

Stretchable Conductive Polymers and Composites Based on PEDOT and PEDOT:PSS

Laure V. Kayser and Darren J. Lipomi*

The conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT), and especially its complex with poly(styrene sulfonate) (PEDOT:PSS), is perhaps the most well-known example of an organic conductor. It is highly conductive, largely transmissive to light, processible in water, and highly flexible. Much recent work on this ubiquitous material has been devoted to increasing its deformability beyond flexibility—a characteristic possessed by any material that is sufficiently thin—toward stretchability, a characteristic that requires engineering of the structure at the molecular- or nanoscale. Stretchability is the enabling characteristic of a range of applications envisioned for PEDOT in energy and healthcare, such as wearable, implantable, and large-area electronic devices. High degrees of mechanical deformability allow intimate contact with biological tissues and solution-processable printing techniques (e.g., roll-to-roll printing). PEDOT:PSS, however, is only stretchable up to around 10%. Here, the strategies that have been reported to enhance the stretchability of conductive polymers and composites based on PEDOT and PEDOT:PSS are highlighted. These strategies include blending with plasticizers or polymers, deposition on elastomers, formation of fibers and gels, and the use of intrinsically stretchable scaffolds for the polymerization of PEDOT.

1. Introduction

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is a commercially available, conductive polyelectrolyte complex.^[1] It has been used in the research laboratory for several decades for applications in electrostatic coatings, organic electrodes, solar cells, and light-emitting diodes. While it is commonly used in flexible devices, it can also be engineered to be useful in applications demanding greater deformability, i.e., stretchability. These applications include wearable and implantable devices for integration with soft and stretchable biological systems and tissues, such as the skin, and large-area devices, such as organic displays and photovoltaic (OPV) cells. The use of PEDOT:PSS as a transparent electrode, for example, allows for the roll-to-roll printing of OPV devices. Several reviews have been published on the development of

PEDOT:PSS, ways of increasing its conductivity, elucidation of its microstructure, and fabrication of new devices.^[1–5] This progress report focuses on the strategies to increase the stretchability of PEDOT or PEDOT:PSS. These strategies include blending with plasticizers or polymers, physical approaches such as wavy device layouts, gelation—often not covered by other discussions on stretchable electronics—and the use of stretchable polymeric matrices for PEDOT.

1.1. Stretchable Electronics

Stretchable electronics refers to electronic devices or materials that have a high deformability, i.e., they can be stretched past some loosely defined engineering strain, usually greater than 10%, with minimal loss in electronic function.^[6–11] Two classes of materials have been explored to generate stretchable devices: inorganic


and organic. Inorganic electronic materials such as metals and silicon are hard and brittle in bulk form. To render these materials stretchable, several compositing strategies have been realized. These approaches include encapsulation or dispersion of inorganic nanoparticles in elastomers.^[12,13] Organic electronic materials such as semiconducting polymers, in contrast, can in principle be rendered stretchable intrinsically without compositing. These approaches use engineering of the molecular structure, such as the length and branching of the alkyl side chain, molecular weight, and the design of block copolymers containing a mix of rigid electronic blocks and soft blocks for stretchability.^[7] In addition, organic electronic materials offer the advantages of electronic tunability by synthesis, ease of processing via spin-coating and ink-jet printing, oxide-free interfaces, and a low impedance.^[14] While the mechanical properties of organic semiconductors are currently the topic of a large and expanding literature,^[7,15,16] until recently, intrinsically stretchable organic conductors have received somewhat less attention.

2. PEDOT and PEDOT:PSS

2.1. Synthesis

Of all organic conductors, the most well-known is PEDOT complexed with PSS, PEDOT:PSS. PEDOT was developed as an

Dr. L. V. Kayser, Prof. D. J. Lipomi
Department of NanoEngineering
University of California San Diego
9500 Gilman Drive, Mail Code 0448, La Jolla, CA 92093-0448, USA
E-mail: dlipomi@eng.ucsd.edu

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201806133>.

DOI: 10.1002/adma.201806133

alternative to polythiophene to reduce α - β and β - β couplings during the oxidative polymerization of thiophene. Because of the substitution of the 3 and 4 positions of the thiophene, PEDOT is also resistant to degradation by oxygen and water.^[2,3] Though intrinsically a semiconductor, PEDOT with conductivities up to 300 S cm^{-1} are obtained when electropolymerized and oxidatively doped in the presence of PF_6^- counterion.^[2] However, PEDOT—in either pristine or doped form—has poor solubility. This problem led to the development of PEDOT:PSS, a polyelectrolyte complex composed of positively charged and p-doped PEDOT, and negatively charged and water-soluble PSS. PSS plays two roles: 1) it acts as a counterion to stabilize doped PEDOT and 2) it provides a matrix for PEDOT to form an aqueous dispersion. PEDOT:PSS is typically synthesized in two steps: preparation of PSS followed by oxidative polymerization of PEDOT which forms a strong electrostatic association with PSS. The most common method of synthesizing PSS is by sulfonation of polystyrene. While this process achieves 80–100% substitution, it also affords crosslinking defects through sulfone groups which bridge the chains.^[17] Alternatively, PSS can be polymerized from sodium 4-vinylbenzenesulfonate followed by acidification. This process leads to a backbone with 100% substitution and no defects. In the second step of the synthesis of PEDOT:PSS, PEDOT is oxidatively polymerized in water using a strong oxidant (sodium or ammonium persulfate) in the presence of the PSS matrix. PEDOT:PSS is commercially available as a water dispersion under the names of Clevios (Heraeus) or Orgacon (Agfa) (it should be noted that for commercially obtained PEDOT:PSS, neither the synthetic route of the PSS nor its molecular weight is generally disclosed). The ubiquity of PEDOT:PSS is due to its ease of processability, high stability under ambient conditions, good transparency in the visible light region, and the range of conductivities that can be achieved, using secondary dopants, which can serve different applications.^[3]

2.2. Microstructure and Conductivity of PEDOT:PSS

PEDOT:PSS has a complex structure due to the intimate association of two polyelectrolytes. The generally accepted model for the structure in solution has small segments of PEDOT in close contact with PSS bundles (Figure 1).^[18] These bundles form a colloid of gel particles in water.^[19] The density of PEDOT is the greatest at the core of the particles, and the density of the hydrophilic PSS is the greatest at the periphery. The deposition and drying of PEDOT:PSS thus result in a pancake-like morphology of grains with a PEDOT-rich core and a PSS-rich shell. The morphology of the films, and hence the conductivity, is largely influenced by the method of processing and any other additives (often called “secondary dopants”) included in the recipe to increase the conductivity.^[4] For example, conductivities as high as 4380 S cm^{-1} have been reported for PEDOT:PSS treated with sulfuric acid, compared to $<10 \text{ S cm}^{-1}$ without any secondary dopant.

