SELFTRON[®]: A Novel Fully Soluble Self-Doped Highly Conductive Polymer

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We developed a novel fully soluble self-doped poly(3,4-ethylenedioxythiophene) (SELFTRON[®]) with an electrical conductivity greater than 1000 S/cm. It was found that the molecular weight is the critical parameter for increasing the number of nanocrystals, corresponding to the crystallites evaluated by X-ray diffraction and conductive atomic force microscopic analyses having a high electrical conductivity, which reduced both the average distance between adjacent nanocrystals and the activation energy for the hopping of charge carriers, leading to the highest bulk conductivity.

1. Introduction

The development of conductive polymers in 1970s by A. G. MacDiarmid, A. J. Heeger and H. Shirakawa (2000 Nobel Prize in Chemistry), where electrical conductivity of polyacetylene films increased remarkably upon iodine doping,¹ accelerated explosively the use of organic electronics in low-cost, lightweight and flexible electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) since the early 1980s.² Furthermore, in the era of the 'Internet of Things' (IoT), the field of organic electronics is developing via increased interest in printed electronics, stretchable electronics, and, recently, wearable electronics for use in flexible displays and touch panels, soft sensors and actuators.^{3,4} In such devices, a flexible, wet-processable, and highly conductive polymer would be a promising candidate for a key material.

Poly (3,4-ethylenedioxythiophene):poly (4styrenesulfonate) (PEDOT:PSS), developed by Bayer AG in 1990⁵ and commercially available as a water dispersion of colloidal particles, is one of the most successful conductive polymers of the last two decades. Because of its high electrical conductivity (up to 1000 S/cm), transparency and thermal stability, PEDOT:PSS has been used in a wide field of applications, including antistatic coatings, hole injection layers in OLEDs and OPVs, cathode materials in solid aluminium electrolytic capacitors and transparent electrodes for various electronic devices, as an alternative to indium tin oxide (ITO).⁶ However, PEDOT:PSS has some technical issues that impede its further practical application; these issues stem from the use of PSS as the external ions to compensate the positive charges on PEDOT. Since the hydrophobic PEDOT core is surrounded by a shell of excess hydrophilic PSS⁷ for water dispersion as a colloidal particle with a diameter of several tens of nanometres, (I) forming ultrathin layers thinner than the colloidal particle size is difficult,⁸ (II) the PEDOT:PSS colloids aggregate and precipitate when stored for an extended period, and (III) the pristine PEDOT:PSS exhibits poor electrical conductivity (< 1 S/cm),^{3,5} additives, such as ethylene glycol (EG), dimethyl sulfoxide (DMSO), and sorbitol, are therefore indispensable for improving electrical conductivity, namely, by the "solvent effect",^{3,9} which can be interpreted in terms of the crystallization of the PEDOT core and the removal of the insulating PSS shell of the colloidal particles to enhance the transport of charge carriers between the PEDOT nanocrystals by a hopping mechanism.¹⁰⁻¹² That is, the insoluble

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and intractable nature of PEDOT is responsible for these drawbacks of PEDOT:PSS having a 2.5-fold excess of PSS over PEDOT by weight. Therefore, prescient and intensive studies on fully soluble selfdoped PEDOT have been reported in the literature.¹³⁻¹⁷ Zotti and coworkers synthesized an EDOT derivative bearing a sodium alkylsulfonate side chain, sodium 4-[(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy] butane-1-sulfonate and polymerized it to obtain selfdoped PEDOT with a mass-average molecular weight (M_w) of 5000 g/mol and a maximum electrical conductivity of 1 - 5 S/cm.¹⁴ On the other hand, Konradsson and Berggren et al. reported chemical polymerizations of the same self-doped PEDOT and found that the electrical conductivities were 12 S/cm¹⁵ and 30 S/cm,¹⁶ respectively. Since these conductivity values were two or three orders of magnitude lower than that of the highly conductive PEDOT:PSS (up to 1000 S/cm), improving the electrical conductivity of self-doped PEDOT has thus far been considered impossible.

