

Understand the Temperature Sensing Behavior of Solid-state Polymerized PEDOT Hybrid Based on X-ray Scattering Studies

Zhen-Hang He^{a,†}, Guang-Feng Liu^{b,†}, Ze-Kun Zhou^a, Zhen Liu^{a*}, Yi-Shu Zeng^a, and Peng Zhang^{a*}

^a School of Materials Science and Engineering, Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Sun Yat-sen University, Guangzhou 510275, China

^b Shanghai Advanced Research Institute (Zhangjiang Laboratory), Chinese Academy of Sciences, Shanghai 201204, China

Electronic Supplementary Information

Abstract Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful conductive polymers that recently has been used in wearable sensors for human health monitoring. In this work, we prepared a series of PEDOT hybrids consisting of PEDOT, sodium poly(styrene sulfonate) (PSSNa) and polyethylene oxide (PEO), and their preparation could be scaled-up *via* an adapted solid-state polymerization process. The resistance of the as-prepared PEDOT:PSS/PEO hybrid shows clear temperature response, *i.e.*, it decreases almost linearly with the temperature increase. To understand this phenomenon, the *in situ* synchrotron radiation wide- and small-angle X-ray scattering (WAXS/SAXS) characterizations were undertaken to study the temperature-dependent microstructure change of the PEDOT:PSS/PEO hybrid. It demonstrated that PEDOT formed conductive paths in the hybrids, which were not destroyed by the PEO crystallization. As temperature increased, the PEO crystals' melting and the accompanying reorganization of PEDOT chains endowed the hybrid sample temperature responsiveness. Based on these fundamental knowledges, the hybrid materials were used to fabricate flexible wearable sensor that showing temperature sensing performance with an accuracy of 1 °C. These findings shed lights on the scalable manufacturing of wearable sensors for body temperature monitoring.

Keywords Solid-state polymerization; PEDOT hybrid; Structure-property correlation; X-ray scattering

Citation: He, Z. H.; Liu, G. F.; Zhou, Z. K.; Liu, Z.; Zeng, Y. S.; Zhang, P. Understand the temperature sensing behavior of solid-state polymerized PEDOT hybrid based on X-ray scattering studies. *Chinese J. Polym. Sci.* 2024, 42, 105–112.

INTRODUCTION

Body temperature (BT) is generally accepted as a very important factor of human health, and abnormal changes in the BT usually reflect the poor health.^[1–4] Recently, monitoring the BT has been studied for pregnancy test,^[5] the mitigation of the COVID-19 spreading,^[6] and so on.^[7–9] For example, Tharakan *et al.*^[10] studied how BT monitoring might inform mortality rate estimates in COVID-19-positive patients. Many of these studies are related to the fever that is defined as “a measured temperature of 38 °C or greater, or feels warm to the “touch”.^[11] By surveying the soaring numbers of BT monitoring literatures,^[1,4,12] some trends of the development of BT sensors are summarized in the following: (1) it should be sensitive in the temperature change at around the body temperature, ~37 °C;^[13] (2) it should be made of non-toxic, stable and biocompatible materials, and the device is flexible,^[14] portable and wearable; (3) the materials' production should be easily

scaled-up, low cost and environmental benign.

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is one of the most successfully commercialized conductive polymer materials. It has been widely used in the broad fields of optoelectronic,^[15,16] thermoelectric,^[17] sensors,^[18–20] and biomedical engineering,^[21,22] due to the integrated capabilities of high intrinsic electron conductivity, optical transparency, improved flexibility and good biocompatibility. Recently, people tried to improve the mechanical performance of the PEDOT:PSS by blending it with small molecules or polymer additives. Among which, poly(ethylene oxide) (PEO) is one of the most popular polymeric additives to enhance the flexibility of the PEDOT:PSS, as summarized by Kayser *et al.*^[23] Typically, the PEDOT:PSS in aqueous dispersion is used for the blending with PEO, which involves the complex solution supramolecular assembly and the structure change from the solution to the dried film states. Such complex processes and inherent uncertainties of the structure change bring us challenges in the materials' property tuning by balancing the mechanical and conductive performances.^[24,25] Meanwhile, it is found that blending with PEO or other polymer additives would decrease the conductivity and functionality of the PEDOT-based hybrids.^[25,26] It is urgent to explore the fundamentals lying behind the hybrids'

* Corresponding authors, E-mail: liuzh287@mail.sysu.edu.cn (Z.L.)
E-mail: zhangpeng3@mail.sysu.edu.cn (P.Z.)

[†] These authors contributed equally to this work.

Received February 28, 2023; Accepted May 25, 2023; Published online July 5, 2023

microstructure and conductivity correlations, *i.e.*, how does the phase separation and ultimately limited connectivity between the conductive PEDOT domains impact the materials' conductivity.

In this work, we developed a new sample preparation protocol by adapting the oxidative polymerization of EDOT^[27] to occur in a solid polymer matrix and by integrating the EDOT polymerization into polymer hybridization. The whole process was achieved *via* a traditional two-roll milling technology, which could be easily scaled-up for the manufacturing of PEDOT:PSS/PEO hybrids. In addition, the solid-state polymerization process avoids the complex structure change due to solvent evaporation. Thus, a series of solid-state PEDOT:PSS/PEO hybrids with varying PEO content were prepared, which endowed a systematic study of the correlations of microstructure and conductivity in PEDOT hybrid. To verify our hypothesis, sophisticated X-ray scattering characterization with synchrotron light was employed. The in-depth structure information helped us to clarify the materials' structure-property correlation. Finally, wearable sensors were successfully fabricated, with a temperature accuracy of 1 °C around the body temperature, to demonstrate the potentials of as-prepared PEDOT:PSS/PEO hybrids in BT monitoring.

EXPERIMENTAL

Materials

3,4-Ethoxylenedioxythiophene (EDOT) (purity: 99%), sodium poly(sodium 4-styrenesulfonate) (PSSNa) ($M_w \sim 7 \times 10^4$, powder), FeCl_3 (purity: $\geq 99.9\%$, metals basis), and poly(ethylene oxide) (PEO) ($M_n \sim 6 \times 10^5$, powder) were purchased from Aladdin (Shanghai Aladdin Biochemical Technology Co., Ltd.). All these chemicals were used without further treatment.