2.3. Stability and Thermal Properties

Early studies on PEDOT with a PF_6^- counteranion, have shown that the conductivity of PEDOT is only weakly dependent on



Laure V. Kayser is a postdoctoral researcher in the group of Prof. Darren Lipomi in the Department of NanoEngineering at the University of California San Diego. She earned her M.Sc. in Chemistry from the University of Strasbourg in 2009 working under Prof. Pierre Braunstein, and her Ph.D. from McGill University in 2016 under Prof. Bruce Arndtsen. Her current research focuses on developing innovative synthetic approaches for stretchable organic electronics.



Darren J. Lipomi is an associate professor in the Department of NanoEngineering at the University of California, San Diego. He earned his Ph.D. in Chemistry from Harvard University in 2010 under George M. Whitesides, and was a postdoctoral fellow at Stanford University from 2010 to 2012 under Zhenan Bao. His current research focuses on the mechanical properties of electronic materials for applications in energy and healthcare.

the temperature.^[20] PEDOT: PF_6^- has a characteristic resistivity ratio of $\rho_r = \rho(1.4 \text{ K})/\rho(291 \text{ K}) = 1.5\text{--}2.8$. Interestingly, and similarly to other high conductivity conjugated polymer, this positive temperature coefficient of resistivity (TCR) becomes negative at temperature below 10 K. Kiebooms et al. showed that these films are stable up to 150°C , above which they gradually decompose until reaching full degradation at 390°C .^[21] They also showed that while the initial conductivity is dependent on the nature of the counteranion (PF_6^- , BF_4^- , or CF_3SO_3^-), the thermal behavior of PEDOT remains roughly similar. For PEDOT:PSS, however, the changes in conductivity as a function of the temperature, the thermal conductivity, and the thermal stability are highly dependent on both the chemical composition and the morphology of the film. For example, Stepien et al. showed that neat films of PEDOT:PSS (Clevios PH1000) gave a maximum conductivity after annealing the films at around 160°C (in air) or 200°C (in nitrogen) before rapidly degrading at higher temperatures.^[22] When treated with dimethylsulfoxide (DMSO), however, the conductivity immediately decreased when the samples were annealed above room temperature, both in air or under nitrogen. They also showed that PEDOT:PSS degrades exponentially over

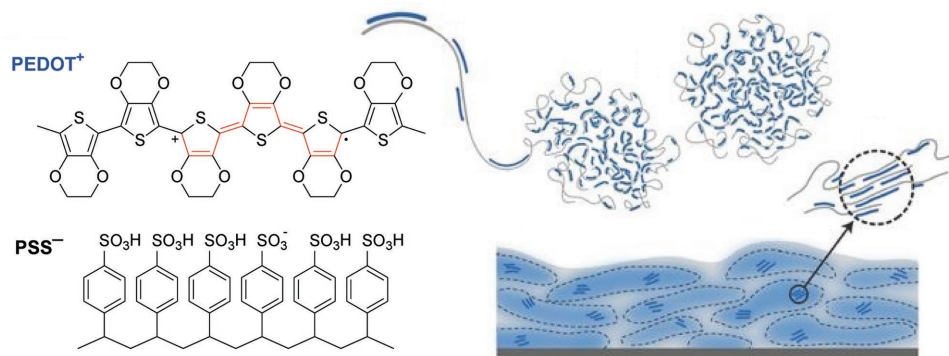


Figure 1. Chemical structure of PEDOT:PSS, its formation of colloidal gel particles when dispersed in water and microstructure of the resulting films with PSS-rich domains (gray) and PEDOT:PSS-rich domains (blue). Reproduced with permission from CC BY 4.0 open access license.^[18]

time between room temperature and 160 °C. They concluded that PEDOT:PSS, at least the formulation tested, should not be used for applications which require prolonged exposure to temperatures above 55 °C. Several other studies reported the thermal stability and/or thermoelectric properties of PEDOT:PSS in different formulations (Clevios PH1000,^[23] Clevios PH500,^[24,25] or Baytron P VP AI 4083^[26]), with sorbitol,^[27] ethylene glycol,^[28] or directly in devices (light-emitting diodes^[29] or organic solar cells^[30,31]).

2.4. Applications in Energy and Electronic Devices

PEDOT:PSS is found in many devices, including solar cells,^[32,33] supercapacitors,^[34] fuel cells,^[35] triboelectric^[36] and thermoelectric generators,^[37] electrochromic devices,^[38] and light-emitting diodes^[39] (Figure 2).^[40–42] The recent development of stretchable PEDOT:PSS has opened new applications in wearable electronics owing to its ease of processing and conformability to the skin.^[6,9] In addition, stretchable forms of PEDOT:PSS can be used in strain sensors and actuators for soft robotics, human–machine interfaces, and electronic skin,^[43–46] including self-powered devices,^[47,48] and can be integrated in fibers and fabrics for electronic textiles.^[49,50]

2.5. Applications in Biology

When used in a biological setting, PEDOT offers several advantages over inorganic materials. It is softer,^[51] thereby reducing the mechanical mismatch with biological tissues which can lead to scarring,^[52] nontoxic,^[53] conducting both electrons and ions,^[54] it has a lower impedance and a higher charge injection capacity than metals,^[55] and it can be chemically tuned to modulate the mechanical and electronic properties or to allow covalent attachment of biomolecules.^[5,56] PEDOT, PEDOT:PSS, and their stretchable derivatives have been extensively reported in bioelectronic applications (Figure 2),^[14,42,57] for example, in electrophysiology,^[58] sensors and actuators for biomedical applications,^[59] ion pumps,^[60] organic electrochemical devices and transistors (OECTs) for biosensing,^[61] tissue engineering,^[62,63] mechanobiology,^[64] neural interfaces,^[65–68] and drug delivery.^[69]

2.6. Mechanical Properties and Methods for Measuring Them

The applicability of PEDOT:PSS in different formulations for stretchable electronics depends on its mechanical properties. The mechanical properties of PEDOT:PSS are highly variable and depend on the ratio of PEDOT to PSS, presence of additives, relative humidity, strain rate, and processing conditions. For example, the mechanical properties under various levels of humidity were determined by Lang et al. using tensile testing of freestanding films.^[70] The authors showed that films of PEDOT:PSS fracture between 2% and 6% strain with a Young's modulus between 0.9 ± 0.2 and 2.9 ± 0.5 GPa at 55% and 23% relative humidity. Under increased levels of humidity, grains of PEDOT:PSS appeared to lose their cohesion, and the mechanical behavior went from brittle to plastic. Zhou et al. obtained results that were consistent with this behavior, and also used dynamic mechanical analysis (DMA) to understand the mechanical response of PEDOT:PSS as a function of temperature.^[71] The authors found that the storage modulus of PEDOT:PSS varied between 1.0 and 7.5 GPa between 250 and –150 °C. In addition, the strain rate should be taken into account when measuring the mechanical properties of PEDOT:PSS. For example, systems with plasticizers can appear to have a much higher strain at failure and toughness by stretching the polymer film at low strain rate over several hours by giving time to the polymer chains to relax.^[72] As an alternative to tensile testing, thin films (<125 nm) of PEDOT:PSS on slabs of poly(dimethylsiloxane) (PDMS) were measured using the buckling method, giving an elastic modulus of 2.26 ± 0.05 GPa.^[73] For PEDOT electrodeposited on metal substrates, however, other methods to characterize the mechanical properties have been proposed. Such methods account for the rough surface of the metal and include nanoindentation,^[74] peak-force quantitative nanomechanical mapping (PF-QNM) in conjunction with atomic force microscopy (AFM) to determine the stiffness modulus,^[51] and thin film cracking to obtain the stiffness, strength, and interfacial shear strength (adhesion).^[75] In all cases, PEDOT and PEDOT:PSS were shown to be brittle, and are not expected to be stretchable, at least in their native forms. The remainder of this progress report will highlight the strategies that have been envisioned to increase the stretchability of PEDOT and PEDOT:PSS.

