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Charge transport and thermoelectric conversion in solution-processed semicrystalline polymer films under electrochemical doping

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Charge transport and thermoelectric conversion mechanisms in doped semicrystalline polymer films are key issues in the field of wearable electronics, whereas the complex film structure consisting of crystalline domains and non-crystalline boundaries prevents sufficient understanding of them. In this study, we fully clarify the roles of the domains and the boundaries in a typical semicrystalline polymer on macroscopic charge transport under continuous electrochemical doping. In the crystalline domains, a multi-step transformation of the transport properties from effectively metallic behavior to weak localization (WL) to variable-range hopping (VRH) is found with decreasing temperature and doping level. On the other hand, at the domain boundaries, the effectively metallic conduction changes directly to VRH. Based on these results, the extremely complicated phase diagram, including the coexistence of the WL and VRH processes, is well explained. The proposed transport mechanism further explains the thermoelectric properties of the film.

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The charge transport mechanism in doped conducting polymer thin films has been a long-pursued issue for over 40 years since the first report of electrical conduction in iodine-doped polyacetylene by Shirakawa and co-workers in 1977¹. Owing to the development of sophisticated materials and doping methods, the transport performance and processability of polymer films have undergone significant improvements, which allow their application to flexible electronic devices such as sensors, transistors, and thermoelectric converters^{2–4}. On the other hand, inhomogeneous film structures, consisting of ordered domains (fibrils or aggregates) and disordered boundary regions, complicate the charge transport mechanism in these materials, which makes it difficult to design high performance devices. This is made evident by the contradictory results between carrier transport properties and other measurements. In the temperature T dependence of the conductivity σ , $d\sigma/dT$, most polymers exhibit a positive $d\sigma/dT$ slope, showing insulating behavior even when highly doped, where the metallic state is detected by other probes such as optical and magnetic measurements^{5–7}. This contradiction must be resolved and a full understanding of the transport mechanism is required in order to improve device performance.

For this purpose, a typical semicrystalline polymer poly(2,5 bis (3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) [pBTTT, Fig. 1a] provides a suitable platform, because it exhibits unique transport properties upon carrier doping. It has been suggested that highly doped pBTTT exhibits a positive $d\sigma/dT$, ascribed to the variable-range hopping (VRH) mechanism, whereas magnetoconductivity (MC) measurements have revealed a phase-correlative transport process consistent with weak localization (WL)^{8–10}, where quantum interference due to coherent back-scattering causes charge localization^{11,12}. This apparent contradiction between the fundamentally different transport mechanisms likely reflects the

effects of domain boundaries on charge transport, although the detailed mechanism is still unclear.

Recently, we have demonstrated pBTTT thin films that exhibit “effectively metallic” behavior, using a continuous electrolyte gating method¹³. Here, we use the term “effectively metallic” because of the observation of the negative $d\sigma/dT$. Since no localization effects are found in this effectively metallic regime, observations of this new type of film gives a valuable opportunity to clarify the effect of domain boundaries on both the carrier transport and thermoelectric properties by controlling the conduction regime from the insulating regime to the effectively metallic regime by changing only the gate voltage (V_G).

In the present study, we combine measurements of the T dependence of the conductivity $\sigma(T)$ and MC measurements to fully reveal the charge transport mechanism for pBTTT thin films doped by the electrolyte gating method over a wide range, including the effectively metallic state, down to low temperatures. In particular, MC measurements of the doped film are crucial because they can directly detect hidden local charge transport processes^{14,15}. Indeed, we observed the coexistence of WL and VRH processes at low temperatures from MC measurements that could not be detected by $\sigma(T)$ measurements. These observations clarify the temperature vs. carrier density phase diagram for electrolyte-gated pBTTT films and reveal the roles of domains and boundaries. Moreover, we have further demonstrated that the reported thermoelectric properties of doped pBTTT films¹³ can be better explained by considering the effect of domain boundaries in the insulating regime.

Results and discussion

Electrolyte-gated transistor fabricated from polymer thin film with effectively metallic conduction. An electrolyte-gated transistor containing pBTTT was fabricated on a glass substrate using

Fig. 1 Conductivity and magnetoconductance measurements by using the ionic-liquid-gated thin-film transistor structure. **a** Chemical structures of poly (2,5 bis (3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT) and constituents of the ion gel, N,N-diethyl-N-methyl-N-(2-methoxymethyl) ammonium (DEME), bis(trifluoromethanesulfonyl)imide (TFSI) and poly(vinylidene fluoride-co-hexafluoropropylene) [p(VDF-HFP)]. **b** Schematic device structure of the ion gel-gated transistor with a side-gate structure. Here, G, S, and D denote gate, source, and drain electrodes, respectively. **c** Photograph of a typical device shown with a 1-mm scale. **d** Transfer characteristics and gate current of the device operated at room temperature. Here, I_D , I_G , V_G , and V_D represent the drain current, gate current, gate voltage, and drain voltage, respectively. The source electrode is grounded. **e** Temperature T dependence of conductivity σ at gate voltage $V_G = -2.2$ V. Inset: effectively metallic magnetoconductance $[\sigma(B) - \sigma(0)] / \sigma(0)$ observed at $V_G = -2.2$ V at 150 K. The solid curve shows the fitting of the experimental data by a quadratic relation of the magnetic field.

