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Electrical Transport Properties of Perchlorate-Doped Oriented Polyacetylene

Takayuki Miyamae,* Takehiko Mori,† Kazuhiko Seki, and Jiro Tanaka††

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01

†Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152

††Department of Materials Science, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-12

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The electrical conductivities of perchlorate-doped highly oriented polyacetylene films were measured from 290 to 1.5 K. The conductivity and its anisotropy were significantly enhanced by stretching. The value of the conductivity was 18000 $\mathrm{S\,cm^{-1}}$ at 190 K, and remained at 14000 $\mathrm{S\,cm^{-1}}$, even at 1.5 K. The extraordinary high conductivity at very low temperature showed that the film is really metallic. The temperature dependence of the conductivity could be expressed as the sum of two terms: One is almost a temperature-independent term, which may be due to a very weakly localized free carrier; the other is due to a three-dimensional variable-range hopping mechanism of a more localized carrier. The conduction mechanism is discussed in terms of the polson model of doped polyacetylene.

The metal-nonmetal transition in a conducting polymer is an attractive subject in condensed-matter physics as well as in the structural chemistry of polymers. Especially polyacetylene ($[\mathrm{CH}]_x$), changes from nonmetallic to metallic states upon increasing the doping level. After a recent substantial improvement in the synthesis of polyacetylene,[1,2] an extensive effort still continues to elucidate the mechanism of the nonmetal-to-metal transition. Although numerous groups have investigated the transport properties,[3—7] a detailed picture of the electrical conductivity has not yet been proposed. A sample having high conductivity showed a metallic temperature dependence of conductivity over the range 300—200 K; below this temperature, however, the conductivity gradually decreases.[8]

In our previous study, the temperature dependence of the conductivity of iodine-doped polyacetylene (made by Shirakawa's method[9]) was analyzed by using one- and two-dimensional variable-range hopping models.[7] In this paper we present the temperature dependence of the electrical conductivity of highly conductive polyacetylene made by Tsukamoto's method,[2] and doped with perchlorate. Perchlorate ion was a good dopant for an optical study based on the transparency in the visible region.[10] It is also useful for conductivity measurements since the maximum value is fairly high. Moreover, it has no spin, while the $\mathrm{FeCl_4}^-$ ion has an effective spin which may influence the conductivity.[8] In our study of the polarized reflection spectra of perchlorate-doped polyacetylene,[10] the change in the optical and electrical properties upon stretching was found to be important for an analysis of the electronic structure and conduction mechanism. The polymer chain becomes more ordered and the interchain contacts are increased by stretching, causing the metallic property to appear. We discuss the effect of the orientation on the conductivity and temperature dependence of the conductivity in connection with the conduction mechanism.

Experimental

The Ziegler–Natta catalyst was prepared according to a technique described by Tsukamoto et al.[2] Polyacetylene films were synthesized in a glove box, where argon gas was circulated through a purification system that could keep the oxygen and water contents below 1.0 ppm, respectively.[1] The catalyst was cast with a uniform thickness of 10 μm on a glass plate by using Doctor Brade (Type YD-2, Yoshimitu Seiki Co., Ltd.). Acetylene monomer gas (six-nine grade) was passed over the catalyst cooled at −10 °C. After polymerization, the films were washed repeatedly with toluene, stretched by hand in the glove box with a stretching ratio of 3—8, and then dried in vacuo. The thickness of the stretched film was ca. 1 μm. The perchlorate doping was carried out in the glove box at room-temperature in an acetonitrile solution of dried copper(II) perchlorate by the same technique as that described previously.[10] The doping levels were determined based on the weight uptake. Polymerization, stretching, washing and perchlorate doping were carried out under a purified argon atmosphere. The temperature dependence of the electrical conductivity was measured by a conventional four-probe method with low-frequency (80 Hz) alternating current under vacuum condition. Electrical contacts were achieved by using silver paste. The temperature was monitored by a copper–constantan thermocouple

(290—30 K) and a calibrated carbon resistor (30—1.4 K).