3. Blending PEDOT:PSS with Additives

3.1. Small Molecule Plasticizers

The addition of small molecule plasticizers can effectively decrease the interaction between polymer chains and increase the free volume, thereby lowering the elastic modulus and enhancing stretchability of the material. Commonly used plasticizers for PEDOT:PSS include xylitol,^[76,77] glycerol,^[78] Triton X-100 (a nonionic surfactant derived from ethylene glycol),^[79,80] and ionic liquids (salts with a melting point below 100 °C).^[81,82] The use of plasticizers allows PEDOT:PSS to be stretched to around 50%. Interestingly, these plasticizers also serve to enhance the conductivity.^[76–82] The enhancement of conductivity with high boiling solvents is believed to originate from dissolution and partial diffusion of insulating PSS domains away from conductive PEDOT, although other mechanisms have been proposed.^[4] Recently, Bao and co-workers have shown that by using water-soluble ionic liquids containing highly acidic anions, the conductivity of PEDOT:PSS could reach 3100 S cm^{−1} when supported on styrene ethylene butylene styrene (SEBS) or 600 S cm^{−1} as freestanding films (Figure 3a).^[82] This difference in conductivity may have arisen from the fact that the supported films were rinsed after spin-coating with additional ionic liquids, which act as secondary

dopants. PEDOT:PSS films doped with these ionic liquids were stretched up to 175% (freestanding films) or 800% (supported). A disadvantage of additives is their propensity to leach into the environment. Loss of the additive not only degrades the properties of the material, but in biological applications also poses health hazards, particularly for ionic liquids.^[83]

3.2. Polymeric Blends

Another route to increasing the stretchability of PEDOT:PSS is by blending with polymers. The requirement for the polymer additive is that it is soluble in water, and thus poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO),^[84] poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) triblock copolymer (PEO–PPO–PEO),^[85] poly(vinyl alcohol) (PVA),^[86] and polyurethane (PUR) have all been used (Figure 3b).^[87–89] While this approach was used to achieve stretchability up to 100% (or higher for PUR with low PEDOT:PSS loadings),^[88] one disadvantage is the decrease in conductivity with increasing amounts of insulating polymer. This decrease in conductivity probably results from phase separation and ultimately limited connectivity between the conductive PEDOT domains. The blending approach is even more difficult with hydrophobic elastomers such as PDMS. Two

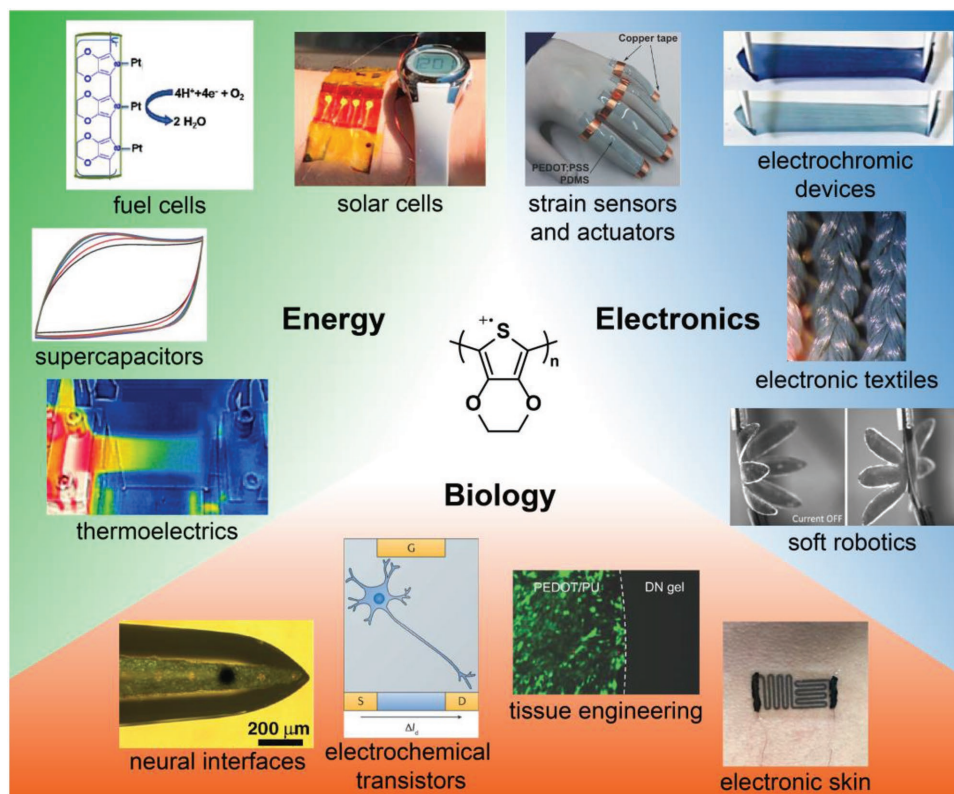


Figure 2. Applications for stretchable and conductive PEDOT in energy, electronics, and biology: thermoelectrics, supercapacitors, fuel cells, solar cells, strain sensors and actuators, electrochromic devices, electronic textiles, soft robotics, electronic skin, tissue engineering, organic electrochemical transistors (OECTs), and neural interfaces. Images reproduced with permission from references:^[37] Copyright 2017, Elsevier;^[35] Copyright 2013, Elsevier;^[33] Copyright 2016, Elsevier;^[44] Copyright 2014, John Wiley and Sons;^[38] Copyright 2017, American Chemical Society;^[119] Copyright 2010, American Chemical Society;^[45] Copyright 2014, Springer Nature;^[63] Copyright 2014, John Wiley and Sons;^[61] Copyright 2018, Springer Nature; and^[68] Copyright 2009, John Wiley and Sons.