an ion gel (Fig. 1a), as illustrated in Fig. 1b. We used a two-terminal method for the $\sigma(T)$ and MC measurements, whose applicability will be discussed later. A photograph of a typical device is shown in Fig. 1c. Details of the fabrication conditions for the device are described in the Methods section. Figure 1d shows the transfer characteristics of the transistor device at room temperature. The drain current can be continuously controlled by applying V_G throughout the electrochemical doping process, where the dopant ions intercalate into the alkyl chain region increasing the lattice constant along lamellar direction, as was confirmed by X-ray diffraction measurements¹³. A *p*-type behavior, i.e., drain current increasing under negative V_G with negligible gate leak current, was observed.

Figure 1e shows $\sigma(T)$ at $V_G = -2.2$ V and the negative $d\sigma/dT$ indicating effectively metallic conduction, observed down to 95 K¹³. In addition, as shown in the inset of Fig. 1e, at 150 K we observed a small but finite negative MC following a simple parabolic magnetic field dependence. The observation of the negative parabolic MC, i.e., positive magnetoresistance, could be either interpreted as that of a metal or a semiconductor. Since we observe a metal-like temperature dependence, not activation-type temperature dependence, of conductivity at this temperature, it is natural to consider that the negative MC is characteristic of the effectively metallic transport¹³, as will be discussed later. Therefore, both the temperature and magnetic field dependences of the conductivity indicate that effectively metallic transport is realized even across the domain boundaries in electrolyte-gated pBTTT films, which contrasts with previous reports on the same material^{8–10}. In field effect transistors of pBTTT based on solid-state insulators, it has been reported that the charge transport is dominantly limited by the potential barriers at the domain boundaries¹⁶, which suggests the possibility of a more efficient interconnection between domains for highly doped electrolyte-gated pBTTT films by planarized tie molecules¹³.

Temperature dependence of conductivity at various doping levels. Figure 2a shows $\sigma(T)$ under various values of V_G plotted on a logarithmic temperature scale measured with two-terminal method. Effectively metallic $\sigma(T)$ was observed for $|V_G| > 1.7$ V. Starting from the effectively metallic conduction, $\sigma(T)$ decreased rather logarithmically by further cooling.

We analyze these results based on the VRH model, in accordance with most previous reports^{8–10}. To evaluate the localization effect within the framework of the VRH model, we examine $\sigma(T)$ according to the Zhabrodskii analysis¹⁷, as shown in Fig. 2b, in which logarithmic derivatives of $\sigma(T)$,

$$W = \frac{d(\log \sigma)}{d(\log T)}, \quad (1)$$

are plotted on a logarithmic scale as functions of $\log T$. The plot shows a straight line with a slope a when $\sigma(T)$ follows the Mott VRH model,

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^a \right], \quad (2)$$

where σ_0 is a temperature-independent factor and T_0 is a characteristic temperature that depends on the localization length and density of states at the Fermi energy. The exponent a represents the dimension of the conduction: $a = 1/4$ for three dimensional (3D) conduction, $a = 1/3$ for 2D, and $a = 1/2$ for 1D¹⁸. In the strongly localized regime where Coulomb interaction is important, Efros and Shklovskii discussed that the exponent is $a = 1/2$ for every dimension (ES-VRH)¹⁹, with $T_0 \equiv T_{ES}$ depending on the localization length and the dielectric constant. As shown in Fig. 2b, Zhabrodskii plots show straight lines below

Fig. 2 Temperature and gate voltage dependence of the conductivity. **a** Semilogarithmic plot of the temperature T dependence of the conductivity $\sigma(T)$ under different gate voltages V_G . The arrows indicate the temperatures of the maximum conductivity for each V_G . $\sigma(T)$ deviates from $\ln T$ dependence at low temperature side. **b** Zhabrodskii plot (a double-logarithmic plot of $W = d(\log \sigma)/d(\log T)$ vs. T) for each V_G . The variable-range hopping exponents a obtained by the analysis are indicated besides each curve.