Sample Preparation with Two-roll Milling

The PEDOT:PSS/PEO hybrid samples were prepared with a two-roll mill (type: 401CE-160, ZhuoSheng Machinery Equipment Co., Ltd., China), with the operating temperature set at 80 °C that was well above the melting point of PEO. A series of solid-state PEDOT:PSS/PEO hybrid samples with fixed molar ratio of $\text{EDOT}:\text{Fe}^{3+}:\text{SS}=1:1:0.31$ and excess amount of PEO (molar ratio of $\text{EDOT}:\text{EO}$ varying from 1:8 to 1:50), were prepared. In a typical case of PEDOT:PSS/PEO hybrid sample, the weighed PSSNa and FeCl_3 were sequentially added to the masticated PEO membrane at 80 °C under violent mixing; after 10 min, the weighed EDOT liquid was added drop by drop *via* a plastic syringe, while the rolls kept on rotating; afterwards, a wooden knife was used to help the compounds' mixing and the typical blue color feature of PEDOT was gradually observed with the progress of oxidative polymerization; finally, the solid-state PEDOT:PSS/PEO hybrid samples were collected. Neat PEO and PEO/ FeCl_3 hybrid sample were prepared in a similar procedure and used as the references. In addition, the PEDOT:PSS/PEO hybrid samples were dried in forced air-drying oven at 110 °C for 12 h and then filmed at 80 °C under pressure (~ 0.1 MPa). Thus, free-standing membrane samples with thickness ~ 150 μm were prepared for the further use. For the UV-Vis-NIR spectroscopy measurements, the solid samples were dispersed in water solution at 90 °C and diluted to 0.083 wt%.

Resistivity Measurement

For the resistivity measurement, the membrane sample was cut into square shape pieces with a dimension of 10 mm. The resistivity of the as-prepared PEDOT:PSS/PEO hybrid membranes were measured with a digital multimeter (RTS-8, Guangzhou Four Probe Technology Co., Ltd., China) by following the four-probe method. To collect the resistivity data as a function of temperature, the membrane samples were sealed in a home-made heating setup, made up of Peltier heating elements and the temperature controlling units.^[28] Meanwhile, the sample was connected to a Fluke multimeter (Fluke 17B+, Fluke Corporation, USA) *via* platinum wires for collecting the resistivity value in the temperature range from 20 °C to 110 °C, 2 °C/step.

UV-Vis-NIR Spectroscopy Measurement

The UV-Vis-NIR spectroscopy data of the solution samples were collected with a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin Elmer, Britain), in transmission mode.

UV-Vis Spectroscopy Measurement

The UV-Vis spectroscopy data of the hybrid samples were collected with a UV-Vis spectrophotometer (UVmini-1280, SHIMADZU, Suzhou, China), in transmission mode.

Differential Scanning Calorimetry Measurement

The crystallization behavior of the hybrid sample was characterized with differential scanning calorimetry (DSC), using a DSC 250 setup (TA Instrument, USA). For the DSC measurement, the weighed (~ 10 mg) sample was sealed in an aluminum pan, dry nitrogen was used as the purging gas and the temperature range was set from -80 °C to 100 °C with a heating/cooling rate of 5 °C/min. Two subsequent heating/cooling cycles were undertaken and the data in the second cycle was used for the crystallization behavior study. The DSC data was analyzed with a Trios software, attached to the DSC setup.

Synchrotron X-ray Scattering Measurement

X-ray scattering experiments with synchrotron light were performed at the BL19U2 beamline of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China).^[29] The sample was held in a Linkam HFSX350 heater and was scanned at the set temperature range from 20 °C to 60 °C, 2 °C/step. In addition, the sample was also measured at high temperatures up to 80 °C. For the scattering experiments, X-ray with wavelength of 1.033 Å penetrated through the sample and the scattering data was collected simultaneously with a Pilatus 300k detector with sample to detector distance (SDD) of 382 ± 1 mm (*i.e.*, WAXS) and with a Pilatus 1M detector with SDD of 2463 ± 1 mm (*i.e.*, SAXS). The SDD calibration was undertaken with silver behenate and LaB_6 . The data analysis was undertaken with a BioXTAS RAW software package (Version 1.6.3).^[30] In addition, the SAXS data was fitted with a SASfit software package and a rod-like model.

Scanning Electron Microscope and Energy Dispersive Spectroscopy Measurement

Scanning electron microscope (SEM) images and energy dispersive spectroscopy (EDS) images were collected with Cold field Emission Scanning Electron Microscope (S-4800, Hitachi). The surface of the samples was treated with platinum (Pt) spray prior to testing.

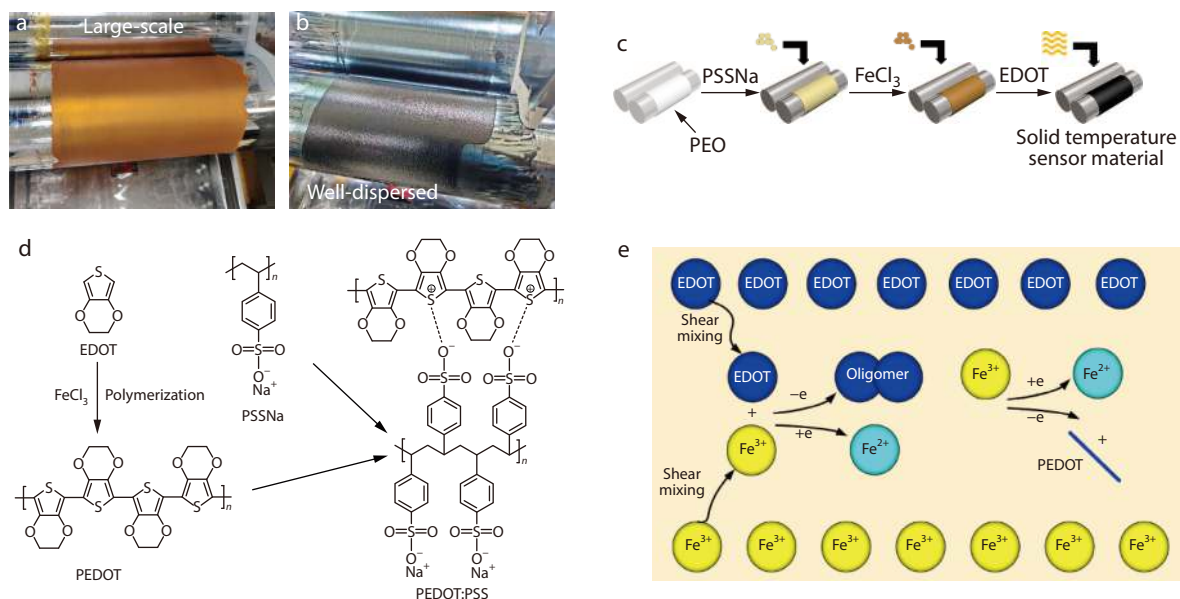


Fig. 1 (a, b) Photos of the scalable manufacturing of solid-state PEDOT:PSS/PEO hybrid based on two-roll milling technology: (a) PSS/PEO/FeCl₃ hybrid and (b) PEDOT:PSS/PEO hybrid; (c) Schematically illustrated production process of the solid-state PEDOT:PSS/PEO hybrid; (d) Schematic illustration of the EDOT polymerization and stabilization with PSS; (e) Proposed solid-state polymerization mechanism of PEDOT.