strategies have been reported to obtain PEDOT:PSS:PDMS. The first approach consisted of forming a PEDOT:PSS aerogel by freeze-drying followed by infiltration of PDMS oligomers into the aerogel pores, followed by crosslinking of the PDMS.^[90] The resulting material could be stretched reversibly up to 10% with ultimate failure at 45%. Another strategy was to enhance the blending of aqueous PEDOT:PSS in PDMS precursor by the addition of an amphiphilic PDMS-*b*-PEO block copolymer.^[91] The optimized ratio of conductivity versus stretchability was obtained by adding 30 wt% PDMS-*b*-PEO, which surprisingly maintained the same conductivity as undoped PEDOT:PSS ($\approx 0.3 \text{ S cm}^{-1}$) and could be stretched up to 75%. PEDOT:PSS could also be blended with hydrophobic and rubbery poly(*n*-butyl acrylate-styrene) (P(BA-*r*-St)) latex-like elastomers to reach an elongation of 97% and a conductivity of 63 S cm^{-1} .^[92]

4. Physical Approaches

4.1. Deposition of PEDOT:PSS on Elastomers

Enhancing the stretchability of PEDOT:PSS using physical approaches (i.e., with no or minimal modification of the molecular structure) is similar to the strategies used by the community associated with stretchable inorganic electronic devices. These approaches use device layouts including metal serpentine, out-of-plane buckles, or “island-bridge” architectures to convert global tensile strains into local bending strains or otherwise to redirect strain energy away from the most sensitive components of the device.^[12,93] While inorganic structures can often be transferred to and from elastomers using kinetically controlled adhesion,^[94] depositing thin films of PEDOT:PSS on elastomers generally requires the use of an adhesion promoter or surfactant. When PEDOT:PSS is deposited directly on PDMS (without surfactant), strains as low as 6% produce a large density of cracks on the surface with an abrupt increase in resistance.^[95] This behavior is similar to that of gold thin films on PDMS which upon stretching form a network of islands and maintain reversibly high conductivity up to 20% strain.^[96] In order to improve the wettability of PEDOT:PSS on hydrophobic silicone elastomers, Zonyl, a nonionic fluorosurfactant, now discontinued and reformulated as Capstone, has been widely used (Figure 4b).^[44,97,98] The addition of Zonyl allows for the

formation of thin layers of PEDOT:PSS (by spin-coating) on PDMS. In addition to enhancing the wettability, Zonyl also acts as a secondary dopant to improve the conductivity. The stretchability and resistance versus strain, however, is highly dependent on the surface treatment of PDMS.^[98] When the surface of PDMS is treated with oxygen plasma, a highly hydrophilic and glassy layer of SiO_x is formed which allows the uniform deposition of PEDOT:PSS:Zonyl. But, when stretched, the behavior of PEDOT:PSS is dominated by this glassy layer and readily forms cracks. Alternatively, the surface of PDMS can be activated by UV/ozone exposition to render the surface mildly hydrophilic without the formation of a glassy layer. In combination with 1% Zonyl, Lipomi et al. found that films of PEDOT:PSS on PDMS could be stretched up to 180% before a complete loss in conductivity.^[98] In this system, tensile strain energy is stored or dissipated by the following three mechanisms: 1) elastic deformation ($<10\%$), 2) plastic deformation, leading to the buckling of PEDOT:PSS on the surface of PDMS (10–50%), and 3) film cracking ($>50\%$). Other treatments for PDMS include activation with hydrochloric acid (HCl)^[98] or methanesulfonic acid,^[99] however, the use of strong acids (HCl) can deteriorate the performance of organic solar cells due to the presence of acidic residues in the vicinity of the active layer. An alternative protocol which did not require surfactants, reported by Zhu et al., consisted in depositing a layer of crosslinked hydrophilic polymer (polyethylene glycol diacrylate or PEGDA) on the surface of PDMS then transferring PEDOT:PSS doped with ethylene glycol by stamping.^[100] An advantage of this approach was that the surface could be patterned by selective photo-crosslinking of PEGDA using masks, although the PDMS still required activation with an oxygen plasma to allow the adhesion of PEGDA. Nonsilicone-based elastomers have also been used as substrates for PEDOT:PSS including SEBS,^[101,102] poly(ethylene terephthalate) (PET),^[103] and polyimide (PI).^[104] In most cases, PEDOT:PSS supported on elastomers led to devices with a limited stretchability due to the intrinsic brittleness of the conductive polymer.

4.2. Encapsulation

In order to reduce cracking of PEDOT:PSS deposited on elastomer, it can be fully encapsulated in the elastomer. Our laboratory previously showed that PEDOT:PSS treated with Capstone

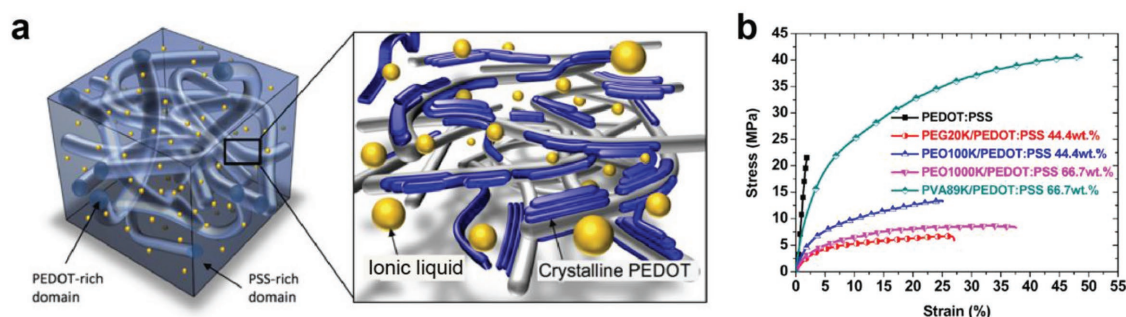


Figure 3. Enhancing the stretchability of PEDOT:PSS by blending with a) ionic liquid plasticizers. Adapted with permission from CC BY-NC 4.0 license.^[82] b) PEG, PEO, or PVA polymers. Reproduced with permission.^[84] Copyright 2015, American Chemical Society.