~ 20 K for $|V_G| > 1.7$ V and ~ 50 K at $V_G = -1.3$ and $V_G = -1.4$ V, with a changing from 0.16 ($V_G = -2.2$ V) to 0.56 ($V_G = -1.4$ V below 15 K). The a and T_0 values are tabulated in Supplementary Table 1 in Supplementary Note 1. At the low gate voltages below $|V_G| = 1.7$ V, the transport at lowest temperature range can be understood by the ES-VRH with exponent $a \sim 0.5$ ^{20,21} while the exponent a decreases to 0.34–0.37 (close to 2D-VRH exponent) at higher temperatures above 15 K. Such temperature dependence of a has also been reported by several groups and ascribed to the crossover from ES-VRH to Mott VRH models^{20,21}. At the highest doping level with $V_G = -2.2$ V the exponent of $a = 0.16$ is lower than that for 3D VRH models, suggesting that the localization effect becomes very weak.

Magnetoconductance. In Fig. 3 we show the MC, $\Delta\sigma(B) = \sigma(B) - \sigma(0)$, under a magnetic field applied perpendicular to the substrate at (a) $V_G = -2.2$ V, (b) $V_G = -1.85$ V, and (c) $V_G = -1.3$ V for various temperatures measured with two-terminal method. At $V_G = -2.2$ V, we observed negative parabolic MC at 150 K, in agreement with the former result¹³. On the other hand, at 100 and 125 K, the MC turned positive, indicating a crossover of the conduction mechanism from the effectively metallic regime to a WL regime. Below 95 K (at 50 and 20 K), we observed a positive MC ascribable to the WL. At low temperature below 10 K, the negative MC component at high field region was observed together with the positive MC at low field region. At $V_G = -1.85$ V,

Fig. 3 Temperature and gate voltage dependence of the magnetoconductivity. The magnetoconductivity $\Delta\sigma = \sigma(B) - \sigma(0)$ under a magnetic field applied perpendicular to the substrate observed at gate voltages **a** $V_G = -2.2$ V, **b** $V_G = -1.85$ V, and **c** $V_G = -1.3$ V. The solid curves represent fits based on the Hikami-Larkin-Nagaoka model.

and $V_G = -1.3$ V, the positive MC was observed also in the temperature range above 20 K, below which the negative MC component coexisted at high field region. At $V_G = -1.3$ V, only the negative MC was observed below 7 K. The MC measurement results for three other voltages, $V_G = -2.0$ V, $V_G = -1.7$ V, and $V_G = -1.4$ V, are described in Supplementary Note 2 and Supplementary Figs. 1 and 2, with the results at these voltages being basically similar to those at $V_G = -2.2$ V, $V_G = -1.85$ V, and $V_G = -1.3$ V, respectively.

Comparison of the $\sigma(T)$ and MC results between two-terminal and four-terminal measurements. The conductivity measurements shown above were carried out with two-terminal method. However, in order to measure the intrinsic electric resistance, four-terminal resistance measurements without the influence of contact resistance are preferred. In order to verify the validity of the results obtained with two-terminal method, we performed four-terminal measurements at gate voltages of $V_G = -2.2$ and -1.7 V, as summarized in Supplementary Note 3. The schematic diagram of the device for four-terminal measurement are shown in Supplementary Fig. 3. Supplementary Fig. 4a, b show the $\sigma(T)$ results by the four-terminal $\sigma_{4t}(T)$ and two-terminal $\sigma_{2t}(T)$ analyses of the same measurement. The behavior of $\sigma_{4t}(T)$ and $\sigma_{2t}(T)$ seems different in appearance, probably due to contact resistance effects. However, the tendency of the effective metallic behavior at high temperature side and decreasing σ with asymptotic $\ln T$ -dependence at low temperatures are common to the two analyses. This is the same as the two-terminal data in Fig. 2 for the spin-coated film. We show the corresponding Zhabrodskii plot in Supplementary Fig. 4c, d. We observed basically similar behavior with straight lines below ~ 20 K for the $\sigma_{4t}(T)$ and $\sigma_{2t}(T)$. This also agrees with those found for the spin-coated film, although the exponents were slightly different.

Supplementary Fig. 5 shows MC results at $V_G = -2.2$ V and -1.7 V by four-terminal (a and c) and two-terminal (b and d) analyses, respectively. The results are qualitatively the same and also common to the two-terminal data in Fig. 3, in the sense that

positive MC was observed above 20 K and mixing negative MC component was observed below 10 K. The similarity of the MC behavior by four-terminal and two-terminal measurements could be ascribed to the negligible magnetic field effect on contact resistances. The negative MC at high temperature side was not observed at 180 K for $V_G = -2.2$ V, which agrees with the absence of the effectively metallic behavior at this temperature. Quantitatively, however, the magnitude of the absolute value of $\Delta\sigma(B) = \sigma(B) - \sigma(0)$ was ten times (at ~ 100 K), several times (at ~ 10 K) larger than that of the two-terminal measurements.

According to the similarity of the tendency of the measured $\sigma(T)$ and MC results, we can justify the use of the results of two-terminal measurements to discuss the overall characteristics of the $\sigma(T)$ and MC changing from effectively metallic to WL and finally to VRH conduction.