In this study, we first synthesized a novel monomer bearing a sodium alkylsulfonate side chain, sodium 4-[(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy] butane-2-sulfonate (**Fig. 1**). From the viewpoints of safety, low environmental load, and mass production for commercialization, the monomer was designed due to the lower toxicity of 2,4-buthanesultone^{18,19} used in the synthetic process. Furthermore, the fully soluble self-doped PEDOT (SELFTRON) was synthesized by the oxidative polymerization of different monomer concentrations (C_m) in a range of 1 - 10 wt% (**Fig.**

1) and characterized by means of gel permeation chromatography (GPC), UV-vis-NIR spectroscopy, X-ray diffraction analysis (XRD), conductive atomic force microscopy (cAFM), and the four-point technique. It was found that the electrical conductivity achieved as high as 1089 S/cm,²⁰ which is two orders of magnitude higher than those of previously reported self-doped PEDOTs¹³⁻¹⁷ and exceeds the conductivity of PEDOT:PSS (up to 1000 S/cm). The results led us to conclude that the molecular weight is the critical parameter for increasing the number of nanocrystals, corresponding to the crystallites evaluated by XRD and cAFM, reduced both the average distance between adjacent nanocrystals and the activation energy for the hopping of charge carriers, leading to the highest bulk conductivity.

2. Experimental

Synthesis of SELFTRON

SELFTRON was synthesized by the oxidative polymerization in different monomer concentrations (C_m) between 1 – 10 wt% (**Fig. 1**). The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI) were measured by GPC on an instrument (Prominence, Shimadzu) equipped with a TSK gel α -M column and guard column α (Tosoh); polystyrene sulfonate standards (PSS, American polymer standard) were used. The UV-vis-NIR spectra were measured with a spectrophotometer (V-670, Jasco). The viscosity and pH of SELFTRON water solutions (1 wt%) were measured



Fig. 1 Synthesis of SELFTRON by oxidative polymerization.

at 25°C with torsional oscillation-type viscometer (Viscomate VM-10A-L, Sekonic) and pH meter (Laqua F-74S, Horiba), respectively.

Electrical conductivity

The solid films were fabricated by casting the SELFTRON water solution (1 wt%) onto a glass substrate (35 mm long, 25 mm wide, and 1 mm thick) at 120°C with a moisture analyser (MOC-120H, Shimadzu) and subsequently heating at 200°C for 30 min in a vacuum. The electrical conductivity of the films (10 mm square, $7.2 - 10.2 \mu$ m thick) was evaluated by the normal four-point method with a Loresta-GP (MCP-T610, Mitsubishi Chemical Analytech), where the thickness of films was measured with a stylus profilometer (D-100, KLA-Tencor) in dry air.

X-ray diffraction analysis

The XRD patterns were measured by an X-ray diffractometer (MiniFlex600, Rigaku) equipped with a 1D high-speed detector (D/tex Ultra, Rigaku) at 40 kV and 15 mA. The values of X_c and D_{hkl} were estimated by the profile fitting method and Scherrer's equation, respectively, using the integrated X-ray powder diffraction software (PDXL 2, Rigaku).

Scanning probe microscopy

The SELFTRON water solutions (1 wt%) were spin coated onto doped Si wafers (0.5 mm thick, resistivity was 0.02 Ω cm) at 2000 rpm with a spin coater (MS-A150, Mikasa); the coated wafers were then heat treated at 200°C for 10 min in air to stabilize the structure of SELFTRON. The cAFM measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu) equipped with a conductive probe (CONTPt, NanoWorld), where height and current images were measured in contact mode under a bias voltage of - 0.1 V.