Wearable Sensor Device

The hybrid materials were wrapped with polyimide (PI) tapes, with conductive copper tapes set in between as the conductive path of the wearable sensor. In addition, the sensor was connected with a DC power source, a temperature control unit (DCU), a N-type metal-oxide-semiconductor (NMOS) logic and a commercial LED light (nominal working voltage and power were 3 V and 3 W, respectively) to fabricate the wearable sensor device.

RESULTS AND DISCUSSION

To explore the correlations between microphase structure and conductivity in the PEDOT-based hybrids for flexible electronics, it is important to prepare a sample system with well-defined chemical composition and simple manufacturing process. In this sense, we adapted the traditional oxidative polymerization of EDOT^[27] with a well-established elastomer compounding protocol, *i.e.*, two-roll milling. As shown in Fig. 1(a), the PSS and PEO were mixed homogeneously first under the strong shearing of the rolls at 80 °C. Note: 80 °C is well above the melting temperature of PEO (*ca.* 68 °C, measured with DSC). Afterwards, the oxidant, FeCl₃, was well distributed in the solid-state polymer matrix under strong shear developed at the mill nip,^[31] as evidenced by the homogeneous color of the mixture (Fig. 1a). Moreover, the EDOT was added gradually to the mixture when the rolls were rotating, which helped its distribution. Under the function of the oxidant and high temperature, the EDOT was gradually polymerized into PEDOT and distributed evenly in the polymer matrix. This phenomenon was manifested with the homogenous dark blue color (unique feature of the PEDOT^[32]) of the as-prepared hybrid sample (Fig. 1b). The whole process of the manufacturing of PEDOT:PSS/PEO hybrid is schematically illustrated in Fig. 1(c). The production of the present setup was estimated to be *ca.* 1.0 kg/h, which could be easily scaled up

with either using mills with a larger roll size or running many mills in parallel. This process can not only produce the PEDOT hybrids in an easy scaling-up way but also provide us a series of solid-state PEDOT:PSS/PEO hybrids with well-defined chemical composition.

For clarity reason, we fixed the molar ratio of EDOT:SS:Fe³⁺=1:0.31:1 and changed the molar ratio of EDOT:EO from 1:8 to 1:50, as indicated in Table 1. Despite to the wet based oxidative polymerization of EDOT, which typically involves much higher molar ratio of SS to disperse the hydrophobic PEDOT in water,^[33] the solid polymerization of EDOT could be dispersed in the polymer matrix under the function of strong shearing. Meanwhile, the blending of a few PSS was expected to improve the compatibility of PEDOT and PEO, and to stabilize the carriers in PEDOT *via* charge interactions, as schematically illustrated in Fig. 1(d).^[24] By referring to the literature,^[32,33] we hypothesized that the solid-state polymerization of PEDOT occurred *via* a mechanism shown in Fig. 1(e). It is expected that the EDOT was oxidized with Fe³⁺ to form the PEDOT dimer or oligomer, which were further oxidized with the Fe³⁺ till the formation of PEDOT polymer in

Table 1 Conductivities of the as-prepared H/PEOn hybrid samples.

Sample ^a	EDOT:Fe ³⁺ :EO:SS	Conductivity (10 ⁻⁵ S/cm)
H/PEO8	1:1:8:0.31	1.24±0.28
H/PEO16	1:1:16:0.31	1.57±0.38
H/PEO30	1:1:30:0.31	2.03±0.16
H/PEO40	1:1:40:0.31	1.67±0.29
H/PEO50	1:1:50:0.31	0.26±0.14
PEO/FeCl ₃	0:1.35:50:0	— ^b
PEO	Neat PEO	— ^b

^a The content of PEO, PEDOT and PSS were calculated as molar ratio of monomers; ^b Conductivity of PEO/FeCl₃ and PEO is out of the range of the multimeter; Note: PEDOT:PSS/PEOn is denoted as H/PEOn where *n* indicates the molar ratio of EO:EDOT.

the PEO matrix. Meanwhile, the oxidized PEDOT was stabilized with the negatively charged PSS.

To verify our hypothesis, we characterized the molecular structure and conductivity of the as-prepared hybrid samples with UV-Vis-NIR and multimeter, respectively. As shown in Table 1, the as-prepared PEDOT hybrids show conductivity values of $\sim 1 \times 10^{-5}$ S/cm in a broad EDOT:EO molar ratio ranging from 1:8 (*H*/PEO8), through 1:16 (*H*/PEO16), 1:30 (*H*/PEO30), 1:40 (*H*/PEO40) to 1:50 (*H*/PEO50). Note: for clarity reason, PEDOT:PSS/PEO_{*n*} is denoted as *H*/PEO_{*n*}, where *n* indicates the molar ratio of EO:EDOT. By comparison, the reference samples without PEDOT, *i.e.*, PEO/FeCl₃ and neat PEO, did not show detectable conductivity value. Thus, we conclude that the *H*/PEO_{*n*} samples show conductive features due to the formation of PEDOT, which is supported by the UV-Vis-NIR spectroscopy data. Clear absorption bands at ~ 800 nm can be found in all the *H*/PEO samples (Fig. 2a). Similar feature was also found in the commercial PEDOT:PSS products, *i.e.*, Heraeus AI4083 and PH1000. Compared to the Heraeus products, the *H*/PEO samples show much weaker absorption signal at ~ 600 nm, which is attributed to the HOMO-LUMO transition in neutral PEDOT chains.^[34] Thus, it is inferred that the PEDOT is in conductive state in the as-prepared *H*/PEO hybrid samples. Our inference is confirmed by the UV-Vis data of the solid *H*/PEO samples (*cf.* Fig. S2 in the electronic supplementary information, ESI). Moreover, the conductivity value of *H*/PEO_{*n*} sample depends on the loading ratio of PEO. For which, the *H*/PEO30 shows the highest conductivity value. This phenomenon could be attributed to the formation of a more ordered structure of PEDOT under the screening function of PEO that is compatible with PEDOT:PSS.^[24]

By comparison, the conductivity value of *H*/PEO_{*n*} sample is much lower than that of PEDOT:PSS sample prepared in either the traditional wet based oxidative polymerization

(~ 0.1 S/cm)^[35] or solid-state polymerization (~ 1 S/cm).^[36] We understand this phenomenon with the fact that the introduction of excess amounts of PEO and PSS disturbed the molecular packing of PEDOT. To prove our hypothesis, we characterized the crystalline structure of the as-prepared PEDOT hybrid samples with wide angle X-ray scattering (WAXS).