Angular dependence of MC. As shown in Fig. 3, and corresponding four-terminal result shown in Supplementary Fig. 5, we observed positive MC in a wide ranges of gate voltages and temperatures. Except the organic magnetoresistance (OMAR) reported in the low magnetic field mT region of the sandwich structure²², the positive MC has been ascribed to the WL effect⁸. Both 2D and 3D, WL shows positive $MC \propto B^2$ at low magnetic field, and $\propto B^{1/2}$ at high magnetic field. Distinguishing which model should be applied is in principle difficult in case the magnetic field is applied only perpendicular to the film. In order to verify the two-dimensionality of the MC in the present film, we conducted angular-dependent MC measurements at 30 K at $V_G = -1.7$ V, where the positive MC was observed, as described in Supplementary Note 4. This measurement was carried out with four-terminal method. We show in Supplementary Fig. 6 that the positive MC decreased with the angle of the magnetic field tilted from the normal to the film. When the magnetic field is parallel to the film, a negative MC was observed. As shown in Supplementary Fig. 7, the positive component of MC is scaled with $\cos^2\theta$, where θ is the angle between the normal of the film and the magnetic field. This means that MC only depends on the

component of magnetic field perpendicular to the film, indicating the 2D nature of MC that is the same as that reported for the F4TCNQ doped PBTTT⁸. The MC can be modeled with positive one due to 2D-WL and negative one due to the electron–electron-interaction (EEI)^{8,11,23}. We note that such 2D carrier transport in a polymer film is enabled because the polymer film takes “edge-on” structure in which the polymer backbone direction with the highest conductivity, and the π -stack direction with the second highest conductivity are both within the 2D plane of the film^{8,13}.

Application of 2D model for the analysis of positive MC by 2D WL model. In the previous subsection, the observed positive MC is confirmed to be ascribed to the 2D-WL, as was reported previously for PBTTT^{8,23}. In 2D-WL, $\sigma(T)$ follows a logarithmic temperature dependence^{11,12}, that is indeed observed down to ~ 20 K for $|V_G| > 1.7$ V, as shown in Fig. 2a, and also by the four-terminal measurement shown in Supplementary Fig. 4a. Because we observe WL behavior with positive MC at lower temperature side of the negative MC as shown in Fig. 3a, the interpretation that the negative MC at 150 K is a sign of the effectively metallic conduction could be rationalized by considering that the influence of WL is suppressed at 150 K.

In the 2D-WL model, the positive MC can be attributed to suppression of the constructive interference loop by the magnetic field based on Hikami–Larkin–Nagaoka’s model in two dimensions (hereafter, the HLN model)¹², in which the magnetic field B dependence of the conductivity increment $\Delta\sigma(B) = \sigma(B) - \sigma(0)$ is written as,

$$\Delta\sigma(B) \propto -\frac{e^2}{2\pi^2\hbar} \left[\log \frac{B_\phi}{B} - \Psi \left(\frac{1}{2} + \frac{B_\phi}{B} \right) \right], \quad (3)$$

where e is the elemental charge, $\hbar$ is the reduced Planck constant, and $\psi(x)$ is the Digamma function. B_ϕ is a characteristic magnetic field dependent on the phase coherence length λ as,

$$B_\phi = \frac{\hbar}{4e\lambda^2}. \quad (4)$$

The existence of such quantum interference effect means the phase-correlative transport extending within the length λ , indicates the evidence for the phase-correlative transport. Here, we rule out the contribution of the term from the spin–orbit coupling which gives rise to antilocalization with negative MC effect, because such effect is usually limited at small magnetic field below 1 T and moreover the spin–orbit interaction is considered to be small in the case of conducting polymers⁸.

Below 95 K (at 50 and 20 K), we observed a positive MC, which follows the HLN model, showing a WL effect. Thus, the carrier conduction in this intermediate temperature region cannot be understood in terms of metallic transport and VRH, but can be ascribed to WL, which is consistent with the $\log T$ dependence of $\sigma(T)$ seen in Fig. 2a. By an analysis according to the HLN model, $\lambda = 3$ –15 nm is deduced ($\lambda = 5$ –20 nm for the four-terminal measurements), as shown in Supplementary Note 5, Supplementary Figs. 8 and 9, which are the same range as reported for chemically doped pPBTTT^{8–10}. Note that the negative MC component originated from EEI is opposite to the positive MC in 2D-WL. Because of such negative component, the magnitude of MC due to WL may be larger below 30 K. As a result, the calculated λ may be longer within a factor of 2. Therefore, maximum value estimated for λ is ~ 40 nm at 20 K.

On the other hand, below 20 K, where the VRH analysis of $\sigma(T)$ become applicable, a mixing of positive and negative components of MC was observed. The positive MC at lower magnetic field can be attributed to WL and negative MC may be ascribed to the EEI effect; however, negative MC contribution from the VRH conduction

should also appear because $\sigma(T)$ shows VRH behavior as verified also in the four-terminal measurement. In VRH, the shrinkage of the wave functions gives rise to the negative MC in which the B dependence of conductivity becomes $\sigma(B)/\sigma(0) \sim -\exp(B^2)$ ¹⁹.