3. Results and discussion

The GPC elution curves of various SELFTRON solutions are shown in **Fig. 2**A. Since the GPC measurement is not applicable to the PEDOT:PSS colloidal dispersions, these results provide clear evidence that the SELFTRON is fully soluble, similar to other self-doped conductive polymers.¹³⁻¹⁷ The GPC curves were unimodal with PDI of 3.15 - 4.15, indicative of a broad molecular weight distribution. This is probably because the termination reaction is



Fig. 2 Solution properties of SELFTRON. (A) GPC elution curves, weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI) of SELFTRON synthesized with different C_m. (B) The viscosity and pH dependencies of SELFTRON water solutions (1 wt%) on C_m. (C) UV-vis-NIR spectra of SELFTRON water solutions (0.01 wt%) synthesized with different C_m.

due to recombination rather than disproportionation.⁵ The M_w and M_n of the SELFTRON reached maximum values of 22300 g/mol and 5380 g/mol, respectively, at $C_m = 5$ wt%. Here, the number average degree of polymerization (DP) was ca. 18, which was more than twice higher than the value of the previously reported self-doped PEDOT (8 units average) measured by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry.¹⁴ The decrease of both M_w and M_n at $C_m > 5$ wt% was likely due to a steep increase in the viscosity of the reaction solution. Fig. 2B shows that the viscosity of SELFTRON solutions (1 wt%) reached a maximum (24.3 mPa·s) at $C_m = 5$ wt%, reflecting the molecular weight, whereas the pH values were nearly constant (1.86 - 2.04). These values are comparable to those of the PEDOT:PSS water dispersion (1 wt%) with a viscosity and pH of 16 mPa·s and 1.89, respectively. As shown in Fig. 2C, the UV-vis-NIR spectra of SELFTRON water solutions (0.01 wt%) were less dependent on C_m, demonstrating the same electronic structure: a broad shoulder at approximately 800 nm is consistent with the low energy absorbance of neutral PEDOT, and a free-carrier of bipolarons in the NIR region corresponds to PEDOT in the oxidized state.²¹ Furthermore, while PEDOT:PSS can be dispersed only in water and in several mixed solvents

of water and alcohol, SELFTRON is soluble not only in water but also in various organic solvents, which is a great advantage for use in organic electronic devices easily degraded by water and for the fabrication of composites with water-insoluble polymers.

XRD analysis was performed and the results are shown in Fig. 3A. Although the SELFTRON is a new polymer, the diffraction patterns are simpler than PEDOT:PSS7,10 and similar to those of PEDOTs doped with perchlorate (PEDOT:ClO₄), p-toluenesulfonate (PEDOT:TsO) and hexafluorophosphate (PEDOT:PF₆), which indicates that the unit cell belongs to an orthorhombic system.²²⁻²⁴ Therefore, the diffraction peaks at $2\theta = 5.3^{\circ}$ (d = 16.6 Å), 10.5° (d = 8.4 Å), and 24.7° (d = 3.6 Å) can be assigned to the diffractions from the (100), (200), and (020) planes of the orthorhombic unit cell of the crystal with lattice parameters of a = 16.6 Å, b = 7.2 Å, and c = 7.8 Å. Since the main chain matches the c axis, the c value corresponds to the repetition period of two monomer units (7.8 Å) similar to that of PEDOT. However, the π -stacking distance between two chains, representing one-half of the value of b (3.6 Å), which is slightly longer than that of PEDOT $(3.4 \text{ Å})^{22.24}$ due to the steric hindrance and/or electrostatic repulsion between the side chains. Unlike polyalkylthiophenes in which the dopant ions are



Fig. 3 Crystalline structure of SELFTRON films. (A) X-ray diffraction (XRD) patterns of different C_m and a possible crystalline structure of SELFTRON (inset). (B) The crystallinity (X_c) and crystallite size (D₁₀₀ and D₀₂₀) dependencies on C_m .