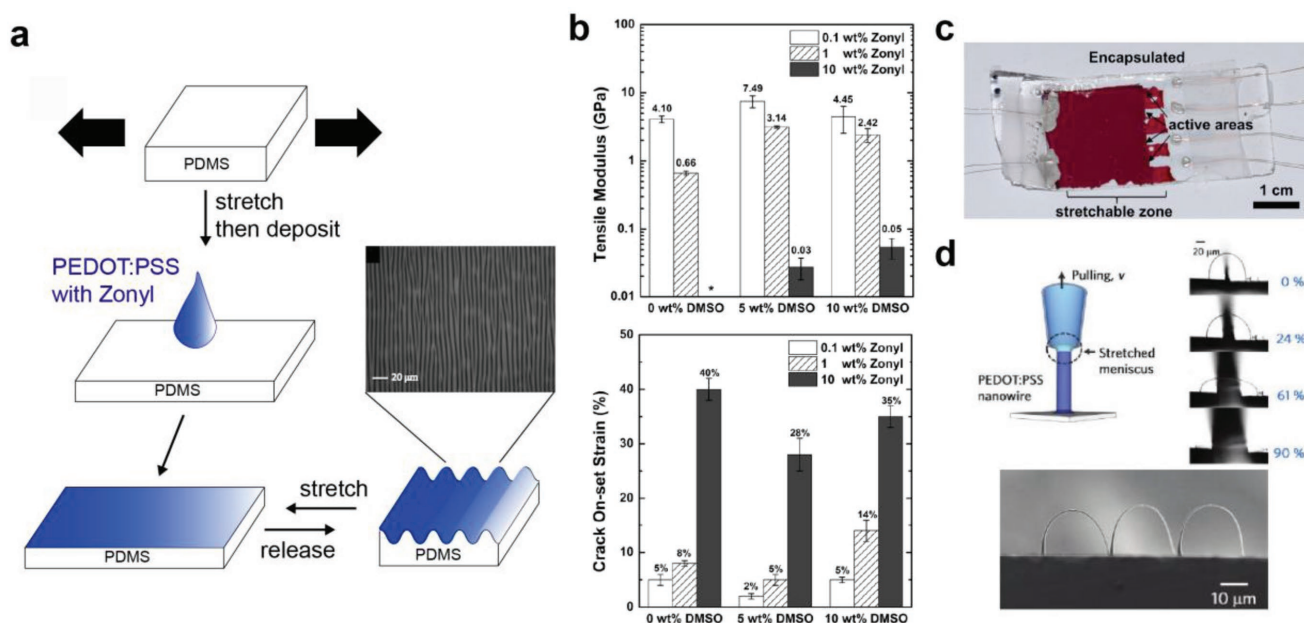


Figure 4. Physical approaches toward stretchable PEDOT. a) Fabrication scheme for stretchable PEDOT:PSS on PDMS by buckling and optical microscopy image of buckled PEDOT:PSS on PDMS. Microscopy image reproduced with permission.^[97] Copyright 2011, John Wiley and Sons. b) Effect of Zonyl concentration on the tensile modulus and crack onset strain of PEDOT:PSS on PDMS using the buckling method. Reproduced with permission.^[44] Copyright 2014, John Wiley and Sons. c) PUR-encapsulated solar cell with PEDOT:PSS electrodes. Reproduced with permission.^[105] Copyright 2016, Elsevier. d) Fabrication and images of 3D PEDOT:PSS nanowires. Reproduced with permission.^[114] Copyright 2012, American Chemical Society.

FS-30—a surfactant equivalent to Zonyl—and stretched up to 50% had shorter cracks ($43 \pm 4 \mu\text{m}$) when encapsulated in polyurethane compared to when only deposited on polyurethane ($89 \pm 10 \mu\text{m}$).^[105] Although the crack onsets are similar, the encapsulation led to shortened cracks and therefore greater retention in conductivity. Encapsulation reduces local strain around defects in the film by encouraging a more even distribution of strain and thus reduces the propagation of cracks. This strategy was used to prepare organic solar cells in which every component was stretchable (Figure 4c). A similar strategy was used by Fan et al. to generate a sensitive and durable strain sensor.^[106] In this device, PEDOT:PSS was incorporated between PVA and PDMS elastomers and strained reversibly up to 30% despite the rapid formation of cracks in the conductive layer.

4.3. Out-of-Plane Buckling

To reduce the cracking of PEDOT:PSS on elastomers, the substrate can be prestrained before deposition. Upon release, films of PEDOT:PSS on elastomers form an out-of-plane wavy pattern on the substrate (the buckling instability, Figure 4a). This effect was first used as a means to measure the mechanical properties of thin films but was later exploited for fabricating a reversibly stretchable organic solar cell with a PEDOT:PSS electrode on PDMS.^[97,107] This strategy was applied to generate stretchable PEDOT:PSS on PET^[108] and hydrogels.^[109] Murtoza et al. used a similar approach containing molded structures for strain relief, such as microridges and trenches.^[110,111]

4.4. In-Plane Serpentes

Hard and rigid materials can be deposited in serpentine patterns on an elastomeric substrate, which allows stretching of the conductive traces with minimal loss in performance. The wavy pattern, instead of a straight line, accommodates strain by rotating in-plane and buckling out-of-plane. This patterning strategy has been applied to patterned PEDOT:PSS on elastomers. Bhandodkar et al. have printed in-plane serpentine interconnects of PEDOT:PSS and Zonyl on PDMS for stretchable electrochemical tattoo-like sensors.^[112] The devices were able to withstand 100% linear strain with negligible loss in electrochemical performance.

4.5. PEDOT:PSS Nanowires, Nanofibers, and Nanotubes

Another strategy to obtain stretchable architectures is to use 1D nanostructures, i.e., nanowires and nanofibers. For a detailed review of strategies to obtain stretchable electronics with conjugated polymers, including with PEDOT:PSS, using 1D nanomaterials, see Lee et al.^[113] Highlights of these strategies include the 3D writing by Kim et al. of single PEDOT:PSS nanoarches (Figure 4d).^[114] The out-of-plane bending motions of the nanowires permit stretching up to 270% strain without any loss in conductivity. Networks of PEDOT:PSS nanofibers can be obtained via electrospinning, however polymeric additives (e.g., PVA) need to be added to enhance binding and to enable the electrospinning process. Such additives resulted in lower conductivities. Alternatively, nanofibers (diameter $\approx 700 \text{ nm}$) of PEDOT:tosylate were obtained by electrospinning an oxidant on

PDMS, followed by vapor phase polymerization of PEDOT.^[115] This method generated a conductive fiber mat on PDMS which could then be stretched up to 140%. Wider PEDOT:PSS fibers can be wet-spun directly from a concentrated solution. This strategy was used by Wang et al. to obtain highly conductive (1770 S cm^{-1}) fibers of PEDOT:PSS after treatment with sulfuric acid.^[116] These fibers, although only intrinsically stretchable up to 23%, could be coiled into spring-like shapes and then stretched up to 400%. Conductive nanotubes of PEDOT can be obtained in a multistep procedure. Abidian et al. used electrospun nanofibers of biodegradable poly(L-lactide) (PLLA) as a template for the electrodeposition of PEDOT.^[117] After the degradation of the PLLA core, PEDOT nanotubes remained. These materials proved efficient as electrode coatings for neural recordings, but their mechanical properties were not determined.