In Fig. 3b we show the MC results at $V_G = -1.85$ V, where $\sigma(T)$ shows effectively metallic behavior down to 145 K and VRH below 20 K. The negligible magnetic field dependence of conductivity at 150 K might be attributed to the effectively metallic transport. A clear positive MC was observed at 125, 100, 50, and 20 K, indicating WL conduction following the HLN model. Below 10 K, a mixture of positive and negative MC, similar to those at $V_G = -2.2$ V, was found.

Finally, in Fig. 3c we show the MC results at $V_G = -1.3$ V, where $\sigma(T)$ showed almost ideal ES-VRH behavior with $a = 0.5$ with crossover to Mott VRH above 15 K but neither metallic nor $\log T$ behavior of $\sigma(T)$ indicating the delocalized transport mechanism was observed. However, in stark contrast to the temperature dependence, a positive MC showing WL was observed at 150, 100, and 50 K, even though $\sigma(T)$ shows VRH behavior, demonstrating that we cannot investigate the transport mechanism of conducting polymers based only on the temperature dependence of the conductivity. Below 20 K, a mixture of positive and negative components of the MC was again observed.

At the lowest temperature region of 7, 5, and 4 K, only a negative MC was observed. Owing to the ES-VRH in this temperature range, we analyze the results based on the ES-VRH model to confirm the origin of the negative components of the MC, summarized in Supplementary Note 6, in which the negative MC is well described by $\sigma(B)/\sigma(0) \sim -\exp(B^2)$ ¹⁹ (Supplementary Fig. 10), showing that the negative components of MC can be ascribed to VRH models. The VRH hopping length is deduced to be ~ 10 nm, which is of the same order as the HLN coherence length λ deduced above and also as those found previously for p3HT²⁰.

Here we summarize the important experimental results. Figure 4a illustrates a T – V_G schematic diagram for the conduction mechanism. We found a successive transformation from effectively “Metallic” to “WL” and finally to “VRH” as T and $|V_G|$ decrease in the diagram. The “WL + VRH” region with coexisting WL and VRH contributions extends over a wide range in the diagram. The VRH component in $\sigma(T)$ and the MC was identified at low temperatures below 20 K. At $V_G = -2.2$ V, the WL contribution in the MC was found at 1.9 K, indicating that the delocalized transport contribution extends down to the lowest temperature. In the “Metallic + WL” region, the coexistence of effectively metallic behavior in $\sigma(T)$ and a positive MC caused by WL was observed. This is in strong contrast to an ordinary metal in which the WL effect is observed only in the temperature range, where $\sigma(T)$ turns to show nonmetallic behavior indicating the effect of the complex film microstructure on the transport properties.

Multistep transformation of the conduction mechanism in semicrystalline polymers. In the following, we discuss the origin of the multistep transformation of the conduction mechanism in the highly doped state at $|V_G| > 1.7$ V. We pay attention to the polymer film structure consisting of crystalline domains and boundaries between them, as illustrated in Fig. 4b–d. For the boundary region, the crystallites are believed to be connected via “tie molecules”^{24–29}, whose local structure crucially affects the transport process¹³. Therefore we must take account of inter-domain charge transport, which can be different from the intradomain transport, to clarify the conduction mechanism for the polymer thin film.

The observation of effectively metallic conduction indicates that delocalized transport prevails throughout the film including

Fig. 4 $T - V_G$ schematic diagram and schematic conduction mechanism at each regime. **a** A temperature T vs. gate voltage V_G schematic diagram of the conduction mechanism consisting of effectively metallic, effectively metallic + weak localization (WL), WL, WL + variable-range hopping (VRH), and VRH regions, based on the magnetoconductivity (MC) measurements. The closed circles, open rectangles, open triangles, and open circles represent the experimental points at which effectively metallic, WL, mixed WL and VRH, and pure VRH behaviors were observed in the MC measurements. MC data other than those shown in Fig. 3 are summarized in Supplementary Note 2, Supplementary Figs. 1 and 2. **b–d** Schematic of the poly(2,5 bis (3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT) film structure consisting of crystalline domains and boundaries surrounding them and the transport mechanism at each temperature range. Pink circles and red lines represent the crystalline domains and polymer chains, respectively. At high temperatures, each crystallite is connected to allow macroscopic delocalized transport, either **b** effectively metallic or **c** WL. The WL conduction occurs when a localized loop path (blue arrows) is formed within the crystallite. **d** At low temperatures, coherency of the conduction across boundaries is lost and each crystallite is isolated by barriers through which VRH conduction occurs.

