All-Polymer Conducting Fibers and 3D Prints via Melt Processing and Templated Polymerization

Anna I. Hofmann,* Ida Östergren, Youngseok Kim, Sven Fauth, Mariavittoria Craighero, Myung-Han Yoon, Anja Lund, and Christian Müller*

ABSTRACT: Because of their attractive mechanical properties, conducting polymers are widely perceived as materials of choice for wearable electronics and electronic textiles. However, most state-of-the-art conducting polymers contain harmful dopants and are only processable from solution but not in bulk, restricting the design possibilities for applications that require conducting micro-to-millimeter scale structures, such as textile fibers or thermoelectric modules. In this work, we present a strategy based on melt processing that enables the fabrication of nonhazardous, all-polymer conducting bulk structures composed of poly(3,4-ethylenedioxythiophene) (PEDOT) polymerized within a Nafton template. Importantly, we employ classical polymer processing techniques including melt extrusion followed by fiber spinning or fused filament 3D printing, which cannot be implemented with the majority of doped polymers. To demonstrate the versatility of our approach, we fabricated melt-spun PEDOT:Nafton fibers, which are highly flexible, retain their conductivity of about 3 S cm$^{-1}$ upon stretching to 100% elongation, and can be used to construct organic electrochemical transistors (OECTs). Furthermore, we demonstrate the precise 3D printing of complex conducting structures from OECTs to centimeter-sized PEDOT:Nafton figureines and millimeter-thick 100-leg thermoelectric modules on textile substrates. Thus, our strategy opens up new possibilities for the design of conducting, all-polymer bulk structures and the development of wearable electronics and electronic textiles.

KEYWORDS: melt processing, conducting elastic PEDOT:Nafton fibers, 3D printing, organic electrochemical transistors (OECTs), electronic textiles
One way to design a chemically stable doped polymer complex and eliminate risks related to the leakage of harmful substances is the use of an all-polymer system, for example, a conjugated polymer doped with a polymeric counter ion. A prominent example for such a conjugated polymer:polyanion complex is poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), which finds widespread use in a myriad of applications; thanks to its high conductivity, excellent chemical stability, biocompatibility, as well as its straightforward and cost-efficient synthesis. However, PEDOT:PSS is only processable from an aqueous dispersion, which limits its use to certain bulk processing methods, such as the solution-casting of tapes or wet-spinning of fibers, some of which reach conductivities of more than $10^3 \, \text{S cm}^{-1}$. Also, blends of PEDOT:PSS and insulating polymers, which display promising electrical and mechanical properties, are mostly processed from solution. More recently, it has been shown that PEDOT can also be complexed with a large variety of other polymeric counter ions, ranging from polyanionic polysaccharides to fluoropolymers such as Nafton, a term commonly used to describe sulfonated tetrafluoroethylene-based copolymers. However, all of these PEDOT complexes are intractable without the use of a solvent and cannot be processed from the melt, which prevents the use of PEDOT for most bulk processing methods that are widely used in polymer technology.

Thus, we set out to develop a novel strategy that permits the fabrication of an all-polymer PEDOT-based bulk material, combining classical melt processing methods with the templated oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT). We chose to work with a thermoplastic fluoropolymer that carries sulfonyl fluoride groups, that is, a Nafton precursor, which can be melt processed into any desired shape. Upon chemical activation, the precursor bulk is transformed into anionic Nafton, which serves as a bulk template during the oxidative dispersion polymerization of EDOT. The obtained PEDOT:Nafton complex is flexible and highly stretchable and shows a bulk conductivity of about 3 S cm$^{-1}$. To illustrate the versatility of our strategy, we prepared conducting fibers, fabricated organic electrochemical transistors (OECTs) and 3D printed different complex bulk structures, including a 100-leg thermoelectric module on a textile substrate.

### RESULTS AND DISCUSSION

We identified Nafton as a suitable candidate for our work because it can serve as a bulk template for PEDOT and shows excellent biocompatibility. The PEDOT:Nafton bulk materials were obtained via a three-step process, consisting of (1) melt processing of the Nafton precursor into the desired shape and (2) an activation step yielding the anionic Nafton, followed by (3) the synthesis of PEDOT within the Nafton template (Figure 1a).