4.6. Conductive Textiles and Fibers

The possibility to obtain conductive fibers has led to the development of conductive textiles for wearable electronics. Applications for electronic textiles (e-textiles) include wearable energy harvesting devices, transistors, memory devices, chemical sensors, and displays.^[49,50,118] The stretchability of a textile derives from two factors: the deformability of the knit or weave pattern,

the intrinsic deformability of the fibers, or both. Several methods have been envisioned to incorporate PEDOT or PEDOT:PSS into textiles. One of the simplest methods is to coat the fibers or the fabric with PEDOT:PSS by immersion or printing and is applicable to textiles such as woven spandex^[119] and nylon (pantyhose),^[58] and nonwoven polyurethane fibers.^[120] Ding et al. showed that the “hard” PEDOT:PSS coating rapidly failed when stretched past 10%, leading to an increase in resistance particularly noticeable in the first cycle of stretching, but the fabric still maintained its conductivity over several cycles.^[120] To increase the stretchability of PEDOT:PSS, it can be blended with PUR before deposition on the fabric. Increased deformability, however, came at the expense of conductivity.^[121] Interfacial energies play a critical role when patterning PEDOT:PSS on textile substrates. Hydrophilic substrates (e.g., linen) will readily absorb aqueous PEDOT:PSS, hence leading to a blurry pattern when printed. Kye et al. addressed this problem by adding graphene oxide to a blend of PEDOT:PSS:PUR to increase the viscosity and conductivity, and decrease the wettability.^[121] Alternatively, stretchable fibers of PEDOT:PSS:PUR were obtained by Seyedin et al. by fiber spinning the composite and subsequently knitting them with or without spandex.^[122] Finally, PEDOT can be polymerized directly onto various fibers and fabrics using oxidative chemical vapor deposition (o-CVD) (Figure 5a).^[123,124] This method allows for the conformable and uniform coating of PEDOT (Figure 5b,c) on various substrates (viscose, polyester,

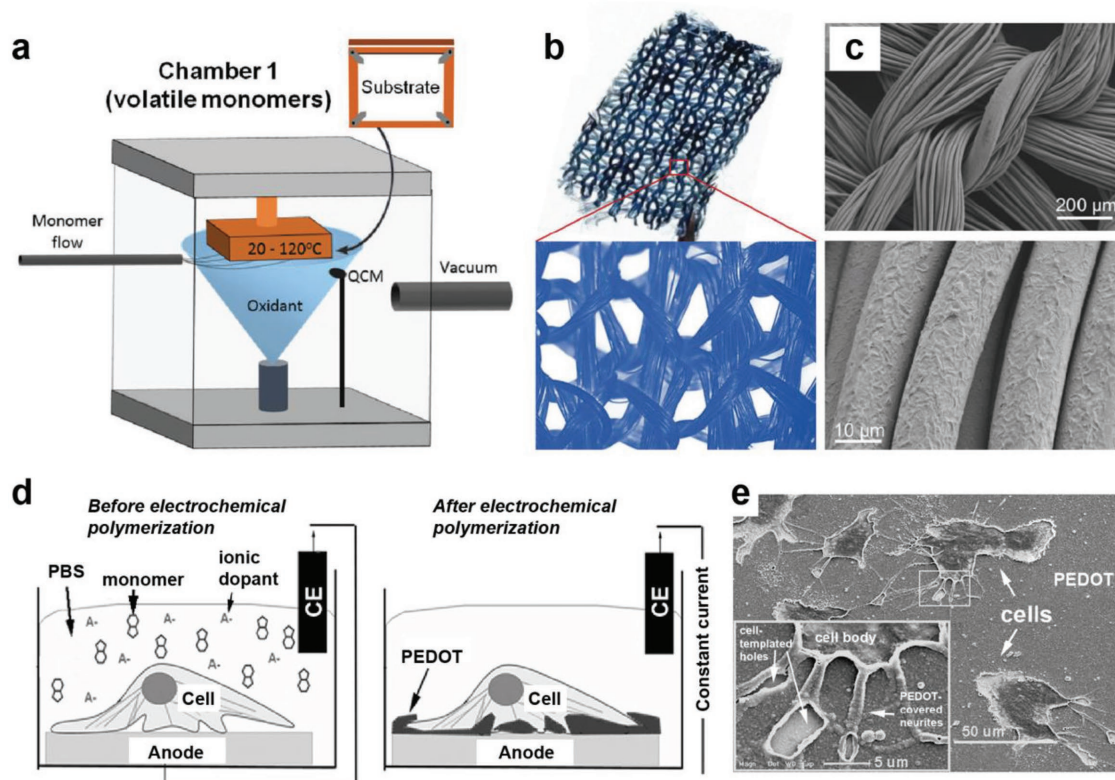


Figure 5. Deposition of PEDOT on textiles and around living cells. a) Schematic of a chemical vapor deposition chamber. b) Picture (top) and optical microscope image (bottom) of a PEDOT-coated woven linen textile. c) SEM images of fibers coated with PEDOT using o-CVD. d) Schematic of the electrochemical polymerization of PEDOT around living neural cells cultured on an electrode. e) Scanning electron microscopy (SEM) images of the neural cells after the electrochemical polymerization of PEDOT. Images in (a)–(c) reproduced with permission.^[123] Copyright 2017, Royal Society of Chemistry. Images in (d) and (e) reproduced with permission.^[127] Copyright 2007, IOP Publishing.

wool, silk, linen, cotton, rayon) regardless of their surface roughness, chemical composition, and surface energy, and was proved feasible on large-area flexible substrates.^[125] Additionally, because only a thin layer of “hard” PEDOT is deposited on the substrate, the mechanical properties are mainly dominated by the substrate, and the fabric maintains the breathability, flexibility, and perceived texture by the wearer while having a conductivity around 300 S cm^{-1} . This method was also able to generate conductive fabrics that are resistant to cold laundering and dry ironing; anticipation of such insults to which materials are exposed in the real world is critical to the development of e-textiles.

4.7. Electropolymerization of PEDOT in Biological Settings

Conducting polymers have been coated on metal electrodes to reduce the impedance, increase the charge injection capacity, and provide a softer interface with biological tissues to reduce the mechanical mismatch with metallic electrodes.^[126] Toward these goals, Martin and co-workers have developed a technique for the electropolymerization of PEDOT on metallic electrodes directly in the presence of living neural cells and tissues (Figure 5d,e).^[127] Using this technique, PEDOT is in close contact with the biological tissues and the electrodes. The authors showed that 50% of the cells exposed to EDOT (0.1 M) remained viable after 72 h and that the neurons were still intact 3 h after the electropolymerization. This strategy proved applicable to the in situ injection of electrodes within individual peripheral nerves.^[128]

5. Hydrogels Based on PEDOT:PSS and PEDOT

Conductive hydrogels have attracted attention for biointegrated applications due to their high mechanical compliance (<100 kPa), which is extraordinary even in the context of the field of stretchable electronics. The large deformability of hydrogels is due to the high content of water. Conductive hydrogels have been particularly used to lower the impedance of electrodes in neural interfaces and for tissue engineering. Several reviews and book chapter already describe the preparation and applications of conductive hydrogels including those based on PEDOT,^[129–133] and nanostructured conductive hydrogels.^[134,135] Different routes have been envisioned to form nanostructured conductive hydrogels. The first and most common method involves the crosslinking of the hydrogel, followed by drying and reswelling in a solution containing the conjugated polymer monomer. The monomer is subsequently polymerized by oxidative polymerization either electrically, by applying a voltage, or electrochemically, using a chemical oxidant. Second, the surface area of the conductive polymer hydrogel can be increased by nano- or microtemplating the formation of the hydrogel, then polymerizing the conductive polymer around the hydrogel after removal of the template. While attractive to precisely control the morphology and structure, this method is difficult to scale up due to the small size of the template. Finally, the hydrogel formation and polymerization of the conductive polymer can be performed simultaneously or in

a two-step process by having all the precursors mixed in the same vessel.