Fig. 2(b) shows the typical crystalline information of the *H*/PEO30 sample at room temperature. The main crystalline peaks are attributed to the typical PEO crystalline reflections (Fig. 2b).^[37–39] This assumption is further supported by the temperature dependent WAXS results, measured from 20 °C to 80 °C. As shown in Fig. 2(c), the typical crystalline peaks diminish with the increase of the temperature. Especially when the temperature was 58 °C, the crystalline peaks disappear. This phenomenon could be rationalized with the melting of PEO crystals at high temperature. The value of the melting temperature is in good consistence with that found in DSC data (*cf.* Fig. S3 in ESI). The melting behavior of the PEO can be represented by the intensity change of the (120) reflection (Fig. 2d) that decreases almost linearly with the increase of temperature (from 30 °C to 42 °C, *cf.* Fig. S4 in ESI), indicating good temperature response around the BT. In the following, we characterized the temperature dependent resistance of the PEDOT:PSS/PEO hybrids with a homemade setup and studied their temperature sensing behaviors.

Fig. 3 shows the typical temperature sensing behavior of the PEDOT:PSS/PEO hybrids. The relative resistance change ($\Delta R/R_0$) versus temperature (*T*) curves are summarized in Fig. 3, where *R*₀, *R_T*, ΔR represent the samples' resistance value at 20 °C, at the set temperature, and the difference between them, respectively. As shown in Fig. 3(a), the $\Delta R/R_0$ increases almost linearly with the temperature increase from 30 °C to 40 °C, and then gradually reaches a plateau with $\Delta R/R_0 = 96.47\%$ when $T \geq 58$ °C. Similar phenomenon is found

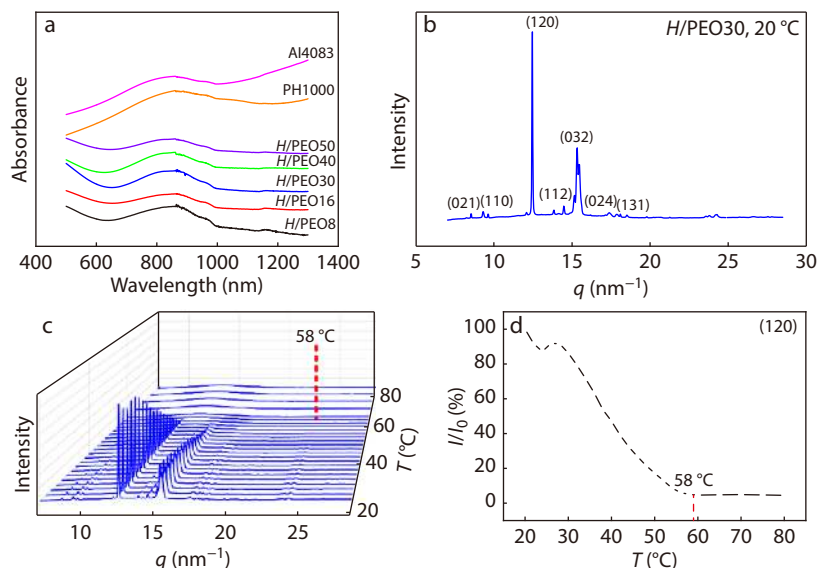


Fig. 2 Molecular structure of the as-prepared hybrid samples. (a) UV-Vis-NIR spectroscopy data of the aqueous solution samples of *H*/PEO and Heraeus products. For clarity reason, the data curves were shifted along the y-axis; (b) Synchrotron radiation WAXS data of *H*/PEO30 at 20 °C, indexed with PEO crystalline reflections; (c) Temperature-dependent WAXS data of *H*/PEO30; (d) Temperature-dependent change of the PEO (120) reflection peak intensity. Note: in panels (c) and (d), the data at 58 °C were marked to indicate the complete disappearing of crystalline signal in the heated sample; PEDOT:PSS/PEO_{*n*} is denoted as *H*/PEO_{*n*} where *n* indicates the molar ratio of EO:EDOT.

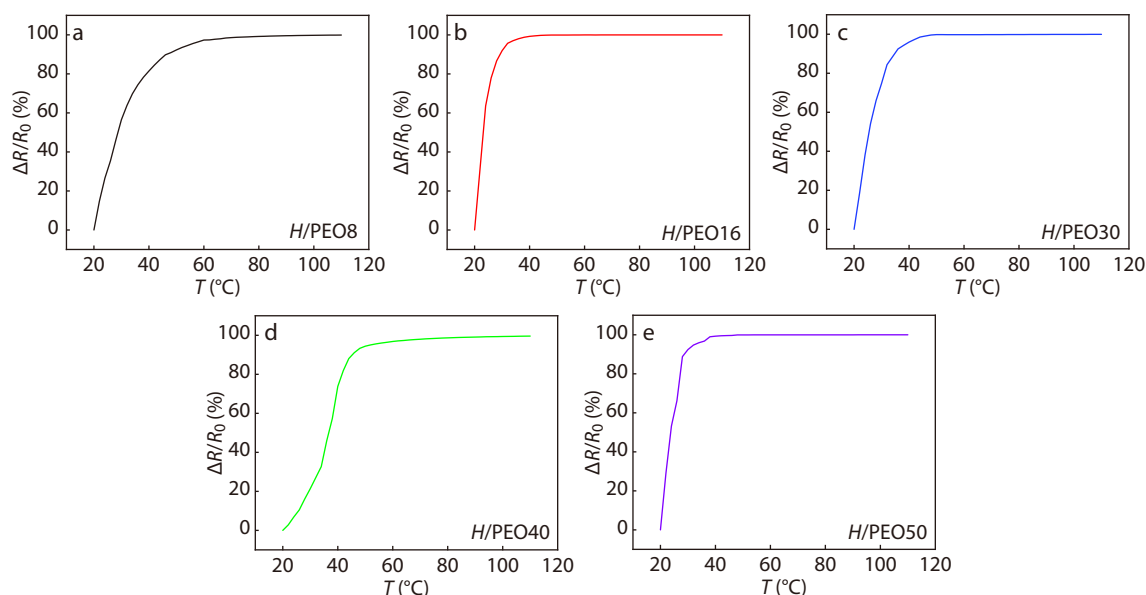


Fig. 3 Typical temperature sensing behavior of (a) H/PEO8, (b) H/PEO16, (c) H/PEO30, (d) H/PEO40 and (e) H/PEO50, indicated by the $\Delta R/R_0$ versus T curves, where R_0 represents samples' resistivity values at 20 °C, and $\Delta R = R_0 - R_t$, R_t is the resistivity values of the samples at set temperature. Note: PEDOT:PSS/PEO n is denoted as H/PEO n where n indicates the molar ratio of EO:EDOT.