To prepare conducting fibers, the Nafton precursor was melt-spun into fibers with a diameter of approximately 200 μm. The precursor fibers were then soaked in an activation bath of H$_2$O/DMSO/KOH, following a well-established activation
procedure. As confirmed by elemental analysis and infrared spectroscopy (Figure S1 and Table S1), the activation process transformed the sulfonyl fluoride groups into sulfonic acid groups, resulting in an ionic Na﻿ nanochannel and disrupts the initial nanostructure of the Na﻿ nanochannel. We argue that the PEDOT penetrates the hydrophilic steps (Figure S3). In contrast, after the PEDOT synthesis, washing it in water, the activated Na﻿ activation process transformed the sulfonyl fluoride groups, resulting in an ionic Na﻿ PEDOT:PSS processed without cosolvents. Furthermore, PEDOT:Nafion displayed a Seebeck coefficient of \( \alpha_{\text{PEDOT:Nafion}} = 12 \pm 2 \mu \text{V K}^{-1} \), indicating that the PEDOT within the complex is highly doped. In order to check the stability over time, we remeasured three different sample batches one year after preparation and found that their conductivity was unchanged (Figure S2). Elemental analysis revealed that the purified bulk material contained approximately one EDOT repeating unit per repeating unit of Na﻿ and that only small amounts of ions (<1 wt %) are present within the complex (Table S1). This translates to a concentration of 12 wt % PEDOT within the PEDOT:Nafion bulk, as compared to as much as 30 wt % in commercial bench-mark PEDOT:PSS.

To elucidate the nanostructure of PEDOT:Nafion, we analyzed the complex by X-ray scattering. The structure of Na﻿ is often described as a polytetrafluoroethylene (PTFE)-like bulk, which is traversed by a hydrophilic network of nanoclusters, formed by the sulfonate side groups. It has been reported that this nanostructure gives rise to a peak at around \( q \approx 5 \text{ nm}^{-1} \) (Figure S3). In contrast, after the PEDOT synthesis, SAXS diffractograms of the resulting bulk PEDOT:Nafion did not display any distinct peak in this \( q \) range (Figure S3). Thus, we argue that the PEDOT penetrates the hydrophilic nanochannels and disrupts the initial nanostructure of the Na﻿ bulk. Wide angle X-ray scattering (WAXS) diffractograms of PEDOT:Nafion displayed a broad scattering peak between \( q \approx 12 \text{ to } 13 \text{ nm}^{-1} \) (\( d \approx 0.5 \text{ nm} \)), which we attribute to the amorphous PTFE-like bulk (Figure S3). The absence of scattering features at around \( q \approx 18 \text{ nm}^{-1} \) (\( d \approx 0.35 \text{ nm} \)) is a sign of a low degree of \( \pi \)-stacking of the PEDOT chains.

We went on to characterize the mechanical properties of the complex and found that PEDOT:Nafion fibers are highly stretchable and display a Young’s modulus \( E \approx 620 \pm 100 \text{ MPa} \) and an elongation at break of more than 100%. Further, the fibers are highly fatigue resistant and can be subjected to at least 100 strain-release cycles with 10% maximum strain without compromising their electrical conductivity (Figure 1b). A direct comparison with pristine-activated Nafion fibers, which are equally elastic (Figure S4), suggests that Nafion is the continuous, loadbearing phase that is impregnated by PEDOT-rich domains. Upon stretching, we observed a reversible increase of the conductivity, opposite to the behavior commonly observed for composite materials made from conducting fillers in an insulating matrix. We argue that upon stretching, PEDOT-rich domains are elongated, which leads to an improved percolation and a reversible increase in the conductivity of the material, similar to the behavior observed for PEDOT:PSS/polyurethane blends by Seyedin et al. Because of their remarkable stretchability, PEDOT:Nafion fibers are of high interest for elastic interconnects in e-textiles and for the fabrication of wearable biosensors, such as sensors based on OECTs. In addition, anionic Nafion swells readily in water and is known for its excellent cation transport properties. Swelling tests on PEDOT:Nafion confirmed that the conducting bulk material retained a high degree of swellability and can take up over 10 wt % of water (Figure S5). Thus, we went on to study the performance of PEDOT:Nafion as a mixed-ion-hole conductor in OECTs operating in the depletion mode. Devices made of a PEDOT:Nafion fiber (\( \sigma = 200 \mu \text{S cm}^{-1} \), channel length \( L \approx 1.5 \text{ mm} \)) displayed an ON/OFF ratio on the order of 10\(^3\) and a maximum transconductance \( g_m \) of 8.6 mS at zero gate voltage (\( V_g = -0.6 \text{ V} \)) (Figure 1c). Hence, the measured transconductance is comparable to the \( g_m \) of microfabricated thin-film devices with channels made from PEDOT:PSS or other PEDOT-based materials. For PEDOT:PSS-based devices, it was observed that \( g_m \) increases with the channel thickness, as a result of the strong swelling and the constant volumetric capacitance (\( C^* \approx 39 \text{ F cm}^{-3} \)) of PEDOT:PSS. Following the trend reported by Rivnay et al., PEDOT:PSS channels with dimensions comparable to our device can be expected to display a \( g_m \) of about 30–40 mS, which is four times higher than the transconductance measured for our device. For further elucidation, we determined the volumetric capacitance of PEDOT:Nafion by analysis of the gate current transient and by impedance spectroscopy and found a \( C^* \approx 15 \text{ F cm}^{-3} \) (Figure S6). Thus, the lower \( g_m \) of our device can be related to a lower volumetric capacitance of PEDOT:Nafion as compared to PEDOT:PSS, which is also in agreement with the lower PEDOT concentration in PEDOT:Nafion. The response time of the PEDOT:Nafion OECTs was in the range of several seconds (\( \tau \approx 18 \text{ s} \)), and cyclability of the devices confirmed that the electrical properties are stable upon immersion in water for at least 3 h (Figure S7).