both the crystalline domains and boundaries (Fig. 4b). The absence of VRH in this high-temperature range indicates that the domains are connected coherently, and the boundary does not limit the effectively metallic conduction. When WL breaks the effectively metallic conduction, carrier localization at the boundary should first be considered. In WL, a constructive quantum interference loop of carriers is expected to be created with a size of the phase coherence length λ along which carriers suffer inelastic scattering by random potentials^{11,12}. If we assume that the scattering centers are located at boundaries, the trajectory should extend over several crystalline domains. However, the size of λ is ~ 10 nm at ~ 100 K, at which the positive MC first appears, as explained in Supplementary Note 5. Such a short λ may be smaller than the typical size of the crystalline domains in pBTTT films evaluated by electron microscopy and NEXAFS mapping measurements^{30–32}. Thus, the 2D loop pathways may be well confined within each crystalline domain, as illustrated in Fig. 4c. In such an intracrystallite loop pathway, intradomain structural disorders such as imperfections, distortions, or stacking faults of polymer chains act as scattering centers. Even though the localization nucleates in the crystalline domain, the connection at the boundary can still allow delocalized transport since the planarized cationic molecules in the highly doped state enable highly efficient interdomain connections¹³.

In the region denoted as “Metallic + WL”, $\sigma(T)$ retains effectively metallic behavior while the MC begins to show WL behavior. This can be understood by considering the difference in the critical temperature of each crystalline domain for the

occurrence of WL, which depends on the concentration of scattering centers. At a specific temperature in the “Metallic + WL” region, WL occurs in some domains while other domains may remain effectively metallic. The $\sigma(T)$ shows the effectively metallic behavior while percolation pathways through effectively metallic domains are connected, even though the WL domain will exhibit a positive MC component. With a further decrease in temperature, the number of crystalline domains showing WL increases and percolative metallic pathways are gradually limited, and finally all the domains show WL. Then $\sigma(T)$ begins to show a logarithmic behavior characteristic of WL.

With a further decrease in temperatures below ~ 20 K, $\sigma(T)$ begins to show VRH behavior and there should appear negative MC contribution ascribable to VRH together with that by EEI effect, coexisting with the positive MC caused by WL. Considering the discussion above, we would expect that WL occurs within the crystalline domain even at low temperature, which is confirmed by ESR measurements showing Pauli spin susceptibility as well as an increase in the linewidth due to phonon scattering of conduction electrons in the heavily doped state of pBTTT^{7,33}. Moreover, it is also reported that the charge transport in pBTTT films is dominantly limited by the potential barriers at the domain boundaries¹⁶. Therefore, the VRH transport can reasonably be ascribed to these barriers, where the tie molecules mediate the charge transport. Although high carrier doping tends to reduce the energy barriers expected at the boundary through planarizing the tie molecules, the effect of barriers at boundaries becomes non-negligible at low temperature, affecting the interdomain charge transport, as schematically illustrated in Fig. 4d^{16,34}. The VRH hopping length deduced by analyzing the negative MC is ~ 10 nm (Supplementary Note 6), which is also a reasonable value considering the distance between boundaries across the crystallite. In addition, VRH conduction, which takes place by thermally assisted tunneling through intercrystallite barriers, is often observed in granular polycrystalline semiconductors^{35,36}.

Even though the effectively metallic transport is not observed in the low-doped state of $|V_G| < 1.7$ V, WL as well as the transformation from WL to VRH are clearly observed with decreasing temperature, similar to the high-doped states. However, at $|V_G| < 1.4$ V, the WL behavior disappears at temperatures below 7 K. In the low-doped regime, there may be trap sites with a depth of ~ 20 meV even within the crystalline domains, as has been reported based on ESR measurements gated by a solid-state insulator^{16,34}. The unfilled trap sites might suppress WL even within the crystalline domains in the low-doped state at low temperatures, resulting in VRH conduction without WL.

As we have seen above, the macroscopic transport must be interpreted in terms of the series connection of transport pathways at the crystalline domains and non-crystalline boundaries. In the crystalline domains, a multistep transformation of the transport properties of effectively metallic conduction via WL to VRH is confirmed with decreasing temperature and doping level. On the other hand, the non-crystalline domain boundaries directly transform the effectively metallic conduction into VRH. The difference in the transformation of the charge transport mechanism between the crystalline domains and non-crystalline boundaries explains the reported contradictions between the VRH-like $\sigma(T)$ and the MC showing WL in previous studies^{8,10}.

We should also discuss the Zhabrodsii analysis of $\sigma(T)$. Because the Zhabrodsii analysis considers only the VRH process, this analysis cannot reflect the conduction when both VRH at the non-crystalline boundaries and WL in the crystalline domains contribute to the carrier transport. Therefore, the elusive exponent $a = 0.16$ at the highest V_G of -2.2 V could also be a result of mixing contributions from VRH and WL.

Thermoelectric conversion mechanism in doped polymer films.