in Figs. 3(b)–3(e), indicating that these are general features of the PEDOT:PSS/PEO hybrids. In addition, the linear response range of the PEDOT:PSS/PEO hybrids varies with the different contents of PEO. For example, as shown in Fig. 3(c), the H/PEO30 sample shows good linear response in a narrow temperature range, *i.e.*, $\Delta R/R_0$ value changes from 84.39% to 95.38% when the temperature increases from 32 °C to 40 °C. More detailed information can be found on the Fig. S5 (in ESI). This temperature range covers well the body temperature, ~37 °C,^[13] which is suitable for the BT monitoring. Similar temperature sensing behavior of PEDOT hybrids have also been reported in the literatures, which demonstrate that the microphase structure plays vital role in the temperature sensing behavior of the PEDOT hybrids.^[40,41] In addition, it is generally accepted that the conductivity of doped PEDOT weakly depends on the temperature change due to its good thermal stability.^[23,42] Moreover, it can be found that the temperature responsive feature of PEDOT:PSS becomes weaker and irregular if we replaced the semi-crystalline PEO matrix with the filter paper (*cf.* Fig. S6 in ESI). It is worth mentioning that the temperature response of our hybrid material showed good environmental stability and repeatability (*cf.* Fig. S7 in ESI).

Thus, we infer that the temperature sensing capabilities of PEDOT:PSS/PEO hybrids are resulting from the microphase structure change during heating. In the following, we decipher the temperature sensing behavior of the PEDOT:PSS/PEO hybrids from the perspectives of the temperature-dependent microphase structure change and corresponding variation of the conductive network.

SAXS is a well-established protocol in characterizing the microstructures of polymer, nanoparticles and so on in solution or solid state.^[43–46] It provides statistical microphase structure (*e.g.*, shape and arrangement) information of the samples. Combined with a heating/cooling system, it helps to study *in situ* the structure evolution as a function of tempera-

ture. Fig. 4(a) shows the synchrotron radiation SAXS data of H/PEO30 sample, in a temperature range from 20 °C to 80 °C. By reviewing the WAXS data of the PEDOT hybrid samples (Fig. 2), we know that the crystallized PEO shows typical crystalline peaks at room temperature. However, there is no crystalline lamellae, typical form of polymer crystal,^[47] observed in the SAXS data (*cf.* Figs. S8 and S9 in ESI). This phenomenon could be rationalized with the irregular shape/size of the PEO crystals, which is probably resulting from the complex crystallization environment in the PEDOT:PSS/PEO hybrids.

Our hypothesis is supported by the following facts. First, the PEDOT:PSS/PEO hybrids show typical conductive feature (Table 1) and it's inferred that the PEDOT forms continuous conductive paths in the hybrid samples, since only PEDOT is conductive. Second, PEO has good compatibility with PEDOT:PSS that has been demonstrated in the previous work.^[48] Third, the PSS is coupled with the PEDOT due to the Coulombic interactions (Fig. 1d). Thus, it is supposed that the PEO crystals are confined in the continuous network formed by the coupled PEDOT and PSS. The PEDOT:PSS network was qualitatively analyzed by fitting the SAXS data with a rod-like model, as demonstrated by Cho *et al.*^[43] and Zhang *et al.*^[49,50] Details about the SAXS data fitting could be found in Fig. S10 (in ESI).

Fig. 4(b) shows the typical fitting parameters of the rod-like structure, with r and L indicate the radius and length values of the rod, respectively. It should be noted that the formation of rod-like structure would promote the formation of a PEDOT conductive network with low thresholding value.^[49,51] By examining the changes of these two parameters as a function of temperature, it can be found that the r value increases almost linearly from 7.3 nm at 20 °C to 8.4 nm at 40 °C and then keeps almost constant till 50 °C. Meanwhile, the L value keeps almost constant at 56 nm from 20 °C to 50 °C. However, when the temperature was above 50 °C, the L value increases

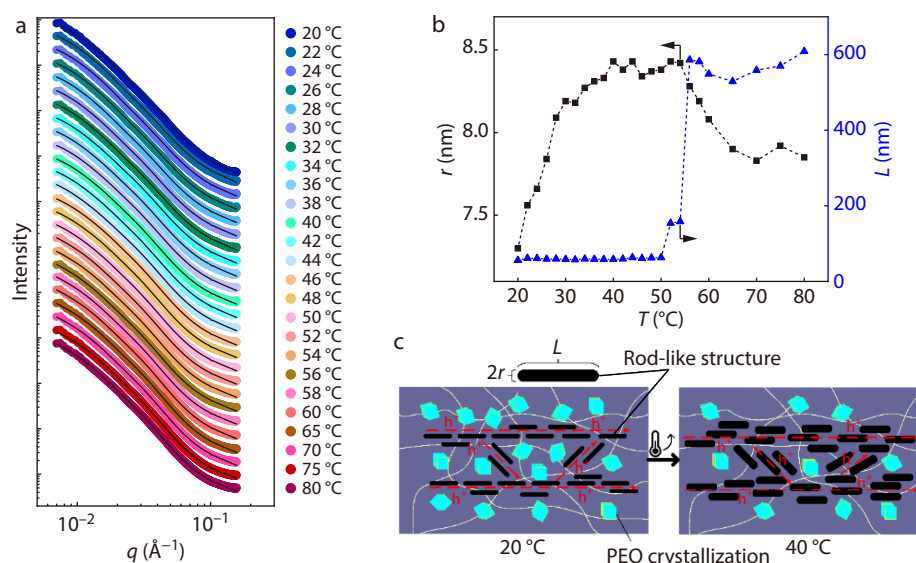


Fig. 4 (a) *In situ* synchrotron radiation SAXS results of H/PEO30 at different temperatures: experimental data (dotted lines) and the fitting results (solid lines). Note: for clarity reason, the curves were shifted vertically. (b) The extracted fitting parameters, radii (r) and length (L) of the rod, from the SAXS data, based on a rod-like model. (c) Schematically illustrated microstructure changes as a response of temperature increase from 20 °C to 40 °C. The dashed-arrow lines indicate the possible conductive paths in the PEDOT:PSS/PEO hybrids.