In order to fabricate more diverse and complex bulk structures, we explored the transferability of our strategy to FFF 3D printing. For successful 3D printing, the thermoplastic polymer must display (1) good adhesion to the printing substrate and (2) sufficiently high stiffness to ensure correct feeding of the filament into the printer head. The Nafion precursor, however, does not adhere well to common print surfaces and is relatively soft (\( E \approx 7.5 \text{ MPa} \)). To overcome
these challenges, we developed a printable polymer blend of the Nafion precursor and an acrylonitrile–butadiene–styrene (ABS) plastic (Figure 3a). ABS, one of the benchmark materials for FFF 3D printing, displays a high stiffness at room temperature ($E \approx 1–3$ GPa) and a processing temperature of 240 °C. Scanning electron microscopy (SEM) images of the precursor/ABS blends depict a phase-separated system, corresponding to a precursor matrix interspersed with micrometer-sized ABS domains (Figure S8). Thus, the stiff ABS domains act as filler particles, which increase the stiffness of the blend. By screening different compositions of precursor/ABS blends, we found that the stiffness of the blend increased significantly for ABS concentrations of more than 20 wt % (Figure 3b). Upon addition of 30 wt % ABS, we obtained a precursor/ABS blend with a Young’s modulus of 20 MPa. This content is high enough to allow for correct feeding of the filament into the printer head and for adherence to ABS, high impact polystyrene (HIPS), and textile substrates (Figure 3b). Thus, we chose to work with a precursor/30 wt % ABS blend, which represents a good compromise between high stiffness and excessive content of the insulating ABS filler material.

We extruded the precursor/ABS blend (30 wt % ABS) into filaments and printed various structures, which were then immersed into the activation bath (see scheme in Figure 3a). Because the activation is controlled by the diffusion of the activation solution into the precursor/ABS bulk, the thickness of the activated layer could be controlled by varying the temperature and the reaction time (Figure 3c). We found that with increasing temperature, the activation reaction proceeded faster into the bulk, which we tentatively assign to improved swelling and diffusion of the alkaline solution into the material, as well as increased reaction kinetics. It should be noted that the thickness of the activated, anionic Nafion defines the thickness of the resulting conducting PEDOT:Nafion layer. Hence, a short activation of 30 min at room temperature, for instance, resulted in a PEDOT layer of 20–30 μm. If the activation was allowed to proceed for several hours at 70 °C, millimeter-thick samples were fully impregnated with PEDOT. Thus, very thick PEDOT:Nafion samples can be obtained by soaking the Nafion precursor in the activation solution for a prolonged time. In this work, we fabricated both micrometer thin conducting PEDOT:Nafion layers ($d_{\text{min}} \approx 10$ μm) as well as millimeter thick conducting bulk structures ($d_{\text{max}} \approx 7$ mm), which opens up many new possibilities for the design of 3D printed structures.

In order to facilitate the diffusion of the EDOT monomer into the Nafion bulk, we chose to remove the ABS from the Nafion/ABS blend because it becomes redundant after printing. Upon leaching in a solution of FeCl$_3$ in dimethyl sulfoxide (DMSO), we obtained a highly porous Nafion bulk (Figure 3d). At the same time, the leaching step introduced Fe$^{3+}$ into the anionic Nafion. Because Fe$^{3+}$ acts as the oxidant in the EDOT polymerization, no additional FeCl$_3$ had to be added to initiate the polymerization reaction. The presence of Fe$^{3+}$ within the Nafion helped to confine the polymerization locally, so that PEDOT was predominantly formed within the Nafion bulk and less in the water phase of the synthesis bath. The obtained porous PEDOT:Nafion bulk displayed a conductivity of $1−5$ S cm$^{-1}$ and a Seebeck coefficient of 10 ± 2 μV K$^{-1}$, which is comparable to the electrical properties of PEDOT:Nafion processed without ABS.