In the above sections, we have discussed the role of the crystalline domains and the non-crystalline boundaries on the macroscopic transport. The transport properties depend strongly on the doping level and temperature through the relative dominance of the interdomain VRH transport. This discussion can be extended to various transport phenomena including thermoelectric conversion properties in doped polymer films. It is widely accepted that structural disorders in polymer films crucially affect the thermoelectric properties, leading to an unusual power-law relation between the Seebeck coefficient (S) and conductivity (σ - S relation) as $S \propto \sigma^{-1/s}$, where s is 3 or 4 in most polymers at room temperature³⁷. Kang and Snyder have proposed that the above unconventional σ - S relation can be well reproduced by considering an energy-dependent unique transport function σ_E ,

$$\sigma_E(E, T) = \sigma_0(T) \times \left(\frac{E - E_t}{k_B T} \right)^s, \quad (5)$$

where k_B is the Boltzmann constant, E_t is the transport level, and $\sigma_0(T)$ is a temperature-dependent but energy-independent parameter³⁸. They explained the observed σ - S relation in many polymers within reasonable statistical errors with $s = 3$, in which the power-law dependence of $S \propto \sigma^{-1/3}$ should be observed in the degeneracy limit. On the other hand, our previous thermoelectric measurements on electrolyte-gated pBTTT seem to exhibit $S \propto \sigma^{-1/4}$ rather than $S \propto \sigma^{-1/3}$ in the lowly doped non-metallic region ($\sigma < 100 \text{ S cm}^{-1}$), as shown in Fig. 5¹³. We suggest that this discrepancy arises from the large contribution of domain boundaries to the thermoelectric properties, which makes it difficult to adopt the single transport function in Eq. (5) to describe the transport in both domains and boundaries. However, our present MC measurements have revealed that the charge transport is macroscopically delocalized near room temperature even at the lowest gate voltage of $V_G = -1.3 \text{ V}$ ($\sigma \sim 20 \text{ S cm}^{-1}$ at 200 K), indicating that no boundary effect should be considered in analyzing the thermoelectric properties in the measured V_G range.

According to the above consideration, we again fit the σ - S relation by the function $S \propto \sigma^{-1/3}$ in Fig. 5. As shown in this figure, the previous experimental data are well reproduced by $S \propto \sigma^{-1/3}$ in the region $20 \text{ S cm}^{-1} < \sigma < 200 \text{ S cm}^{-1}$. We stress here that this conductivity range almost corresponds with the region

Fig. 5 Thermoelectric property of the polymer as a function of conductivity. Electrical conductivity σ dependence of the Seebeck coefficient S at room temperature obtained with the electrolyte gating technique reported previously¹³. Variable-range hopping (VRH), weak localization (WL) and effectively metallic regimes according to the room temperature σ values are denoted on top of the figure based on the conductivity and magnetoconductivity measurements. We can find a narrow σ range where the σ - S relation follows $S \propto \sigma^{-1/3}$ between $20 < \sigma < 200 \text{ S cm}^{-1}$ (solid red line), which corresponds to the σ range where WL conduction is observed.

where the charge transport is homogeneously explained by WL at room temperature. The observed deviation for conductivities higher than 200 S cm^{-1} can be reasonably ascribed to a transition to effectively metallic state, where the Mott equation is expected to give a $S \propto \sigma^{-1}$ relation¹³. For the lower conductivity region below 20 S cm^{-1} , the $S \propto \sigma^{-1/3}$ relation becomes again incapable of explaining the experimental data. Although Kang and Snyder's model predicts a deviation from $S \propto \sigma^{-1/3}$ in low-doped states approaching the conventional $S \propto \ln \sigma$ relation for a thermally activated system, it should occur at much smaller conductivities (or larger Seebeck coefficient) because no signature of thermally activated transport has been observed within our conductivity measurements. Moreover, based on the linewidth broadening of the ESR signal, the delocalized charge transport within the domain is suggested even down to at least 1 S cm^{-1} ¹³. Therefore, since the σ - S relation in the low-conductivity region still seems to follow the $S \propto \sigma^{-1/4}$ relation, it is possible to consider that the unusual $S \propto \sigma^{-1/4}$ relation applies in a system where the domain boundary limits the charge transport in doped polycrystalline films and possibly causes a VRH contribution.