Results and Discussion

Temperature Dependence of the Conductivity of Perchlorate-Doped Polyacetylene. Figure 1 shows the temperature dependence of the conductivity of perchlorate-doped with polyacetylene, $[\mathrm{CH(ClO_4)}_y]_x$, parallel to the stretching direction. The doping was carried out immediately after synthesis. Films (a) (y=0.074) and (b) (y=0.082) were doped to a saturated level, but film (b) was exposed to air for 30 min after doping. Film (c) was also a freshly prepared sample doped to y=0.022. The orientational order parameter ($\overline{P}_2$ (for the definition of $\overline{P}_2$, see Appendix)) of these films were estimated from the infrared absorption spectra to be 0.68. The room-temperature conductivity ($\sigma(T)$, Fig. 1 (a)) is 17000 $\mathrm{S\,cm^{-1}}$, and increases upon cooling, as in the case of $\mathrm{FeCl_4^-}$-doped polyacetylene.[11] This shows the maximum value to be at 190 K ($\sigma_{190\,\mathrm{K}}/\sigma_{\mathrm{RT}}=1.09$), as shown in the inset of Fig. 1; it then decreases to $\sigma_{1.5\,\mathrm{K}}/\sigma_{\mathrm{RT}}=0.84$ at 1.5 K. High conductivity ($\sigma>10^4$ $\mathrm{S\,cm^{-1}}$) down to 1.5 K implies that the heavily perchlorate-doped stretched polyacetylene is a metal with a weak localization of carriers. The temperature dependence of the conductivity is illustrated in Fig. 2 by a $\ln\sigma$ plot to $1/T$. The activation energy (ΔE) for curve (a) in the 3—1.5 K region is only 1.2 μeV, which is obtained by the fitting to

$$\sigma=\sigma_0\exp\left(-\Delta E/k_{\mathrm{B}}T\right). \qquad (1)$$

This means that most of the carriers are very weakly localized, even in the 1 K region. We also analyzed the conductivities of other films at very low temperature, and found σ_0 and ΔE of Eq. 1, as shown in Table 1. The most ordered heavily doped film (Fig. 1 (a) and (b), $\overline{P}_2$=0.68) shows a large σ_0 for the chain direction. In a previous study on the reflection spectra, we found that elongation of the film increases the inter- and intrachain interaction, producing a metallic reflectance.[10] The elongation results in an increase of σ_0 along the chain direction. In this respect, perchlorate-doped polyacetylene is highly anisotropic. It is remarkable that neither phonon scattering nor electron–electron scattering were found at very low temperature.

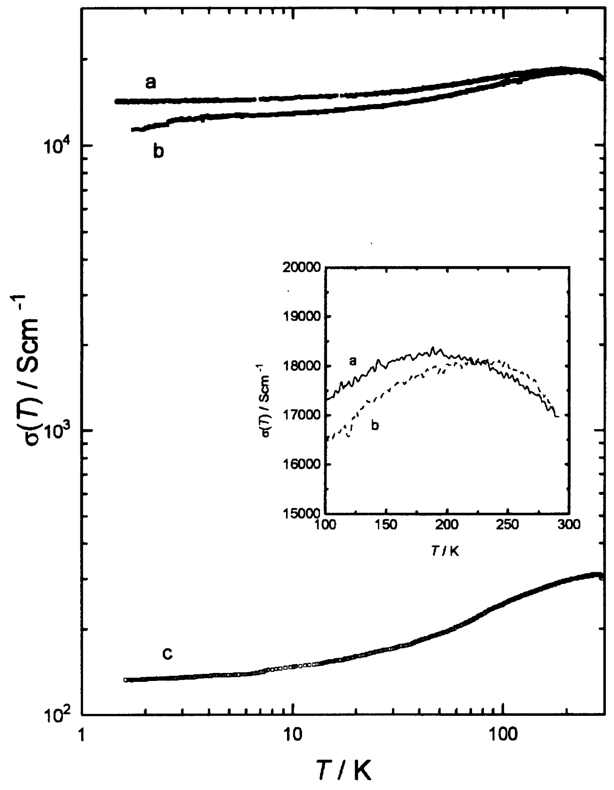

Fig. 1. Temperature dependence of conductivity parallel to the stretching direction; (a) stretched fresh sample, y=0.074, (b) y=0.083 (measured after 30 min exposure to air), and (c) y=0.022. The inset shows the expansion of the region from room temperature to 100 K.