We went on to test the electrochemical response of the printed material within OECT devices (Figure S9). In order to keep the channel dimensions similar to our fiber OECTs, we measured printed lines (width 1 mm) with a 30 μm thick, porous PEDOT:Nafion layer and a channel length of 1.5 mm. The 3D printed devices displayed an ON/OFF ratio of about $10^2$ ($V_D = -0.6$ V, $V_G = 0.6$ V) and a maximum transconductance of 6.0 mS at $V_G = 0.1$ V ($V_D = -0.6$ V) at a time response in the range of 1 min ($\tau \approx 55$ s). Thus, the
electrochemical response of PEDOT:Nafion was not drastically affected by the differences in processing.

In a final set of experiments, we aimed at illustrating that our 3D printing process can be used for the fabrication of complex architectures. To highlight the excellent printability of the material, we fabricated a conducting duckling, which we call a (con)duckling (Figure 4a), and a carbon nanotube-like structure (Figure 4b), which comprised details in the millimeter-range and could be printed with high precision. As a proof of concept, illustrating the potential for functional devices, we also 3D printed a set of thermoelectric modules. For organic materials, the optimal leg length is typically found in the millimeter range, a size that is difficult to realize with in-plane or 2D printed and folded modules but is perfectly suitable for 3D printing. We chose to fabricate an out-of-plane thermoelectric module with a leg length of 1.6 mm. The module was printed onto a textile substrate (a prewashed polyester fleece) and comprised 100 leg pairs (Figure 4c). In the first step, PEDOT:Nafion legs, which served as the p-type material, were prepared on top of the textile. In the second step, we printed interconnecting, pseudo n-type legs onto the PEDOT:Nafion structures using a commercial ABS/Carbon black composite which displays a Seebeck coefficient close to 0 (\( \alpha_{\text{ABS/CB}} = 1 \pm 1 \, \mu V \, \text{K}^{-1} \), \( \sigma_{\text{ABS/CB}} = 0.003 \, \text{S cm}^{-1} \)). In order to improve the thermoelectric performance of the module, the print was immersed into a base bath, which resulted in a slight dedoping of the PEDOT:Nafion and an increase of its Seebeck coefficient \( \alpha_{\text{PEDOT/Nafion}} \) from 10 to 15 \( \mu V \, \text{K}^{-1} \) without a notable decrease of its conductivity. As expected, the thermoelectric properties of the ABS/carbon black composite were not affected by the base treatment.

To measure the thermoelectric performance, the module was then sandwiched between a hot-plate (textile side) and a heat sink, and the temperature difference \( \Delta T_{\text{hot-cold}} \) between them was monitored by two thermocouples. The output voltage increased linearly from 9 mV for \( \Delta T_{\text{hot-cold}} = 10 \, \text{°C} \) to 39 mV for \( \Delta T_{\text{hot-cold}} = 53 \, \text{°C} \) (Figure 4d). Thus, in the case of small temperature gradients, the obtained output voltage was close to the expected value of \( V_{\text{out}}/\Delta T = N(\alpha_{\text{PEDOT/Nafion}} - \alpha_{\text{ABS/CB}}) = 1400 \, \mu V \, \text{K}^{-1} \), where \( N \) is the number of leg pairs. Only at larger temperature gradients, the obtained voltage output started to deviate considerably from the estimated value. We explain this discrepancy with a non-negligible thermal contact resistance between the module and the heat source and sink, which reduces the temperature difference \( \Delta T_{\text{leg}} \) that the thermoelectric legs experience (cf. Figure 4e; the measured and calculated power output match if \( \Delta T_{\text{leg}} \approx 0.5 \cdot \Delta T_{\text{hot-cold}} \) is assumed). As a result of the low conductivity of the ABS/carbon black composite, the module displayed a considerable internal resistance \( R_i \), of about 400 kΩ, which can be regarded as the main limiting factor for the power output of the device. We would like to point out that our module fabrication process is reproducible as evidenced by the very similar performance of a second, identical thermoelectric module (Figure 4d), affirming the robustness of our 3D printing method.

### CONCLUSIONS

In conclusion, we have demonstrated an innovative strategy that enables the fabrication of flexible and conducting polymer architectures via bulk processing using the polymer complex PEDOT:Nafion. Melt-spun PEDOT:Nafion fibers displayed conductivities of about 3 S cm\(^{-1}\), retained their conductivity...
output power was estimated using the equation $P = \frac{V_{in}^2}{R_L + R_i}$, where $R_L$ is the load resistance and $R_i$ is the internal resistance of the device. The temperature dependence of the output power was found to be significant, with a maximum output power of 260 °C being observed. A textile substrate was used for the thermoelectric module, with a polyester fleece being employed as the evaporation of water.

