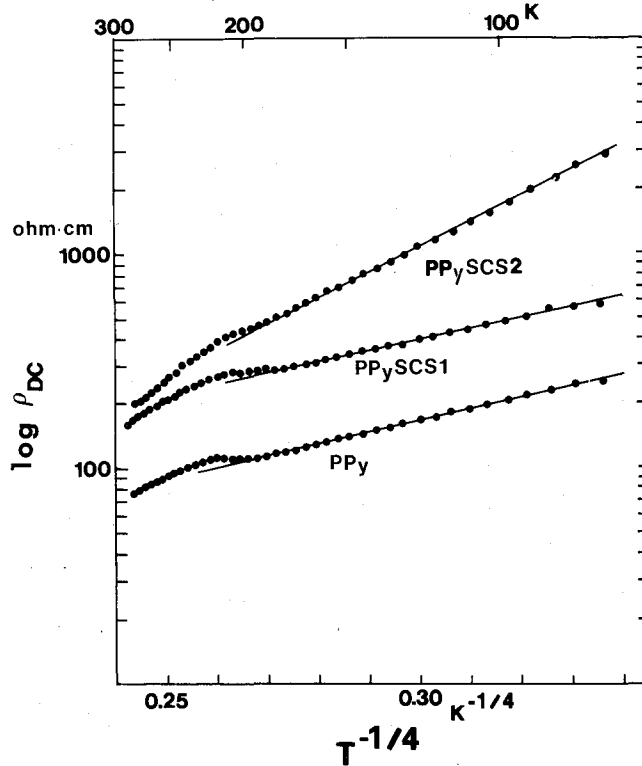
Fig. 6. Log(ρ_{DC}) vs. $T^{-1/4}$ plot based on Mott's variable range hopping in three dimension. Better linearity in a wider temperature region is observed than the cases of Figs. 4 and 5.

observed below 200 K in Fig. 6 of the resistivity-temperature relation. The deviation of experimental data from the line observed still in higher temperature may be caused by other conduction process, such as ionic conduction. This better fitting in a wider temperature range suggests the conduction mechanism due to variable range hopping in three-dimension as reported for other polypyrroles[7],

$$\rho_{DC} = C_0 T^{1/2} \exp(\frac{T_0}{T})^{1/4}, \tag{4}$$

where C_0 is the constant and

$$T_0 = \frac{\beta \alpha^3}{k\ N(E_F)}, \tag{5}$$

where α^{-1} is the decay length of the localized state, $N(E_F)$ the density of states at Fermi level E_F and β the numerical constant of about 16. T_0 can be evaluated from eq. (4) with the slope in log($\rho_{DC}/T^{1/2}$) vs. $(1/T)^{1/4}$ plot. Then α^{-1} is calculated using this T_0 from eq. (5) for three samples as in Table III, assuming $N(E_F)=3\times10^{21}/$ eV·cm³, because the degree of oxidation is the same for all polymer. In this assumption, however, $N(E_F)$ is over estimated, because one extra charge is assumed to be

Table III. T_0 are calculated from the slopes in the figure of $\log(\rho_{DC}/T^{1/2})$ vs. $T^{-1/4}$ plot. $N(E_F)/\alpha^3$ are calculated from the T_0. In the last column of the table, α^{-1} were calculated, assuming $N(E_F)=3\times10^{21}$/eV·cm³, though these values of $N(E_F)$ should be the maximum value estimated from the following assumptions. A extra charge is produced in a volume of $1.7\times0.47\times0.47$ nm³, which is determined from the value of oxidation and the density of the polymer, and the charges from the localized electronic states at Fermi level.

	T_0 (K)	$N(E_F)/\alpha^3$ (ev^{-1})	α^{-1} (nm)
PPy	1.4×10^5	1.3	0.78
PPySCS1	1.2×10^5	1.5	0.82
PPySCS2	1.4×10^6	0.13	0.36
PPyTMV	2.2×10^4	8.4	1.5
PPyIMO	2.9×10^3	64.0	2.9

produced in a volume of $1.7\times0.47\times0.47$ nm³ and to contribute wholly for localized electronic states at Fermi level. That means that real α^{-1} should be certainly longer than the estimated value shown in the table. Nevertheless, these T_0 and α^{-1} values are the same order of magnitude comparing with the values for other polypyrroles already reported[8]. In the cases of PPySCS1 and PPySCS2, it can be seen rigorously that the smaller polypyrrole particles give larger T_0 values and smaller α^{-1} values.