A comparison of curves (a) and (b) of Fig. 1 shows the effect of oxidation by air. A decrease in the conductivity of the film of Fig. 1 (b) was noticed below 230 K, while that of curve (a) was found from 190 K. This may mean that the conductivity mechanism which dominates in the low-temperature region is influenced more by air. The activation energy for 2.5—5 K, estimated by the plot of Fig. 2 (b), was 7.2 μeV. This value is six-times larger than that of curve (a), suggesting the formation of deeper traps by oxidation in film (b) than

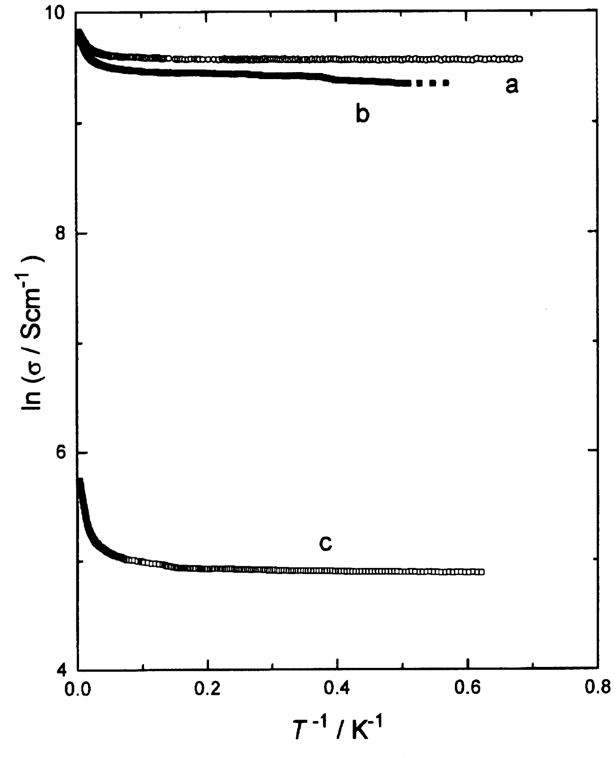

Fig. 2. $\ln\sigma$ against $1/T$ for the $[\mathrm{CH(ClO_4)}_y]_x$; (a) y=0.074, (b) y=0.083 (measured after 30 min exposure to air), and (c) y=0.022.

Table 1. Parameters of the Modified Three-Dimensional Variable Range Hopping Model

Sample	$\overline{P}_2$ [a)]	ΔE / 10^{-6} eV	T_1 / K	σ_0 / S cm^{-1}	T_0 / K	ln (A) [b)]	α / 10^5 cm^{-1}	L / Å	R / Å	ν_0 / cm^{-1}
y=0.074 fresh film (a) [c)]	0.681	1.2	30	14200	32700	14.61	77.1	13.0	17.4	149200
y=0.083 film (b) parallel [d)]	0.554	7.2	5	8200	18670	14.31	64.1	15.6	18.3	100400
perpendicular		9.0	2	220	26500	11.78	71.9	13.9	17.7	8500
y=0.072 parallel	0.681	10	10	12000	17000	14.36	62.0	16.1	18.4	104800
perpendicular		13	2	50	30500	10.81	75.3	13.3	17.5	3300
y=0.070 unstretched	0.0	17.8	5	70	29300	12.15	83.3	12.0	15.7	11200

a) For the definition of $\overline{P}_2$, see Appendix. b) For 3D VRH model $A=0.39[N(\varepsilon_F)/\alpha k_B T]^{1/2}\ \nu_0 e^2$. $N(\varepsilon_F)$=0.22 states/eV·(C atom) (for stretched sample) and 0.31 state/eV·(C atom) (for unstretched sample), respectively.[14] The lattice parameters are taken to a=8.0, b=8.6, and c=2.46 Å. c) These parameters are obtained from the curve of Fig. 1 (a). d) These parameters are obtained from the curve of Fig. 1 (b).