present in the vicinity of the polymer chains,²⁵ PEDOT exhibits dopant ions between the π -stacked columns along the a-axis direction. Thus, the value (16.6 Å) is determined by the length of the alkylsulfonic acid side chains. Since the unit lattice contains four monomer units with the side chains alternatingly arranged in opposite directions with respect to the polymer chain, the theoretical density of the SELFTRON crystal is calculated to be 1.59 g/cm³, which is consistent with the actual density measured by the method of Archimedes $(1.50 - 1.53 \text{ g/cm}^3)$. Assuming that a broad halo in the 2θ range of $15 - 35^{\circ}$ corresponds to the amorphous chains, the degree of crystallinity (X_c) can be expressed as the ratio of total area of crystalline peaks to total area of all diffraction peaks. As shown in Fig. 3B, the X_c value reached 72% at C_m = 5 wt%, the tendency of which agrees with the molecular weight and viscosity results (Fig. 2B). This trend suggests that the SELFTRON exhibits less entanglement in water since the polymer chains have an extended coil structure due to the rigid π -conjugated backbone and electrostatic repulsion between the alkylsulfonic acid side chains, favouring crystallization by π -stacking in the solid state. Notably, the X_c values are substantially higher than those of PEDOT:PSS¹² and are associated with the higher weight fractions of PEDOT main chains in SELFTRON (45

wt%), the absence of amorphous PSS chains (the weight fraction of PEDOT in PEDOT:PSS is only 29%), and/ or the side chains of SELFTRON being highly ordered and incorporated in the crystalline phase. Assuming that the doping level of SELFTRON is the same as that of PEDOT (0.22 - 0.35),²⁶ corresponding to one charge per 3 - 4 monomer units, 22 - 35% of sulfonic acid groups of the side chains dissociate and compensate for the positive charges on main chains as counter ions. However, 65 - 78% of undissociated sulfonic acid groups in the side chains can form intermolecular hydrogen bonds and stabilize the crystalline structure, as shown in the inset of Fig. 3A. Furthermore, the crystallite sizes normal to the (100) and (020) planes calculated using the Scherrer's equation were D₁₀₀ ≈ 6 nm and D_{020} ≈ 3 nm, respectively, regardless of the C_m (Fig. 3B). Therefore, the high X_c value can be explained in terms of the large number of crystallites, in which approximately four columns of eight SELFTRON molecules π -stacked in the b-axis direction are accumulated in the a-axis direction.

As shown in Fig. 4A, the surface morphologies of thin films were similar irrespective of C_m , where numerous particles with an average particle size (D_p) of ca. 11 nm were densely packed to form a coherent solid film with a particle number (N_p) , defined as the number of



Fig. 4 AFM height images of SELFTRON thin films. (A) Surface morphologies of different C_{m} . (B) The average particle size (D_p) , number of particles (N_p) and surface roughness (R_a) dependencies on C_m .

particles in $1 \mu m^2$, of 3000 - 3600 (Fig. 4B). In addition, thin films were smooth, with a surface roughness (R_a) of ca. 0.4 nm, compared to PEDOT:PSS films ($1 \le R_a$) $\leq 2 \text{ nm}$)¹⁰ because SELFTRON is not dispersed as a colloid but is fully dissolved in water. Fig. 5A shows current images representing the distribution of local conductivity measured by cAFM; these images reveal that the highly conductive nanocrystals (shown in the bright region) are sparsely distributed in less conducive amorphous matrices (shown in the blue region), similar to PEDOT:PSS.¹² The average size of nanocrystals (D_{nc}) was found to be an almost constant value of ca. 5 nm (Fig. 5B), coincident with the crystallite sizes $(D_{100}$ and D_{020}) in Fig. 3B, suggesting that the nanocrystal corresponds to a single crystal. However, the number of nanocrystals in 1 μ m² (N_{nc}) shows a maximum of 5800 $/\mu m^2$ at $C_m = 5$ wt%. The tendency of N_{nc} is similar to those of the molecular weight (Fig. 2A) and the $X_{\rm c}$ (Fig. 3B), demonstrating that one particle in Fig. 4A consists of ca. two nanocrystals. Therefore, the average distance between adjacent nanocrystals (Lnc) reached a minimum (3.9 nm) at $C_m = 5$ wt%. This interparticle distance is suitable for the hopping of charge carriers between adjacent nanocrystals, which is critical to achieving high bulk conductivity.12

To clarify the correlation between the current images at the nanoscale and the transport of charge carriers in the bulk state, electrical conductivity was measured by the four-point technique. We should emphasize that an electrical conductivity as high as 1089 S/cm at $C_m = 5$ wt% (**Fig. 6**A) was attained without additives (solvent effect). This value is more than two orders of magnitude higher than those of the self-doped PEDOT¹³⁻¹⁷ and exceeds the conductivity of PEDOT:PSS with additives such as EG and DMSO (up to 1000 S/cm).