Mechanical Testing. The mechanical stability of the PEDOT:Naion composite was evaluated using a DMA Q800 (TA Instruments) with a ramped force of 0.5 N m⁻¹. The dynamic mechanical properties were determined by subjecting the composite to 100 cycles of 6 s displacement to 10% strain followed by 30 s rest. The electrical resistance was measured using a Keysight U1253B multimeter collecting 1 data point s⁻¹. The results were found to be accurate within a range of ±0.5%.

Electrical Characterization. The electrical conductivity of PEDOT:Naion films was measured using a Keithley 2400 SMU. The conductivity was found to be dependent on the film thickness and substrate material. The conductivity was found to be highest for PEDOT:Naion films on glass substrates, with a conductivity of 0.15 S cm⁻¹. The conductivity was found to decrease as the substrate thickness increased.
X-ray Scattering. SAXS diffractograms were obtained using a Mat:Nordic (SAXSLAB) equipped with a Rigaku 003+ high brilliance microfocus Cu-radiation source (wavelength = 1.5406 Å) and a Pilatus 300K detector placed at a distance of 1050 mm from the sample. WAXS images were obtained at the D-line at the Cornell High Energy Synchrotron Source (CHESS) at Cornell University. The measurements were performed with a synchrotron radiation of a wavelength of 1.155 Å. A Pilatus 200 K detector with pixel size of 172 μm × 172 μm was used to collect scattered X-ray from the sample at a sample to detector distance of 177.2 mm.

Elemental Analysis. Elemental analysis was performed using inductively coupled plasma–mass spectrosometry on dried samples (60 °C, > 4 h) at Mikrolab Kolbe, Germany.

Attenuated Total Reflection–Fourier Transform Infrared Spectroscopy. Infrared absorption measurements were performed on bulk samples (dimensions ca. 2 mm × 5 mm × 1 mm) using a Frontier FTIR Spectrometer from PerkinElmer equipped with a GladiATR attachment from Pike Technologies.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b20615.

FTIR absorption spectra, elemental analysis, WAXS and SAXS diffractograms, mechanical properties of PEDOT:Nafion fibers, water uptake of PEDOT:Nafion, capacitance measurements, scanning electron micrographs, and OECT device characterization (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Anna I. Hofmann — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden; orcid.org/0000-0002-4480-6028; Email: hofanna@chalmers.se

Christian Müller — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden; orcid.org/0000-0001-7859-7909; Email: christian.mueller@chalmers.se

Authors

Ida Östergren — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

Youngseok Kim — School of Materials Science and Engineering, Gwangju Institute of Science and Technology, 61005 Gwangju, Republic of Korea

Sven Fauth — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

Mariavittoria Craighero — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

Myung-Han Yoon — School of Materials Science and Engineering, Gwangju Institute of Science and Technology, 61005 Gwangju, Republic of Korea; orcid.org/0000-0001-7205-3054

Anja Lund — Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.9b20615

Author Contributions

A.I.H. and I.O. contributed equally.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge financial support from the Swedish Research Council through grant no. 2016-06146, the Swedish Foundation for Strategic Research through grant no. RMA 15-0052, the Knut and Alice Wallenberg Foundation through a Wallenberg Academy Fellowship, and the European Research Council (ERC) under grant agreement no. 637624. Furthermore, we thank the Cornell High Energy Synchrotron Source (CHESS) (supported by the NSF & NIH/NIGMS via NSF award DMR-1332208) for providing experimental time for WAXS measurements. SAXS measurements and electron microscopy were performed at the Chalmers Material Analysis Laboratory (CMAI). Furthermore, we thank Dr. Hengda Sun and Dr. Simone Fabiano from Linköping University for discussions regarding the design of bulk OECTs, and Lanxess for providing the Lewatit S108H ion exchange resin.

**REFERENCES**

(1) Kroon, R.; Mengistie, D. A.; Kiefer, D.; Hynynen, J.; Ryan, J. D.; Yu, L.; Müller, C. Thermoelectric Plasics: From Design to Synthesis, Processing and Structure—Property Relationships. Chem. Soc. Rev. 2016, 45, 6147–6164.

(2) Russ, B.; Glaudell, A.; Urban, J. J.; Chabinyc, M. L.; Segalman, R. A. Organic Thermoelectric Materials for Energy Harvesting and Temperature Control. Nat. Rev. Mater. 2016, 1, 16050–21158.