in film (a). Air oxidation enhances sp^3 defects in the conjugated double bonds of the polyacetylene chain.[12] Curve (c) of Fig. 1 shows the conductivity of a less-doped film (y=0.02); it indicates that a really metallic state is not realized at this level of doping. The room-temperature conductivity of y=0.022 was 300 S cm^{-1}; the conductivity decreased monotonically from room-temperature to 1.5 K with $\sigma_{1.5\,\mathrm{K}}/\sigma_{\mathrm{RT}}=0.44$

Above 10 K, the more tightly bound electrons are activated; the activation energy (ΔE) estimated from Fig. 2 and Eq. 1 is 0.88 meV for curve (a). Accordingly, the conduction mechanism in doped polyacetylene may be considered based on two terms: one is almost the temperature-independent conduction mentioned above; the other is a process requiring thermal activation. In fact, the contribution from the latter, which can be described by three-dimensional variable-range hopping (3D-VRH) conduction, becomes significant for a higher temperature region as shown below.

Variable-Range Hopping Analysis of the Conductivity of Oriented Polyacetylene. Following Mott's treatment,[13] the 3D-VRH conductivity is given by

$$\sigma(T)=0.39[N(\varepsilon_F)/\alpha k_B T]^{1/2}\nu_0 e^2 \exp\left[-(T_0/T)^{1/4}\right], \quad (2)$$

where $T_0=16\alpha^3/k_B N(\varepsilon_F)$, α^{-1} is the decay length of a localized state, or $L=\alpha^{-1}$ is the localization length (we will use this terminology in the following discussion), ν_0 is the hopping attempt frequency, and $N(\varepsilon_F)$ is the density of states near to ε_F per unit volume.[4] The optimum hopping distance (R) is given by

$$R=\left(\frac{3}{2\pi\alpha N(\varepsilon_F)k_B T}\right)^{1/4}. \quad (3)$$

We applied Eqs. 2 and 3 to the values of the conductivity after subtracting the contribution of the almost temperature-independent conduction expressed by Eq. 1 by using σ_0 and ΔE of Table 1. The residual conductivities follow the good relation of Eq. 2 fairly well, as shown in Fig. 3. It is remarkable that the relation between $\ln\sigma T^{1/2}$ and $T^{-1/4}$ holds over a wide temperature range. In this analysis we used the value of the density of states ($N(\varepsilon_F)$), to be 0.22 and 0.31 state/eV·(C atom), for the stretched and unstretched films, respectively, at the saturated doping level.[14] The lattice parameters for two CH chains are assumed to be as shown in Table 1.[15]

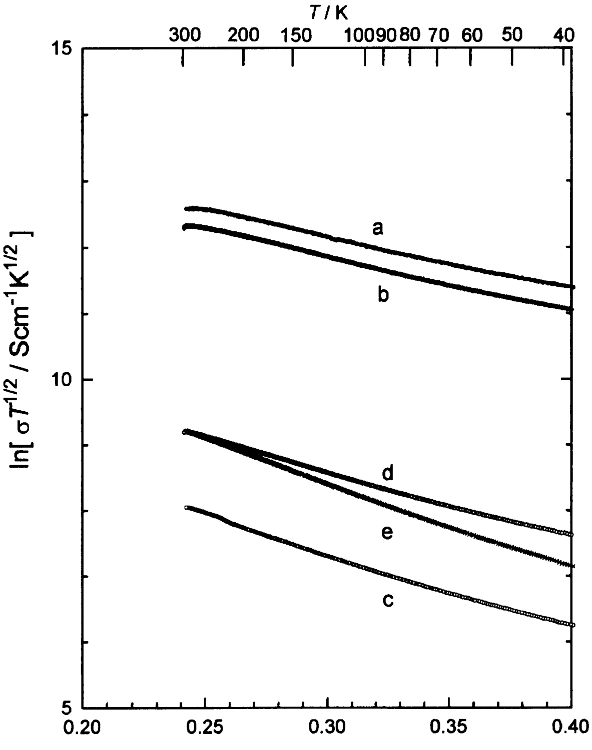

Fig. 3. $\ln\sigma(T)T^{1/2}$ against $T^{-1/4}$ plots for perchlorate-doped polyacetylene; (a) $\overline{P}_2=0.68$ parallel to the stretching direction. (b) $\overline{P}_2$=0.55 parallel to the stretching direction, (c) perpendicular to the stretching direction of (a), (d) perpendicular to the stretching direction of (b), and (e) unstretched film.