4. Comparison with Other Polypyrroles

For comparison, polypyrroles with different morphology were polymerized using IMO or TMV with FeCl₃ as the oxidizing agent. In both cases, the degrees of oxidation are about 0.25, about 25% of monomeric units are oxidized from elementary analysis (Table I). Figures 7 and 8 show morphologies of the polypyrrole polymerized with IMO (PPyIMO) and with TMV (PPyTMV), respectively. In the case of PPyIMO, polypyrrole particles are formed, and at the same time rod-like polypyrroles are produced as shown in Fig. 7. These rod-like polypyrrole seem to be resulted from the polymerization on an aggregate of IMO molecules, because about 2.5 nm lattice fringes relating to the side-packing spacing in aggregated IMO molecules[9] are observed in the rod-like polypyrroles. Thus PPyIMO has a bigger morphology in length than PPy, PPySCS1 and PPySCS2. Pyrrole was not polymerized into a rod-like form with TMV, though expected from the molecular shape of TMV shown in the inset of Fig. 8. Instead they compose bigger powdery irregular-shaped particles than polypyrroles polymerized without TMV.

Temperature dependence of DC-resistivity in PPyIMO and PPyTMV reveals that the conduction mechanism is described again by Mott's model and T_0 is much smaller in PPyIMO and PPyTMV than in PPySCS1 and PPySCS2 as shown in Fig. 9. Thus α^{-1} are larger in these cases, though the polypyrroles were produced with the same degrees of oxidation.

A large variation in T_0 values from specimen to specimen is probably caused by a morphological factor. Polypyrrole is known to be polymerized usually in the form of aggregate of irregular powdery particles from usual chemical procedures. As shown in
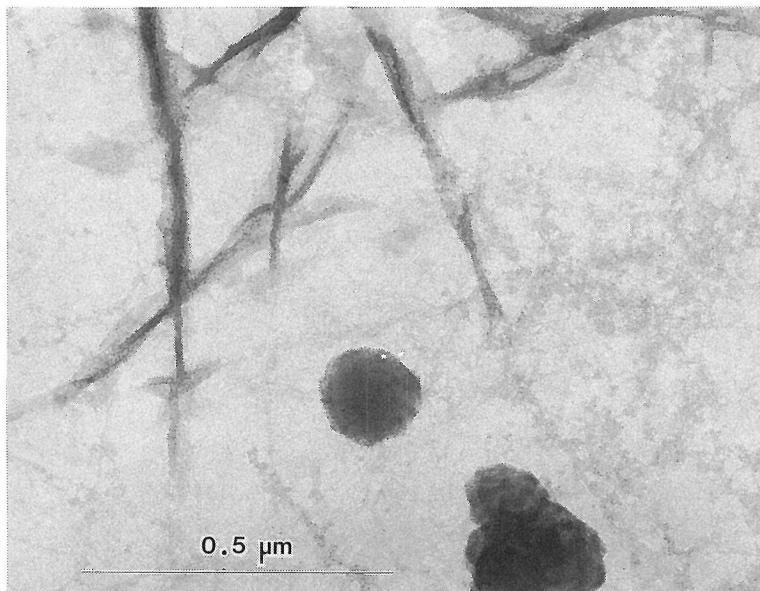
Fig. 7. Polypyrrole polymerized with IMO (PPyIMO). Electron microscopic observation shows the co-existence of irregular powder and rod-like particles.
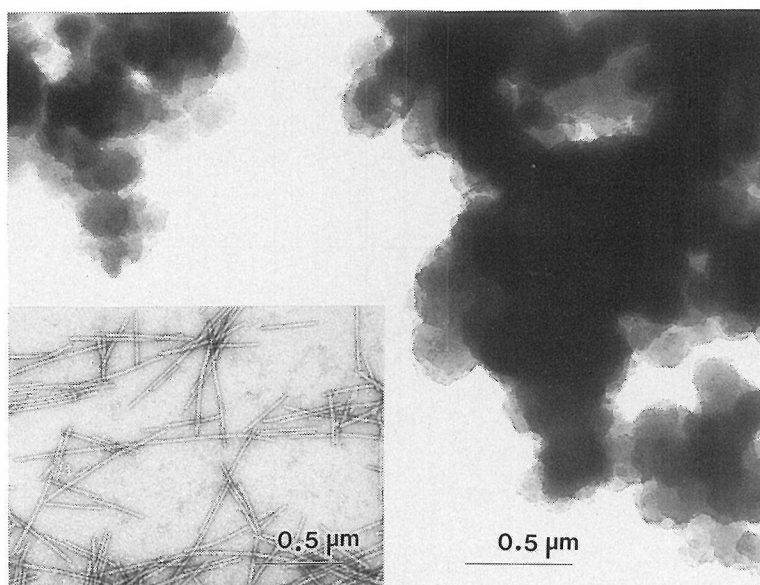

Fig. 8. Polypyrrole polymerized with TMV (PPyTMV). Though TMV has regular rod-like molecular shape shown in the inset, PPyTMV is again powdery irregular particles.