sharply to 586.1 nm at 56 °C and then keeps almost constant at higher temperatures. Note: the fitted L values of 586.1 nm exceed the detectable range of the SAXS measurements, which should be further verified with ultra-small angle X-ray scattering measurement that is out the scope of the present work. By reviewing the temperature sensing behavior of H/PEO30 (Fig. 3c), it is inferred that the temperature sensing capability of the hybrid samples around BT is strongly correlated with the r values, *i.e.*, the higher the r value the lower the resistance value. By reviewing the WAXS data (Fig. 2), this phenomenon could be rationalized with the fact that the melting of PEO crystals with temperature increase endows the PEDOT:PSS rearrangement to forge dense conductive paths (Fig. 4c). Moreover, complete melting of PEO at 58 °C does not made the samples' resistivity decrease significantly,

indicating that the continuous network formed already at lower temperatures (Fig. 4c). The distribution of sulfur elements (representing PEDOT and PSS) in EDS data also demonstrated the formation of conductive networks (*cf.* Fig. S11 in ESI). Our hypothesis agrees with the fact that H/PEO30 has similar resistivity values with that of H/PEO8 and H/PEO40 (Table 1), which have different loading values of PEO. In addition, the formation of continuous conductive network in PEDOT:PSS/PEO samples has been demonstrated by Sanviti *et al.* with conductive atomic force microscopy data.^[25]

In the following, we fabricated a flexible device with the H/PEO30 sample and testified its potential applications in wearable sensor. As shown in Fig. 5(a), the H/PEO30 sample was connected with the copper foil electrodes and then sealed with Kapton foils in both sides, to fabricate the wear-

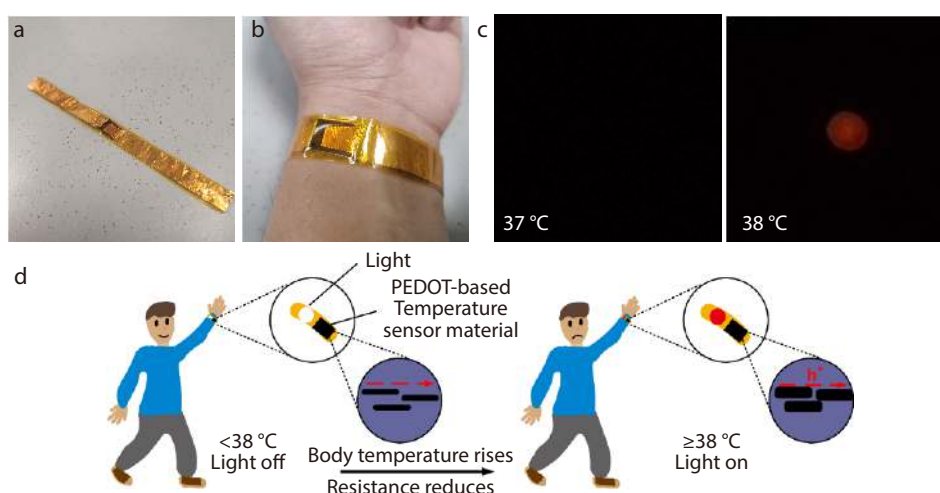


Fig. 5 Photos of the flexible wearable sensor (a) before and (b) after wearing on the wrist; (c) Photos of the LED light showing the temperature sensing capabilities of the as-prepared flexible wearable sensor; (d) Schematic illustration showing the potential applications of as-prepared PEDOT:PSS/PEO hybrids in wearable temperature sensors for BT monitoring.

able sensor. The as-prepared sensor device has good flexibility, which can be easily worn on the wrist (Fig. 5b). In addition, by connecting the sensor with a homemade signal enlargement and logic system (cf. Fig. S12 in ESI), it is demonstrated that the sensor shows good detection capability around the BT change. As indicated by the LED light in Fig. 5(c), the light turns on immediately when the temperature of the study subject reached 38 °C since the change of the sensor's resistance. At the same time, our devices showed good environmental stability (cf. Fig. S13 in ESI). Similar findings have been demonstrated by Daoud *et al.*^[52] and Yu *et al.*^[53] Thus, the change of the temperature can be visualized with the LED light, with accuracy within ± 1 °C. Note: a heater was employed as the heat source rather than human wrist, for the convenience of temperature control. The present finding indicates the potential applications of as-prepared PEDOT:PSS/PEO hybrids in wearable temperature sensors, as schematically demonstrated in Fig. 5(d).

CONCLUSIONS

In this work, a new protocol for the scalable manufacturing of PEDOT hybrid materials based on solid-state polymerization and two-roll milling have been developed. The success of the PEDOT polymerization was confirmed by the UV-Vis-NIR spectroscopy and conductivity data. In addition, the as-prepared PEDOT hybrids showed clear temperature responsiveness, which was slightly influenced by the loading of the PEO content. This phenomenon was rationalized with the temperature-dependent *in situ* study results based on synchrotron radiation WAXS and SAXS characterization. The PEDOT formed continuous conductive paths during the sample preparation, which were accompanied by irregular PEO crystals. The PEO crystals' melting resulting from temperature increase would trigger the PEDOT chain rearrangements to form closely packed microdomains, indicated by the radius value of the rod. These structure features enabled the as-prepared PEDOT:PSS/PEO hybrids temperature responsiveness around the body temperature. Moreover, these hybrid materials could be fabricated into flexible wearable sensors to monitor the body temperature change. These findings would help the design and preparation of PEDOT hybrids for their applications in wearable sensors and so on.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-3005-4>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. U2032101 and 11905306),

Fundamental Research Funds for the Central Universities (No. 19lgpy14) and "100 Top Talents Program" of Sun Yat-sen University. Ms. Huiyun Deng is thanked for her help during the sample preparation. This work was carried out with the support of 19U2 beamline at Shanghai Synchrotron Radiation Facility.