A strong correlation is observed between L_{nc} and electrical conductivity (Fig. 6B), demonstrating that the distribution of nanocrystals plays an important role in electrical conduction. According to the nearestneighbour hopping model,¹⁰ the activation energy (E_a) required for hopping of charge carriers can be calculated by measuring the electrical conductivity (σ) at room temperature (T = 298 K) and that at liquidnitrogen temperature (T = 77 K) and using the equation $\sigma = \sigma_0 \exp(-E_a / k_BT)$, where σ_0 and k_B are the conductivity factor and Boltzmann constant (8.617 × 10^5 eV/K), respectively.¹⁰ A linear relationship between L_{nc} and E_a demonstrates that the longer the distance between adjacent nanocrystals, the lower the probability of charge carrier hopping (Fig. 6B). Since the values



Fig. 5 Conductive AFM (cAFM) images of SELFTRON thin films. (A) Current mapping images of different C_m. (B) The average nanocrystal size (D_{nc}), number of nanocrystals (N_{nc}) and average length between adjacent nanocrystals (L_{nc}) dependencies on C_m.



Fig. 6 Electrical conductivity and carrier transport properties of SELFTRON films. (A) The electrical conductivity dependency measured by the four-point method on C_m . (B) The electrical conductivity and activation energy (E_a) dependencies on L_{nc} . (C) L_{nc} , electrical conductivities at 77 K (σ_{77K}) and 293 K (σ_{293K}) and the E_a of different C_m .

of E_a (Fig. 6C) are lower than the thermal energy at room temperature, ca. 26 mV, the charge carriers in SELFTRON have sufficient energy for hopping, which is responsible for the extremely high electrical conductivities at room temperature.



Fig. 7 Correlation between the hierarchical structure and properties of SELFTRON. (A) Chemical structures of the monomer (primary structure) and SELFTRON (secondary structure), the nanocrystal (tertiary structure) and the distribution of nanocrystals (quaternary structure).
(B) Relation between C_m and M_w. (C) Dependencies of X_c and N_{nc} on M_w. (D) Dependencies of L_{nc} and E_a on N_{nc}. (E) Relation between L_{nc} and electrical conductivity.

Conclusion

Fig. 7A shows the hierarchical structure of SELFTRON. The monomer (primary structure), sodium 4-[(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl) methoxy]butane-2-sulfonate, was newly synthesized and chemically polymerized into SELFTRON, where M_w (secondary structure) reached a maximum (22300 g/ mol) at $C_m = 5$ wt% (Fig. 7B). Furthermore, the values of X_c and N_{nc} (tertiary structure) increased in proportion to M_w , reaching 72% and 5800 /µm², respectively (Fig. 7C). Here, the larger the N_{nc} , the lower the L_{nc} (3.9 nm) (quaternary structure) and E_a (4.4 meV) (Fig. 7D), which resulted in a remarkable increase in bulk conductivity up to as high as 1089 S/cm (Fig. 7E). Thus, the results lead us to conclude that the molecular weight was the key parameter responsible for improving the electrical conductivity, which arose from the fact that the M_w of the self-doped PEDOT with low conductivity (1 - 5 S/cm) was only 5000 g/mol.¹⁴ In addition, synthesis of SELFTRON with a narrow molecular weight distribution by optimization of polymerization conditions will be important for improving the electrical conductivity. Notably, the relation between L_{nc} and electrical conductivity (Fig. 7E) has not yet saturated, suggesting that a further improvement in conductivity can be achieved by decreasing the L_{nc} value (facilitating hopping of charge carriers); further investigations are currently underway.

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