Combining Eqs. 1 and 2, the conductivity is given by

$$\sigma(T)=\sigma_0 \mathrm{e}^{-\Delta E/k_B T} +0.39[N(\varepsilon_F)L/k_B T]^{1/2}\nu_0 e^2 \mathrm{e}^{-(T_0/T)^{1/4}}. \quad (4)$$

The calculated conductivities with the parameters of

Table 1 are shown in Fig. 4 together with experimental points, which illustrates the good agreement between the experimental and calculated values throughout the examined temperature range. Above 200 K, the observed conductivity ($\sigma(T)$) decreased, which may have been caused by phonon scattering. The rotational motion of the perchlorate ion may be freed above 186 K,[16] leading to enhanced phonon scattering above this particular temperature. For film (c), the conductivity increased monotonously to 290 K; this may mean that the dominant conduction mechanism is not the same.

Concerning the temperature dependence of different conduction mechanisms, one is T^{-1} and the other is $T^{-1/4}$ on the exponent; this has been discussed in detail by Mott.[17] In Table 1 gives the cross-over temperature (T_1) from a nearly free to the VRH conduction according to this type of analysis. Below T_1 the conduction of a nearly free, or very weakly localized, carrier is dominant. The weakly localized carrier has an extended localization length (L), which it is effective for transport at a very low temperature, where thermal excitation is not available. From an activation energy of 1.2 μeV below 3 K, the value of L at 1.5—3 K was estimated using

$$\Delta E \approx \frac{1}{L^3 N(\varepsilon_{\mathrm{F}})} \qquad (5)$$

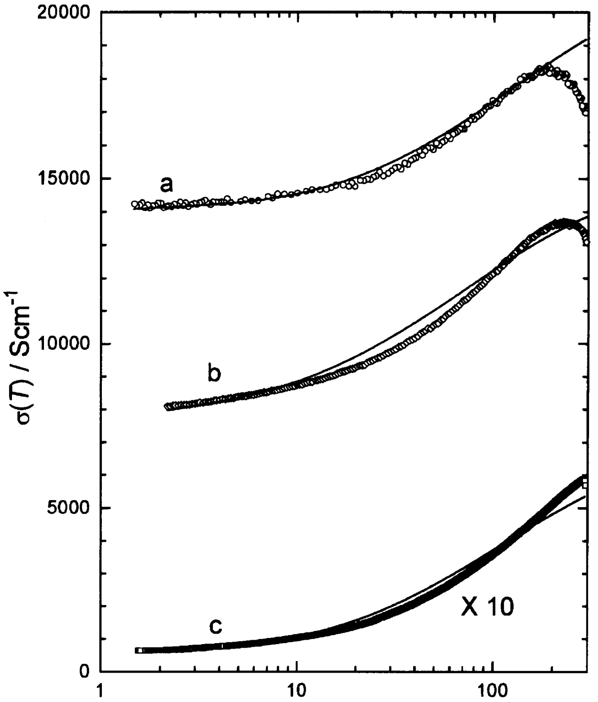

Fig. 4. Observed and calculated temperature dependence of conductivity; (a) y=0.074, $\overline{P}_2$=0.68 parallel to the stretching direction of fresh sample. (b) y=0.072, $\overline{P}_2$=0.55 (measured after 30 min exposure to air), and (c) y=0.07 unstretched. The solid lines are simulated temperature dependences of conductivity. For details, see text.

to be as large as 680 Å. In a stretched fresh film, the $T^{-1/4}$ dependence exists above T_1=30 K.

More reliable values for L and R above T_1 were obtained by an analysis using Eq. 4, and are tabulated in Table 1. These values are 13 and 18 Å, respectively, which had implications in an estimate using the polson model of the minimum L and R, being ca. 13 and 18 Å.