Fig. 1, PPy is the powdery particles largely varied in dimension and their mean size is about 100 nm. On the other hand, PPySCS1 and PPySCS2 form regular spheres of about 100 nm and 40 nm in diameter, respectively. The inner structure is supposed to be uniform or homogeneous in the particles of PPy, PPySCS1 and PPySCS2, so that
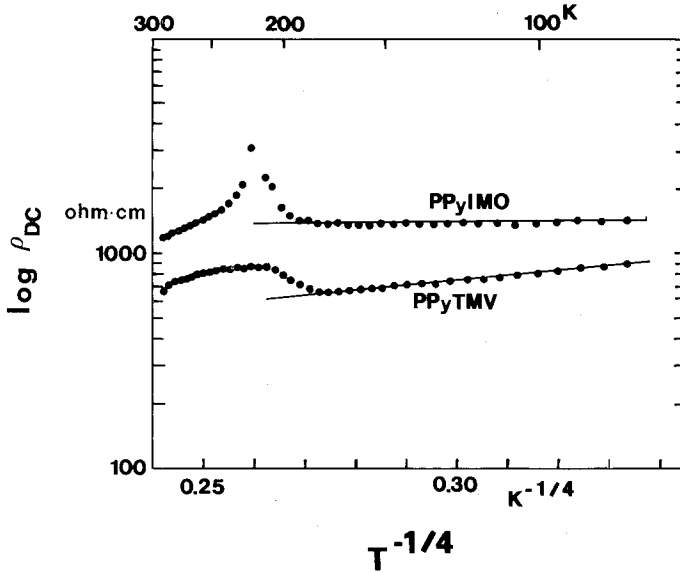
Fig. 9 Log(ρ_{DC}) vs. $T^{-1/4}$ plot for PPyIMO and PPyTMV based on the variable range hopping model.

the boundary condition between particles is considered to affect the macroscopic phenomena such as a bulk resistivity. The conduction path will be rather restricted and cut off in the bulk cluster depending on the morphology. Here a formation of infinite cluster (network) is prevented and a fraction of bonds is suppressed by discontinuous boundaries between particles. The T_0 derived from the slopes in the experimental log
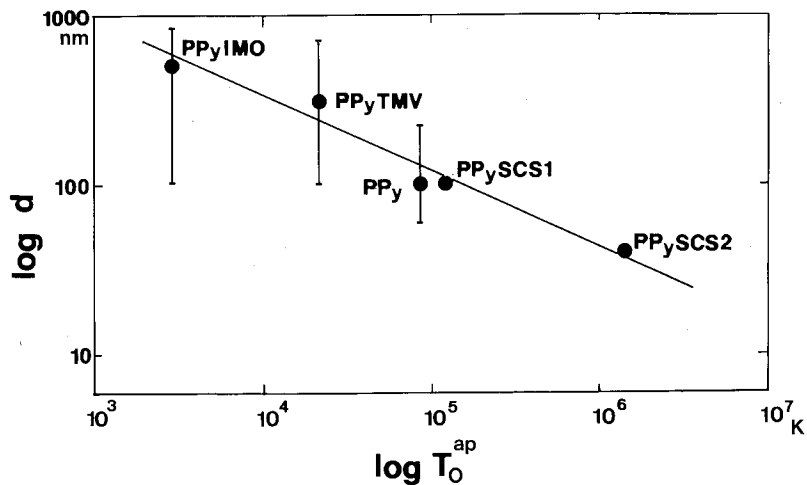
Fig. 10. Dependence of T_0^{ap} on the dimension d of polypyrrole particles. From eq.(6), log(d) is expected to be proportional to $(1/4w)$ log(T_0^{ap}). Vertical bars represent the distribution of particle dimenion. w can be estimated about 0.54 from the slope.

$(\rho_{DC}/T^{1/2})$ vs. $(T^{-1/4})$ should be modified to include the size dependence of resistivity in amorphous semiconductors[5] as,

$$T_0{}^{ap} = T_0 \ \{1 + D(\ \langle r \rangle /d)^w\}^4 \approx T_0 D(\ \langle r \rangle /d)^{4w} \tag{6}$$

where $T_0{}^{ap}$ is the apparent T_0, d the domain size, $\langle r \rangle$ the mean hopping length, D the unknown coefficient and w the numerical constants of about 1.0.

Assuming d is given by the particle size determined by electron microscopic observation; the diameter of spheres in PPySCS1 and PPySCS2, the averaged diameter of powdery particles in PPy and PPyTMV and long dimension of rod-like PPyIMO are plotted against $T_0{}^{ap}$ in Fig. 10, where an approximate linear relation is observed in $\log(d)$ vs. $\text{Log}(T_0{}^{ap})$ plot. This result suggests that the variation in T_0 values is due to the size effect. From this figure, w was estimated as about 0.54, which is in an acceptable range of w.

CONCLUDING REMARKS

DC-resistivity was measured for several polypyrroles, which have different morphologies; an irregular powdery, a regular spherical or a rod-like morphology. The conduction mechanism seems to follow Mott's variable range hopping process in all polypyrroles. T_0 in Mott's equation depends on the morphology and follows approximately eq. (6), which was derived to include the size dependence of resistivity, based on percolation theory. Bigger particle seems to suppress the temperature dependence of resistivity. AC-resistivity measurement is now in progress to clarify the size effect.

ACKNOWLEGEMENT

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