(3) Seyedin, S.; Razal, J. M.; Innis, P. C.; Jeirani, Chen, Z.; Hamed, M. M.; Müller, C. Electrically Conducting Fibres for E-Textiles: An Open Playground for Conjugated Polymers and Carbon Nanomaterials. Mater. Sci. Eng. R 2018, 126, 1–29.

(4) Wang, B.; Facchetti, A. Mechanically Flexible Conductors for Stretchable and Wearable E-Skin and E-Textile Devices. Adv. Mater. 2019, 31, 1901408.

(5) Matsushita, N.; Chen, X.; Yao, Z.; Someya, T. Materials and Structural Designs of Stretchable Conductors. Chem. Soc. Rev. 2019, 48, 2946–2966.

(6) Berggren, M.; Richter-Dahlfors, A. Organic Bioelectronics. Adv. Mater. 2007, 19, 3201–3213.

(7) Rivnay, J.; Salleo, A.; Owens, R. M.; Berggren, M.; Malliaras, G. G. Organic Electrochemical Transistors. Nat. Rev. Mater. 2018, 3, 17086.

(8) Bubnova, O.; Crispin, X. Towards Polymer-Based Organic Thermoelectric Generators. Energy Environ. Sci. 2012, 5, 9345–9362.

(9) Mayer, P. M.; Ram, R. J. Optimization of Heat Sink–Limited Thermoelectric Generators. Nanoscale Microscale Thermophys. Eng. 2006, 10, 143–155.

(10) Ferhat, M.; Perego, A.; Lanzani, G.; Caironi, M. Organic Flexible Thermoelectric Generators: From Modeling, a Roadmap towards Applications. Sustainable Energy Fuels 2017, 1, 174–190.

(11) Beirne, S.; Wallace, G. G. Knitted Strain Sensor Textiles of Highly Conductive All-Polymeric Fibers. ACS Appl. Mater. Interfaces 2015, 7, 21150–21158.

(12) Russ, B.; Glaudell, A.; Urban, J. J.; Chabinyc, M. L.; Segalman, R. A. Organic Thermoelectric Materials for Energy Harvesting and Temperature Control. Nat. Rev. Mater. 2016, 1, 16050–21158.

(13) Beretta, D.; Perego, A.; Lanzani, G.; Caironi, M. Organic Thermoelectric Materials for Energy Harvesting and Temperature Control. Nat. Rev. Mater. 2016, 1, 16050–21158.

(14) Hynynen, J.; Jaatinen, T.; Hynynen, J.; Ryan, J. D.; Yu, L.; Müller, C. Thermoelectric Plasics: From Design to Synthesis, Processing and Structure—Property Relationships. Chem. Soc. Rev. 2016, 45, 6147–6164.
Thermoelectric Power Factor of Tensile Drawn Poly(3-Hexylthiophene). ACS Macro Lett. 2019, 8, 70–76.

(15) Brandão, L.; Viana, J.; Bucknall, D. G.; Bernardo, G. Solventless Processing of Conjugated Polymers - A Review. Synth. Met. 2014, 197, 23–33.

(16) O’Carroll, D.; Lieberwirth, I.; Redmond, G. Melt-Processed Polyfluorene Nanowires as Active Waveguides. Small 2007, 3, 1178–1183.

(17) Kroon, R.; Ryan, J. D.; Kiefer, D.; Yu, L.; Hynynen, E.; Müller, C. Bulk Doping of Millimeter-Thick Conjugated Polymer Foams for Plastic Thermoelectrics. Adv. Funct. Mater. 2017, 27, 1704183.

(18) Holness, F. B.; Price, A. D. Direct Ink Writing of 3D Conductive Polyolinate Structures and Rheological Modelling. Smart Mater. Struct. 2018, 27, 015006.

(19) Titelman, G. I.; Zilberman, M.; Siegmann, A.; Haba, Y.; Narkis, M. Thermal Dynamic Processing of Polyamylene with Dodecylbenzene Sulfonic Acid. J. Appl. Polym. Sci. 1997, 66, 2199–2208.

(20) Cao, Y.; Smith, P.; Heeger, A. J. Counterion-Induced Processibility of Conducting Polyamylene and of Conducting Polymers of Polyamylene in Bulk Polymers. Synth. Met. 1992, 48, 91–97.

(21) Drozda, T.; Wick, C.; Benedict, J. T.; Veilleux, R. F.; Bakerjian, R. Tool and Manufacturing Engineers Handbook: A Reference Book for Manufacturing Engineers, Managers, and Technicians; Society of Manufacturing Engineers, 1983.

(22) Jacobs, I. E.; Moule, A. J. Controlling Molecular Doping in Organic Semiconductors. Adv. Mater. 2017, 29, 1703065.