5.1. Ionically Crosslinked PEDOT:PSS Hydrogels

Hydrogels can be formed directly from PEDOT:PSS, simply by the addition of ions. In 1998, Ghosh et al. showed that the addition of Mg^{2+} ions induces the gelation of PEDOT:PSS in a poly(vinylpyrrolidone) matrix by ionically crosslinking the negatively charged PSS with positive ions.^[136] This electrostatic effect on the phase behavior of PEDOT:PSS was later studied in detail by Leaf and Muthukumar.^[137] Different types of additives have been shown to induce gelation of PEDOT:PSS including Ca^{2+} , $\text{Fe}^{2+/3+}$, $\text{Ru}^{2+/3+}$, ionic liquids, and sulfuric acid.^[138–140] The hydrogel treated with sulfuric acid showed the highest conductivity (880 S m^{-1}) at extremely low solid content (4 wt%).^[140] The mechanical properties of the hydrated hydrogel were not reported but air-dried fibers had a Young's modulus of 6.5 GPa, fail at 14.6% strain, and had a conductivity of $8 \times 10^4 \text{ S m}^{-1}$. When fully hydrated, however, ionically crosslinked PEDOT:PSS hydrogels are typically very weak and difficult to handle.

5.2. Double Network Hydrogels

To increase the toughness of conductive hydrogels, PEDOT:PSS or PEDOT can be incorporated in a nonconductive hydrogel, forming an interpenetrating network (IPN) or double network hydrogel.^[141–143] This strategy leads to tougher conductive hydrogels which could be strained past 50% but have a lower conductivity (typically between 10^{-3} and 10 S m^{-1}). Recently, Feig et al. reported a more conductive ($>10 \text{ S m}^{-1}$) IPN hydrogel by first ionically crosslinking PEDOT:PSS with an ionic liquid followed by polymerization of crosslinked polyacrylic acid.^[144] This IPN allowed for high mechanical stability and strength while maintaining good conductivity. An interesting variant of the double network hydrogels involved the use a dynamic assembly process to enable healing.^[145] Wu et al. reported the synthesis of a thermoplastic PEDOT:PSS IPN with a supramolecularly crosslinked polymer which healed at 90°C (Figure 6a). This material showed good conductivity ($\approx 1 \text{ S m}^{-1}$) and high stretchability (up to 1300%) and could be 3D-printed by melt extrusion.^[146] Another example by Zhang and co-workers uses PEG-functionalized positively charged peptides to form an injectable self-assembled hydrogel in the presence of PEDOT:PSS. The hydrogel rapidly healed below 37°C and supported the adhesion, survival, and growth of mesenchymal stromal cells.^[147] The development of biocompatible (and biodegradable) conductive hydrogels is crucial to the study of cells and biointegrated electronics. While PEDOT:PSS has been shown to be biocompatible, most efforts have been directed toward its integration in bioderived hydrogels such as gelatin (GelMA),^[148] crosslinked silk fibroin,^[149] poly- γ -glutamic acid crosslinked with cystamine,^[150] and carboxymethyl chitosan.^[151] These materials, although they showed good biocompatibility in vitro, could trigger the formation of scar tissue when implanted due to inflammatory responses.^[67] The long-term stability

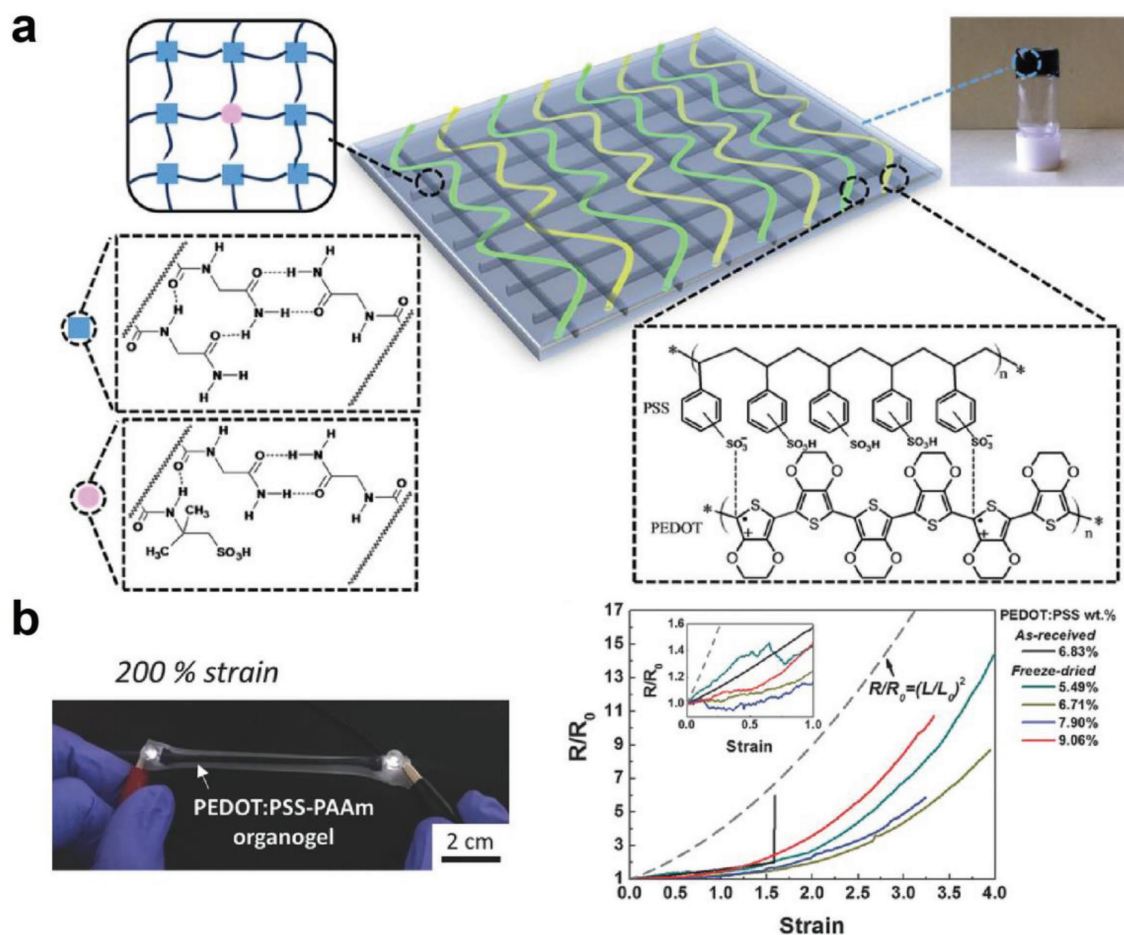


Figure 6. Examples of conductive gels with PEDOT:PSS. a) Thermoprocessible supramolecular PEDOT:PSS hydrogel with self-healing properties. Reproduced with permission from CC-BY 4.0 open access license.^[146] b) PEDOT:PSS-PAAm (polyacrylamide) organogel with low sensitivity to strain. Reproduced with permission.^[154] Copyright 2015, John Wiley and Sons.