Finally, we discuss the approach for improving thermoelectric device performance based on our results. As we recently reported, the output power of pBTTT films is maximized at around the borderline of the transformation from WL to the effectively metallic phase¹³, and the contribution from the boundaries might be relatively small based on our above consideration because the boundaries already transform to the effectively metallic phase. Therefore, the maximum thermoelectric power factor can be boosted by improving the transport properties of the WL regime, which is controlled by the phase coherence length λ . The conductivity decrease in the WL regime is given by,

$$\Delta\sigma = -\frac{e^2}{\pi^2 \hbar} \log \frac{\lambda}{l}, \quad (6)$$

where l is the carrier mean free path between elastic scatterings. A larger l with respect to λ leads to a smaller decrease and a higher σ in the WL regime¹¹, resulting in a larger power factor. This clearly indicates that an appropriate approach for improving the thermoelectric device performance is to increase the elastic mean free path by reducing the density of scattering centers within the crystalline domains, which might be caused by structural disorders such as imperfections, distortions, or stacking faults of the polymer chains. In addition, because the mean free path might also be limited by the size of the crystalline domains, a larger domain size is desirable. Because both reducing the density of scattering centers and enlarging the domain size can be realized by improving the material crystallinity, a novel film growth method might be a key issue toward future high-performance thermoelectric devices.

To conclude, we have investigated the charge transport mechanism in pBTTT polymer films from the T dependence of $\sigma(T)$ and MC under electrochemical doping by ion-gel gating. Under heavily doped conditions at $|V_G| > 1.7 \text{ V}$, the effectively metallic conduction observed at high temperatures changes to WL and finally to VRH as the temperature decreases, while the VRH coexists with WL. The macroscopic observation of effectively metallic conduction at high temperatures, as well as the WL process, indicates phase-correlative transport even across domain boundaries, whereas the connectivity between the domains becomes worse at low temperatures resulting in a contribution from the VRH process occurring at the domain boundaries. Thus, the non-crystalline domain boundaries directly transform the effectively metallic conduction to VRH. The domain connectivity tends to become poorer as the doping level decreases due to the higher potential barriers at the boundaries. The change in the relative dominance of the conduction at the

domain boundaries can explain the apparent contradiction between the VRH-like $\sigma(T)$ and MC indicating delocalized transport, which has been reported in previous studies of doped pBTTT films. Furthermore, a description of the charge transport mechanism is crucial for understanding the thermoelectric properties of doped polycrystalline polymer films.

Methods

Transistor fabrication. pBTTT with hexadecyl side chains (Fig. 1a, molecular weight ~83,000) was purchased from Merck and used as received. The device structure is illustrated in Fig. 1b and a photograph of a typical device is shown in Fig. 1c. We used a two-terminal method for the electrical measurements. Au/Cr source, drain, and gate electrodes of thickness 30 nm were evaporated on an Eagle-XG glass (Corning, surface roughness 1 nm). The channel length and channel width were 40 μm and 2 mm, respectively. After UV/O₃ treatment, the glass substrate was immersed in a 20- μl toluene solution of octadecyltrichlorosilane at 60 °C for 3 h. Then the pBTTT was spin-coated (4000 rpm for 90 s) from dichlorobenzene solution (7.5 mg ml⁻¹). The thickness of the polymer film was evaluated to be 20 nm by a surface profiler. The film was heated in dried N₂ into the mesophase at 215 °C for 20 min and cooled down slowly. Subsequently, an ion gel film with a thickness of thickness of ~1 μm prepared from a 1:1 mixture of [N,N-diethyl-N-methyl-N-(2-methoxymethyl)ammonium][bis(tri-fluoromethanesulfonyl)imide] [(DEME)(TFSI)] (Nissinbo Holdings Inc.) and poly(vinylidene fluoride-co-hexafluoropropylene) [p(VDF-HFP)] (Sigma Aldrich) (Fig. 1a) was laminated on the polymer film in contact with the gate electrode to form a transistor. The use of a thin ion gel reduces surface tension at the polymer/insulator interface produced by different thermal expansion coefficients, which prevents sample cracking in low-temperature measurements.

Conductivity and magnetoconductance measurements. For the temperature dependence of the conductivity and MC measurements, the device was enclosed in a PPMS cryostat (Quantum Design) and V_G was applied at room temperature. After waiting until the gate current fell to a low stationary value (typically 20 min), the sample was cooled at a rate of 5 K min⁻¹ down to 180 K. The conductivity above 180 K was measured by a pseudo four-probe method under the application of V_G using a semiconductor parametric analyzer (Agilent B1500A) and a nanovoltmeter (Hewlett-Packard 34420A). Below 180 K, where the ion gel is frozen, the cooling rate was reduced to 0.3–0.5 K min⁻¹ and the conductivity was directly measured by a PPMS system (model 6000). The MC was measured under magnetic field applied perpendicular to the film. All conductivity measurements were performed in the ohmic regime with a small drain current between 0.005 and 100 μA depending on the resistance value of the film.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

H.I. and H.M. determined the temperature dependence of the conductivity, and carried out the magnetoresistance measurements. H.I. and K.W. made additional four-terminal measurements and angle-dependent measurements. H.I. and H.T. designed the total experiments. H.I. wrote the manuscript with input from all co-authors. T.T. supervised the project. All authors discussed the results and approved the manuscript draft.

Competing interests

The authors declare no competing interests.

Additional information

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