(23) Green, R. A.; Lovell, N. H.; Wallace, G. G.; Poole-Warren, L. A. Conducting Polymers for Neural Interfaces: Challenges in Developing an Effective Long-Term Implant. Biomaterials 2008, 29, 3393–3399.

(24) Njuguna, J.; Ansari, F.; Sachse, S.; Zhu, H.; Rodriguez, V. M. Nanomaterials, Nanofillers, and Nanocomposites: Types and Properties. In Health and Environmental Safety of Nanomaterials: Polymer Nanocomposites and Other Materials Containing Nanoparticles; Ngjuna, J., Pielichowski, K., Zhu, H., Eds.; Woodhead Publishing, 2014; pp 3–27.

(25) Elschnier, A.; Kirchmeyer, S.; Lovenich, W.; Merker, U.; Reuter, K. PEDOT: Principles and Applications of an Intrinsically Conductive Polymer; CRC Press, 2010.

(26) Richardson-Burns, S. M.; Hendricks, J. L.; Foster, B.; Povlich, L. K.; Kim, D.-H.; Martin, D. C. Polymerization of the Conducting Polymer Poly(3,4-Ethylenedioxythiophene) (PEDOT) around Living Neural Cells. Biomaterials 2007, 28, 1539–1552.

(27) Fujie, T. Development of Free-Standing Polymer Nanoshapes for Advanced Medical and Health-Care Applications. Polym. J. 2016, 48, 773–780.

(28) Greco, F.; Zucca, A.; Taccola, S.; Menciassi, A.; Fujie, T.; Haniu, H.; Takeoka, S.; Dario, P.; Mattoli, V. Ultra-Thin Conductive Free-Standing PEDOT/PSS Nanofilms. Soft Matter 2011, 7, 10642–10650.

(29) Kee, S.; Kim, H.; Paleti, S. H. K.; El Labban, A.; Neophytou, M.; Enwas, A.; Alshaffaf, H. N.; Baran, D. Highly Stretchable and Air-Stable PEDOT:PSS/Ionic Liquid Composites for Efficient Thermoelectric Response of PEDOT:PSS/Polyurethane Blends. Adv. Funct. Mater. 2018, 28, 1704285.

(30) Seyed, M. Z.; Razal, J. M.; Innis, P. C.; Wallace, G. G. Strain-Responsive Polyurethane/PEDOT Elastomeric Composite Fibers with High Electrical Conductivity. Adv. Funct. Mater. 2014, 24, 2957–2966.

(31) Hofmann, A. I.; Smaal, W. T. T.; Muntz, M.; Katsigianopoulos, D.; Brochon, C.; Schütze, F.; Hild, O. R.; Cloutet, E.; Hadziioannou, G. An Alternative Anionic Polyelectrolyte for Aqueous PEDOT Dispersions: Toward Printable Transparent Electrodes. Angew. Chem., Int. Ed. 2015, 54, 8506–8510.

(32) del Aguila, I.; Malliaras, G. G.; Mecerreyes, D. Conductive Poly(3,4-Ethylenedioxythiophene) (PEDOT-Based) Polymers and Their Applications in Bioelectronics. In Smart Polymers and Their Applications; Aguilar, M. R., San Román, J., Eds.; Woodhead Publishing, 2019; pp 191–218.

(33) Hofmann, A. I.; Katsigianopoulos, D.; Muntz, M.; Petsagkourakis, I.; Pecastaings, G.; Fleury, G.; Schatz, C.; Pavlopoulou, E.; Brochon, C.; Hadziioannou, G.; et al. Toward Stretchable Self-Powered Sensors Based on the Thermoelectric Response of PEDOT:PSS/Polyurethane Blends. Adv. Funct. Mater. 2018, 29, 1704285.

(34) Zhang, J.; Seyedin, S.; Qin, S.; Lynch, P. A.; Wang, Z.; Yang, W.; Wang, X.; Razal, J. M. Fast and Scalable Wet-Spinning of Highly Conductive PEDOT:PSS Fibers Enables Versatile Applications. J. Mater. Chem. A 2019, 7, 6401–6410.

(35) Saraba-Riquelme, R.; Shali, M.; Brill, J. W.; Weisenberger, M. C. Effect of Drawing on the Electrical, Thermoelectrical, and Mechanical Properties of Wet-Spun PEDOT:PSS Fibers. ACS Appl. Mater. Inter. 2019, 11, 2157–2167.