Effect of Stretching and Anisotropy of the Conductivity. The room-temperature conductivity of unstretched fims is only 500 S cm^{-1}. By stretching the film, the room-temperature conductivity parallel to the stretching direction is increased by a factor of 30—40, and a metallic property appears as shown in Fig. 1. The anisotropy of the conductivity is given by the ratio of the conductivity parallel and perpendicular to the stretching direction ($\sigma_{//}/\sigma_{\perp}$); its temperature dependence is shown in Fig. 5. The most ordered film ($\overline{P}_2$=0.68) exhibited a conspicuous temperature dependence, as shown in curve (a) of Fig. 5. The anisotropy was 92 at 280 K and 250 at 1.5 K. A strongly oriented, but mediumly-doped film of y=0.039 ($\overline{P}_2$=0.68) showed a similar behavior, as shown in Fig. 5 (b). In contrast, the anisotropy of a less-stretched film ($\overline{P}_2$=0.55) was almost constant (22—35), as shown in Fig. 5 (c).

In the preceding section the conductivity is expressed using two terms. At very low temperature, conduction by extended carriers dominates, whereas above 30 K, the 3D-VRH term becomes significant. The temperature dependence of anisotropy suggests that the extended carrier moves along the chain with a large anisotropy of 250 at very low temperature, while the

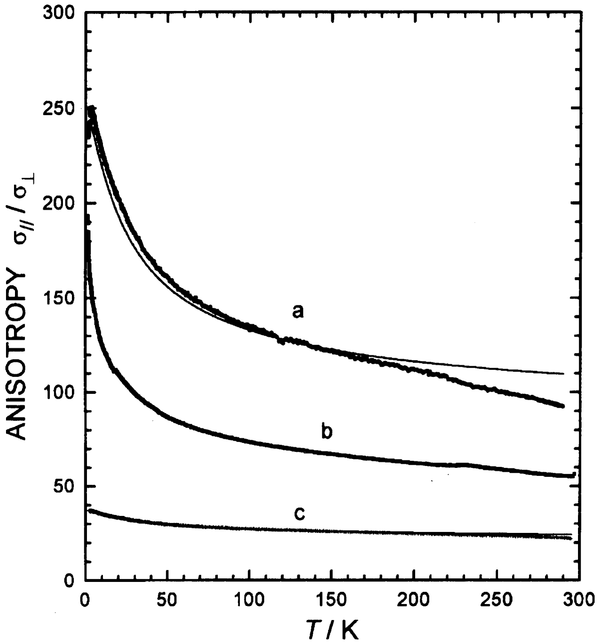

Fig. 5. Observed and calculated temperature dependence of anisotropic ratio for perchlorate-doped $(\mathrm{CH})_x$; (a) $\overline{P}_2$=0.68, y=0.083, (b) $\overline{P}_2$=0.68, y=0.039, and (c) $\overline{P}_2$=0.55, y=0.072.

VRH conduction involves interchain hopping. The anisotropy of the conductivity can be reasonably explained using the parameters given in Table 1; the calculated anisotropy for curves (a) and (c) for heavily doped films are shown by solid lines in the Fig. 5; they show satisfactory agreement with the observed values. The result provides additional support for Eq. 4, and the overall scenario of the conduction mechanism.

The σ_0 values dramatically increase by extensive stretching, as shown in Table 1; the σ_0 of a $\overline{P}_2=0.68$ film is 12000 $\mathrm{S\,cm^{-1}}$, a $\overline{P}_2=0.55$ film is 8200 $\mathrm{S\,cm^{-1}}$, and an unstretched ($\overline{P}_2=0$) one is only 70 $\mathrm{S\,cm^{-1}}$, respectively. The metallic conductivity appears due to an extended ordering of fibril, which enhances the interchain interaction.

Perpendicular to the stretching direction, the values of R and L are of the same order of magnitude as for the parallel direction, indicating that a 3D nature of the interaction is conceivable. However, hopping to the perpendicular direction requires slightly larger activation energy, as indicated by the larger T_0 in Table 1. The hopping frequency (ν_0) in the direction perpendicular to the stretching direction is apparently more than one order of magnitude smaller than that in the parallel direction; this means that the phonon density of states is larger along the chain direction.