REFERENCES

- Lou, Z.; Wang, L.; Jiang, K.; Wei, Z.; Shen, G. Reviews of wearable healthcare systems: materials, devices and system integration. *Mater. Sci. Eng. R Rep.* **2020**, *140*, 100523.
- Ma, L. Y.; Soin, N. Recent progress in printed physical sensing electronics for wearable health-monitoring devices: a review. *IEEE Sens. J.* **2022**, *22*, 3844–3859.
- Nakata, S.; Arie, T.; Akita, S.; Takei, K. Wearable, flexible, and multifunctional healthcare device with an ISFET chemical sensor for simultaneous sweat pH and skin temperature monitoring. *ACS Sens.* **2017**, *2*, 443–448.
- Ates, H. C.; Nguyen, P. Q.; Gonzalez-Macia, L.; Morales-Narváez, E.; Güder, F.; Collins, J. J.; Dincer, C. End-to-end design of wearable sensors. *Nat. Rev. Mater.* **2022**, *7*, 887–907.
- Grant, A.; Smarr, B. Feasibility of continuous distal body temperature for passive, early pregnancy detection. *PLOS Digit. Health.* **2022**, *1*, e0000034.
- Tang, Z.; Kong, N.; Zhang, X.; Liu, Y.; Hu, P.; Mou, S.; Liljeström, P.; Shi, J.; Tan, W.; Kim, J. S.; Cao, Y.; Langer, R.; Leong, K. W.; Farokhzad, O. C.; Tao, W. A materials-science perspective on tackling COVID-19. *Nat. Rev. Mater.* **2020**, *5*, 847–860.
- Gao, W.; Emaminejad, S.; Nyein, H. Y. Y.; Challa, S.; Chen, K.; Peck, A.; Fahad, H. M.; Ota, H.; Shiraki, H.; Kiriya, D.; Lien, D. H.; Brooks, G. A.; Davis, R. W.; Javey, A. Fully integrated wearable sensor arrays for multiplexed *in situ* perspiration analysis. *Nature* **2016**, *529*, 509–514.
- Hasanpour, S.; Karperien, L.; Walsh, T.; Jahanshahi, M.; Hadisi, Z.; Neale, K. J.; Christie, B. R.; Djilali, N.; Akbari, M. A hybrid thread-based temperature and humidity sensor for continuous wound monitoring. *Sens. Actuators B* **2022**, *370*, 132414.
- T, K.; Rajini, G. K.; Maji, D. Cost-effective, disposable, flexible, and printable MWCNT-based wearable sensor for human body temperature monitoring. *IEEE Sens. J.* **2022**, *22*, 16756–16763.
- Tharakan, S.; Nomoto, K.; Miyashita, S.; Ishikawa, K. Body temperature correlates with mortality in COVID-19 patients. *Crit. Care* **2020**, *24*, 298.
- Smarr, B. L.; Aschbacher, K.; Fisher, S. M.; Chowdhary, A.; Dilchert, S.; Puldon, K.; Rao, A.; Hecht, F. M.; Mason, A. E. Feasibility of continuous fever monitoring using wearable devices. *Sci. Rep.* **2020**, *10*, 21640.
- Honda, W.; Harada, S.; Arie, T.; Akita, S.; Takei, K. Wearable, human-interactive, health-monitoring, wireless devices fabricated by macroscale printing techniques. *Adv. Funct. Mater.* **2014**, *24*, 3299–3304.
- Hall, J. E.; Hall, M. E. *Guyton and Hall textbook of medical physiology e-Book*. Elsevier Health Sciences: **2020**.
- Su, Y.; Ma, C.; Chen, J.; Wu, H.; Luo, W.; Peng, Y.; Luo, Z.; Li, L.; Tan, Y.; Omisore, O. M.; Zhu, Z.; Wang, L.; Li, H. Printable, highly sensitive flexible temperature sensors for human body temperature monitoring: a review. *Nanoscale Res. Lett.* **2020**, *15*, 200.
- Xia, Y.; Sun, K.; Ouyang, J. Solution-processed metallic conducting polymer films as transparent electrode of optoelectronic devices. *Adv. Mater.* **2012**, *24*, 2436–2440.
- Meng, X.; Xing, Z.; Hu, X.; Chen, Y. Large-area flexible organic solar cells: printing technologies and modular design. *Chinese J.*