(36) Hansen, T. S.; West, K.; Hassager, O.; Larsen, N. B. Highly Stretchable and Conductive Polymeric Material Made from Poly(3,4-Ethylenedioxythiophene) and Polyurethane Elastomers. Adv. Funct. Mater. 2007, 17, 3069–3073.

(37) Tanori, P. J.; Santaguidiana, G.; Wan, K.; Calado, P.; Qin, M.; Zhang, H.; Pugno, N. M.; Palma, M.; Stengl-Stutzman, N.; Heeney, M.; et al. Toward Stretchable Self-Powered Sensors Based on the Thermoelectric Response of PEDOT:PSS/Polyurethane Blends. Adv. Funct. Mater. 2018, 28, 1704285.
(50) Carrico, J. D.; Traeden, N. W.; Aureli, M.; Leang, K. K. Fused Filament 3D Printing of Ionic Polymer-Metal Composites (IPMCs). Smart Mater. Struct. 2015, 24, 125021.

(51) Elliott, J. A.; James, P. J.; McMaster, T. J.; Newton, J. M.; Elliott, A. M. S.; Hanna, S.; Miles, M. J. Hydrolysis of the Nafion Precursor Studied by X-Ray Scattering and in-Situ Atomic Force Microscopy. E-Polymers 2001, 1, 022.

(52) Salerno, H. L. S.; Beyer, F. L.; Elabd, Y. A. Anion Exchange Membranes Derived from Nafion Precursor for the Alkaline Fuel Cell. J. Polym. Sci., Part B: Polym. Phys. 2012, 50, 552–562.

(53) Mauritz, K. A.; Moore, R. B. State of Understanding of Nafion. Chem. Rev. 2004, 104, 4535–4586.

(54) Crispin, X.; Jakobsson, F. L. E.; Crispin, A.; Grim, P. C. M.; Andersson, P.; Volodin, A.; van Haesendonck, C.; Van der Auweraer, M.; Salaneev, W. R.; Berggren, M. The Origin of the High Conductivity of Poly(3,4-Ethylenedioxythiophene)—Poly(Styrenesulfonate) (PEDOT–PSS) Plastic Electrodes. Chem. Mater. 2006, 18, 4354–4360.

(55) Elliott, J. A.; Wu, D.; Paddison, S. J.; Moore, R. B. A Unified Morphological Description of Nafion Membranes from SAXS and Mesoscale Simulations. Soft Matter 2011, 7, 6820–6827.

(56) Haubold, H.-G.; Vad, T.; Jungbluth, H.; Hiller, P. Nanostructure of NAFION: A SAXS Study. Electrochim. Acta 2001, 46, 1559–1563.

(57) Gruger, A.; Régis, A.; Schmatko, T.; Colomban, P. Nanostructure of Nafion Membranes at Different States of Hydration: An IR and Raman Study. Vib. Spectrosc. 2001, 26, 215–225.

(58) Kim, S.-M.; Kim, C.-H.; Kim, Y.; Kim, N.; Lee, W.-J.; Lee, E.-H.; Kim, D.; Park, S.; Lee, K.; Rivnay, J.; et al. Influence of PEDOT:PSS Crystallinity and Composition on Electrochemical Transistor Performance and Long-Term Stability. Nat. Commun. 2018, 9, 3858.

(59) Proctor, C. M.; Rivnay, J.; Malliaras, G. G. Understanding Volumetric Capacitance in Conducting Polymers. J. Polym. Sci., Part B: Polym. Phys. 2016, 54, 1433–1436.

(60) Rivnay, J.; Leleux, P.; Ferro, M.; Sensolo, M.; Williamson, A.; Koutsouras, D. A.; Khodagholy, D.; Ramuz, M.; Strakosha, O.; Owens, R. M.; et al. High-Performance Transistors for Bioelectronics through Tuning of Channel Thickness. Sci. Adv. 2015, 1, No. e1400251.

(61) Beretta, D.; Neophytou, N.; Hodges, J. M.; Kanatzidis, M. G.; Narducci, D.; Martin- Gonzalez, M.; Beeckman, M.; Balke, B.; Cerretti, G.; Tremel, W.; et al. Thermoelectrics: From History, a Window to the Future. Mater. Sci. Eng., R 2019, 138, 100501.

(62) Bahk, J.-H.; Fang, H.; Yazawa, K.; Shakouri, A. Flexible Thermoelectric Materials and Device Optimization for Wearable Energy Harvesting. J. Mater. Chem. C 2015, 3, 10362–10374.

(63) Fan, Z.; Li, P.; Du, D.; Ouyang, J. Significantly Enhanced Thermoelectric Properties of PEDOT:PSS Films through Sequential Post-Treatments with Common Acids and Bases. Adv. Energy Mater. 2017, 7, 1602116.