By transmission electron microscope (TEM) observations of an ultra-thin stretched film,[18] a small part of fibril was found to still exist along the perpendicular direction. The electrical conductivity for the perpendicular direction may be caused by this component, rather than an intrinsic property of perpendicular transport in a less-ordered system. However, the trend of the temperature-dependent anisotropy conductivity of Fig. 5 (a) is not compatible with the expected behavior based on this mis-oriented fibril transport, since the anisotropy of the conductivity shows a temperature dependence in the low-temperature region. In a previous study of the reflection spectra of highly oriented polyacetylene,[10] the real part of the dielectric function of a highly ordered film showed a negative value for the perpendicular direction in the far-infrared region. This implies that a metallic state is realized even for the perpendicular direction in a highly ordered system. The temperature dependence of the anisotropy, and a similar localization length for parallel and perpendicular directions, suggests that hopping to an adjacent chain (interchain hopping) occurs significantly, as well as does intrachain hopping in the high-temperature region.

Polson Model of Perchlorate-Doped Polyacetylene. By studying the optical and structual aspects of doped polyacetylene, we proposed the polson model.[19—21] The characteristic point of the model is that an unpaired electron is enclosed by two charged soliton structures which comprise dopant-coordinated allylic groups. Figure 6 shows an idealized model of a polson–antipolson chain (a) and interchain contacts in the ordered fibril structure (b).

Although the crystal structure of perchlorate-doped polyacetylene is not perfectly determined,[15] we can estimate the structure based on the dopant concentration and polson model. Saturated perchlorate-doped polyacetylene contains 8 mole percent per repeat unit of the $[\mathrm{CH}]_x$ chain. Accordingly, twenty-five carbon atoms involving two dopant-coordinated groups form a polson unit. This chain unit may be the smallest polson structure in the perchlorate-doped polyacetylene, suggesting that the minimum polson unit length is ca. 30 Å, since each C–C bond length would be ca. 1.2 Å along the chain direction. If we consider more strictly the structure of the polson unit (Fig. 6), an unpaired electron is contained within 11 carbon atoms between the dopants, and a value of 13 Å found for L, as mentioned in the preceding section. The carrier (an unpaired electron) in the polson unit moves freely within the unit, making the minimum L to be ca. 13 Å. The hopping distance ($R\approx 18$ Å) to the nearest neighbor is naturally explained in Fig. 6 by hopping to the inter- or intrachain neighboring polson unit.

Along the one-dimensional polson chain, we can estimate the conductivity using

$$\sigma = \frac{e^2}{4\pi^3\hbar}\nu_{\mathrm{F}} S_{\mathrm{F}} \tau, \qquad (6)$$

where ν_{F} is the Fermi velocity, S_{F} the area of the Fermi surface, and τ the relaxation time of a free carrier.

From an energy-band calculation of the one-dimensional polson chain,[20,21] we estimated ν_{F} to be 10^8 $\mathrm{cm\,s^{-1}}$; τ was estimated to be 10^{-13} s by an optical experiment.[10,21] By using the lattice parameters of $a=8.0$, $b=8.4$, and $c=2.46$ Å, the conductivity was estimated as 2×10^5 $\mathrm{S\,cm^{-1}}$. The experimentally obtained σ_0 is one order of magnitude smaller than this value, presumably because of scattering due to impurities and defects in the π-conjugated system. However, a pretty good agreement between the theoretical and experimental values supports the picture of a one-dimensional metallic band of the polson chain structure.

A one-dimensional metal is not stable to a Peierls distorsion, and it thus seems paradoxical that the doped polyacetylene shows a highly anisotropic conduction. In fact, high metallic conductivity is realized by extensive stretching with intimate contact among the chain, thus expanding the dimensionality due to the interchain interaction. The interchain contact is essential for realizing a metallic state. Therefore, the doped polyacetylene should be regarded as being a three-dimensional metal with a large anisotropy, but not as being a one-dimensional conductor.