- Polym. Sci.* **2022**, 40, 1522–1566.
- 17 Bubnova, O.; Khan, Z. U.; Malti, A.; Braun, S.; Fahlman, M.; Berggren, M.; Crispin, X. Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene). *Nat. Mater.* **2011**, 10, 429–433.
 - 18 Bai, H.; Shi, G. Gas sensors based on conducting polymers. *Sens.* **2007**, 7, 267–307.
 - 19 Lu, Y.; Wen, Y. P.; Lu, B. Y.; Duan, X. M.; Xu, J. K.; Zhang, L.; Huang, Y. Electrosynthesis and characterization of poly(hydroxymethylated-3,4-ethylenedioxythiophene) film in aqueous micellar solution and its biosensing application. *Chinese J. Polym. Sci.* **2012**, 30, 824–836.
 - 20 Jian, M.; Zhang, Y.; Liu, Z. Natural biopolymers for flexible sensing and energy devices. *Chinese J. Polym. Sci.* **2020**, 38, 459–490.
 - 21 Dimov, I. B.; Moser, M.; Malliaras, G. G.; McCulloch, I. Semiconducting polymers for neural applications. *Chem. Rev.* **2022**, 122, 4356–4396.
 - 22 Guimard, N. K.; Gomez, N.; Schmidt, C. E. Conducting polymers in biomedical engineering. *Prog. Polym. Sci.* **2007**, 32, 876–921.
 - 23 Kayser, L. V.; Lipomi, D. J. Stretchable conductive polymers and composites based on PEDOT and PEDOT:PSS. *Adv. Mater.* **2019**, 31, 1806133.
 - 24 Li, P.; Sun, K.; Ouyang, J. Stretchable and conductive polymer films prepared by solution blending. *ACS Appl. Mater. Interfaces* **2015**, 7, 18415–18423.
 - 25 Sanviti, M.; Martínez-Tong, D. E.; Rebollar, E.; Ezquerro, T. A.; García-Gutiérrez, M. C. Crystallization and phase separation in PEDOT:PSS/PEO blend thin films: influence on mechanical and electrical properties at the nanoscale. *Polymer* **2022**, 262, 125475.
 - 26 Lo, L. W.; Zhao, J.; Wan, H.; Wang, Y.; Chakrabarty, S.; Wang, C. An inkjet-printed PEDOT:PSS-based stretchable conductor for wearable health monitoring device applications. *ACS Appl. Mater. Interfaces* **2021**, 13, 21693–21702.
 - 27 Corradi, R.; Armes, S. P. Chemical synthesis of poly(3,4-ethylenedioxythiophene). *Synth. Met.* **1997**, 84, 453–454.
 - 28 Zhou, Z.; Tao, Z.; Zhang, L.; Zheng, X.; Xiao, X.; Liu, Z.; Li, X.; Liu, G.; Zhao, P.; Zhang, P. Scalable manufacturing of solid polymer electrolytes with superior room-temperature ionic conductivity. *ACS Appl. Mater. Interfaces* **2022**, 14, 32994–33003.
 - 29 Li, Y. W.; Liu, G. F.; Wu, H. J.; Zhou, P.; Hong, C. X.; Li, N.; Bian, F. G. BL19U2: small-angle X-ray scattering beamline for biological macromolecules in solution at SSRF. *Nucl. Sci. Tech.* **2020**, 31, 117.
 - 30 Hopkins, J. B.; Gillilan, R. E.; Skou, S. BioXTAS RAW: improvements to a free open-source program for small-angle X-ray scattering data reduction and analysis. *J. Appl. Crystallogr.* **2017**, 50, 1545–1553.
 - 31 Wu, X.; Liu, H.; Tang, Z.; Guo, B. Scalable fabrication of thermally conductive elastomer/boron nitride nanosheets composites by slurry compounding. *Compos. Sci. Technol.* **2016**, 123, 179–186.
 - 32 Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Adv. Mater.* **2000**, 12, 481–494.
 - 33 Gueye, M. N.; Carella, A.; Faure-Vincent, J.; Demadrille, R.; Simonato, J. P. Progress in understanding structure and transport properties of PEDOT-based materials: a critical review. *Prog. Mater. Sci.* **2020**, 108, 100616.
 - 34 Zozoulenko, I.; Singh, A.; Singh, S. K.; Gueskine, V.; Crispin, X.; Berggren, M. Polarons, bipolarons, and absorption spectroscopy of PEDOT. *ACS Appl. Mater. Interfaces* **2019**, 1, 83–94.
 - 35 Elschner, A.; Kirchmeyer, S.; Lovenich, W.; Merker, U.; Reuter, K. *PEDOT: principles and applications of an intrinsically conductive polymer*. CRC Press: **2010**.
 - 36 Meng, H.; Perepichka, D. F.; Wudl, F. Facile solid-state synthesis of highly conducting poly(ethylenedioxythiophene). *Angew. Chem., Int. Ed.* **2003**, 42, 658–661.
 - 37 Dörr, T. S.; Pelz, A.; Zhang, P.; Kraus, T.; Winter, M.; Wiemhöfer, H. D. An ambient temperature electrolyte with superior lithium ion conductivity based on a self-assembled block copolymer. *Chem. Eur. J.* **2018**, 24, 8061–8065.
 - 38 Zardalidis, G.; Mars, J.; Allgaier, J.; Mezger, M.; Richter, D.; Floudas, G. Influence of chain topology on polymer crystallization: poly(ethylene oxide) (PEO) rings vs. linear chains. *Soft Matter* **2016**, 12, 8124–8134.
 - 39 Takahashi, Y.; Tadokoro, H. Structural studies of polyethers, $-(CH_2)_m-O-)_n$. X. Crystal structure of poly(ethylene oxide). *Macromolecules* **1973**, 6, 672–675.
 - 40 Liu, Z.; Wu, L.; Qian, J.; Peng, J.; Liu, R.; Xu, Y.; Shi, X.; Qi, C.; Ye, S. Tuned transport behavior of the IPA-treated PEDOT:PSS flexible temperature sensor via screen printing. *J. Electron. Mater.* **2021**, 50, 2356–2364.
 - 41 Zhang, F.; Hu, H.; Islam, M.; Peng, S.; Wu, S.; Lim, S.; Zhou, Y.; Wang, C. H. Multi-modal strain and temperature sensor by hybridizing reduced graphene oxide and PEDOT:PSS. *Compos. Sci. Technol.* **2020**, 187, 107959.
 - 42 Kiebooms, R.; Aleshin, A.; Hutchison, K.; Wudl, F.; Heeger, A. Doped poly(3,4-ethylenedioxythiophene) films: thermal, electromagnetic and morphological analysis. *Synth. Met.* **1999**, 101, 436–437.
 - 43 Ju, D.; Kim, D.; Yook, H.; Han, J. W.; Cho, K. Controlling electrostatic interaction in PEDOT:PSS to overcome thermoelectric tradeoff relation. *Adv. Funct. Mater.* **2019**, 29, 1905590.
 - 44 Chu, B.; Hsiao, B. S. Small-angle X-ray scattering of polymers. *Chem. Rev.* **2001**, 101, 1727–1762.
 - 45 Li, T.; Senesi, A. J.; Lee, B. Small angle X-ray scattering for nanoparticle research. *Chem. Rev.* **2016**, 116, 11128–11180.
 - 46 Zhang, P.; Zou, R.; Wu, S.; Meyer, L. A.; Wang, J.; Kraus, T. Gold nanopores exploring the ice structure in the aqueous dispersion of poly(ethylene glycol)-gold hybrid nanoparticles. *Langmuir* **2022**, 38, 2460–2466.
 - 47 Yeh, S.-W.; Wu, T. L.; Wei, K. H.; Sun, Y. S.; Liang, K. S. Effect of incorporated CdS nanoparticles on the crystallinity and morphology of poly(styrene-*b*-ethylene oxide) diblock copolymers. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, 43, 1220–1229.
 - 48 Fu, K.; Lv, R.; Na, B.; Zou, S.; Zeng, R.; Wang, B.; Liu, H. Mixed ion-electron conducting PEO/PEDOT:PSS miscible blends with intense electrochromic response. *Polymer* **2019**, 184, 121900.
 - 49 Li, X.; Zou, R.; Liu, Z.; Mata, J.; Storer, B.; Chen, Y.; Qi, W.; Zhou, Z.; Zhang, P. Deciphering the superior thermoelectric property of post-treatment-free PEDOT:PSS/IL hybrid by X-ray and neutron scattering characterization. *npj Flexible Electron.* **2022**, 6, 6.
 - 50 Liu, Z.; Li, X.; Zou, R.; Zhou, Z.; Ma, Q.; Zhang, P. Deciphering the quaternary structure of PEDOT:PSS aqueous dispersion with small-angle scattering. *Polymer* **2022**, 261, 125415.
 - 51 Li, X.; He, Z.; Liu, Z.; Chen, Y.; Zhou, Z.; Chen, G.; Qi, W.; Rauber, D.; W. M. Kay, C.; Zhang, P. High-performance post-treatment-free PEDOT based thermoelectric with the establishment of long-range ordered conductive paths. *Chem. Eng. J.* **2023**, 454, 140047.
 - 52 Daoud, W. A.; Xin, J. H.; Szeto, Y. S. Polyethylenedioxythiophene coatings for humidity, temperature and strain sensing polyamide fibers. *Sens. Actuators B* **2005**, 109, 329–333.
 - 53 Yu, Y.; Peng, S.; Blanloeuil, P.; Wu, S.; Wang, C. H. Wearable temperature sensors with enhanced sensitivity by engineering microcrack morphology in PEDOT:PSS-PDMS sensors. *ACS Appl. Mater. Interfaces* **2020**, 12, 36578–36588.