Conclusion

The electrical conductivities of heavily perchlorate-doped highly oriented polyacetylene films were measured at 290—1.5 K; the maximum value was 19000

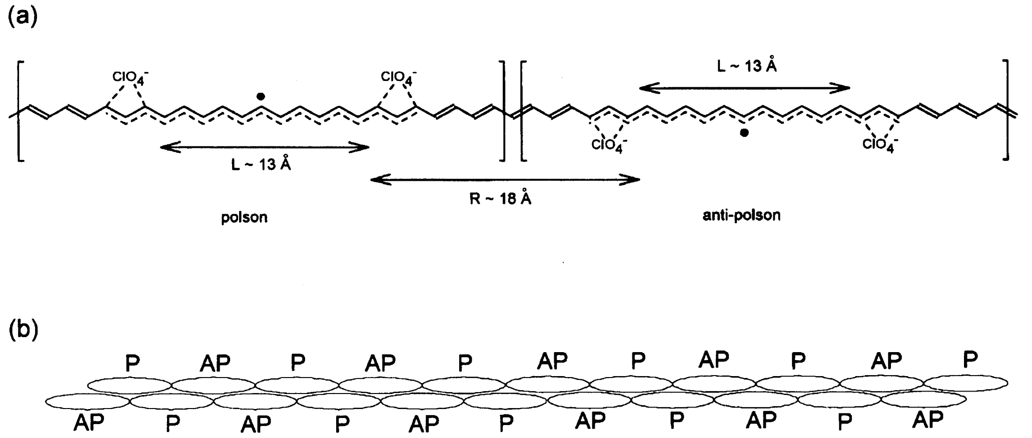

Fig. 6. Structural formula for perchlorate ions in doped polyacetylene (a) and the interchain contact between the nearest neighbor polson–antipolson chain of doped polyacetylene (b). Unpaired electrons are shown by block circles.

$\mathrm{S\,cm^{-1}}$ at 190 K. Metallic conductivity with a large anisotropy was realized by extensive stretching. The temperature dependence of the conductivity was analyzed by a neat formula, in which almost temperature-independent and a variable-range hopping (VRH) terms are included. The conduction at very low temperature is highly anisotropic, since three-dimensional VRH is suppressed at low temperature. Although the conductivity is much larger along the chain direction than in the perpendicular direction, heavily doped polyacetylene is never a one-dimensional conductor, since the metallic property is caused by the interchain and interfibril contact with stretching. Moreover, the conductivity for the perpendicular direction could be explained by a three-dimensional VRH mechanism. The free carriers, which are very weakly localized, are considered in the polson unit, and the polson chain may form a metallic energy band.

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Appendix

The definition of the order parameter ($\overline{P}_2$) was given by Jen et al.,[24] and was explained in our previous paper.[10] By fixing the z-axis parallel to the stretching direction, the second-order parameter ($\overline{P}_2$), which is a Legendre polynomial, is given by

$$\overline{P}_2 = \langle P_2(\cos\theta)\rangle = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{A1}$$

where θ is the angle between the axis of the individual polymer chain direction and the macroscopic symmetry axis, and $\langle\cdots\rangle$ is the thermal average. It is assumed that the polymer chains are linear and that each chain has a series of independent absorbing groups in which the transition dipole moments are inclined at a common angle (α) to the chain axis. Following this model, the $\overline{P}_2$ and the observed dichroic ratio (R) are given by

$$\overline{P}_2 = \frac{(2\cot^2\alpha + 2)(R-1)}{(2\cot^2\alpha - 1)(R+2)}. \tag{A2}$$

The $\overline{P}_2$ of an undoped film was estimated by the dichroic ratio R of the bands at 738 $\mathrm{cm^{-1}}$ (CH out-of-plane vibration band of *cis*-polyacetylene) and 1029 $\mathrm{cm^{-1}}$ (CH out-of-plane vibration band of *trans*-polyacetylene).[9] These bands are polarized perpendicular to the polyacetylene chain. The angle θ represents an average angle of disorientation of the chain to the stretching direction. From the dichroic ratio, we could obtain the second-order parameter as follows by allowing α to tend to be zero:[25]

$$\overline{P}_2 = \frac{(R-1)}{(R+2)}. \tag{A3}$$

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