and performance in vivo of conductive hydrogel implants still remain a challenge.

5.3. Hydrogels from Functionalized EDOT, Organogels, and Aerogels

An alternative approach to conductive hydrogels is by the crosslinking of PEDOT bearing carboxylic acids and methacrylamide functional groups (f-PEDOT) with PEG-diacrylate and acrylic acid.^[152,153] This approach, while requiring a longer synthetic sequence than for the IPN, allowed anchoring of the conductive polymer in the hydrogel to prevent leaching of the polymer during swelling. The presence of water and ions in solution is beneficial for applications in bioelectronics since the devices operate in a wet environment and rely on both electronic and ionic conductivities. For applications which require a DC current or when devices must operate in a dry environment, however, hydrogels are not suitable. The water content—which can rapidly decrease when the hydrogel is not immersed—affects greatly the mechanical and electronic properties of the hydrogel. Moreover, the application of a DC current, even at low voltage, can induce electrochemical

reactions and therefore is limited by the electrochemical window of the electrolyte. To circumvent these issues, Lee et al. reported the synthesis of a PEDOT:PSS/acrylamide (PEDOT:PSS-PAAm) organogel (Figure 6b).^[154] The organogel did not contain residual mobile ions and used glycerol—a high boiling solvent—as an alternative to water. It could be stretched up to 400% and its conductivity showed minimal sensitivity to strain even when repeatedly stretched to 50%, with an initial conductivity of 1 S m^{-1} . The use of solvent can be avoided altogether by using aerogels. These lightweight, porous materials can be formed from PEDOT:PSS directly, however, they are very brittle.^[90] To increase the stretchability, Crispin and co-workers used a blend of PEDOT:PSS, cellulose nanofibrils, and glycidoxypyl trimethoxysilane (GOPS, a common crosslinker for PEDOT:PSS) and obtained aerogels with good conductivity ($\approx 10 \text{ S m}^{-1}$) that sustained up to 90% compression.^[155]

6. Elastomeric Polymer Matrices for PEDOT

Another commonly used strategy to obtain stretchable PEDOT is to polymerize it directly in an elastomeric matrix in the presence of small molecule oxidant and dopant such as

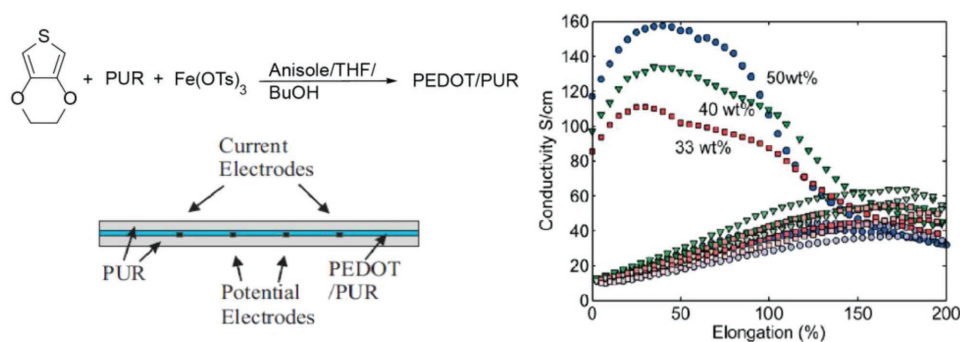


Figure 7. In situ polymerization of PEDOT in polyurethane (PUR) and conductivity versus strain of PEDOT/PUR. Reproduced with permission.^[156] Copyright 2007, John Wiley and Sons.

Fe(III) tosylate ($\text{Fe}(\text{OTs})_3$) (Figure 7). This procedure was first developed by Hansen et al. with elastomeric PURs to obtain conductive elastomers with a conductivity up to 160 S cm^{-1} and stretchability up to 200%.^[156] It has since been used to obtain stretchable conductive materials on hydrogels for tissue engineering^[63] and electrochromic displays,^[38] or embedded in PDMS for stretchable interconnects.^[157] This strategy, although efficient, generates relatively thick films from organic solvents and cannot be processed in the same way as PEDOT:PSS, which is water-soluble: it requires post-casting polymerization and purification—typically boiling the film in water—to remove excess oxidant and monomer. Moreover, it relies on mobile small molecule dopants (tosylate) which could leach out and deteriorate the material under certain conditions. Alternatively, a polymeric dopant, a polyionic liquid (PIL), has been used, which also enhanced the compatibility of PEDOT:PIL with hydrophobic elastomers.^[158] The PEDOT:PIL/PEEA (poly(ether-*b*-ester)) blend was processed as a paste in propylene carbonate to obtain stretchable materials (up to 350%) but suffered from a high surface resistivity ($4 \times 10^8 \Omega \text{ sq}^{-1}$).

7. Intrinsically Stretchable Polymeric Matrix and Dopant – PSS Block Copolymer

We recently reported the use of a PSS-based block copolymer to achieve stretchable PEDOT:PSS (Figure 8).^[159] A block copolymer comprised of “hard” PSS and “soft” poly(polyethylene glycol methyl ether acrylate) (PPEGMEA) was synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization (Figure 8a). PSS-*b*-PPEGMEA acted simultaneously as a stretchable matrix for PEDOT as well as a stabilizer for doped PEDOT. PEDOT:PSS-*b*-PPEGMEA offers several advantages: it did not require additional additives (dopants or plasticizers), could be processed in water, and had a lower Young's modulus ($\approx 41 \text{ MPa}$) than PEDOT:PSS ($\approx 280 \text{ MPa}$). When compared to PEDOT:PSS and a blend of PEDOT:PSS with PPEGMEA, the block copolymer exhibited a higher toughness (up to 10.1 MJ m^{-3}) and stretchability (up to 128%) (Figure 8b–d). Although the conductivity of the block copolymer was reduced, this approach provides a new pathway toward stretchable organic conductors.

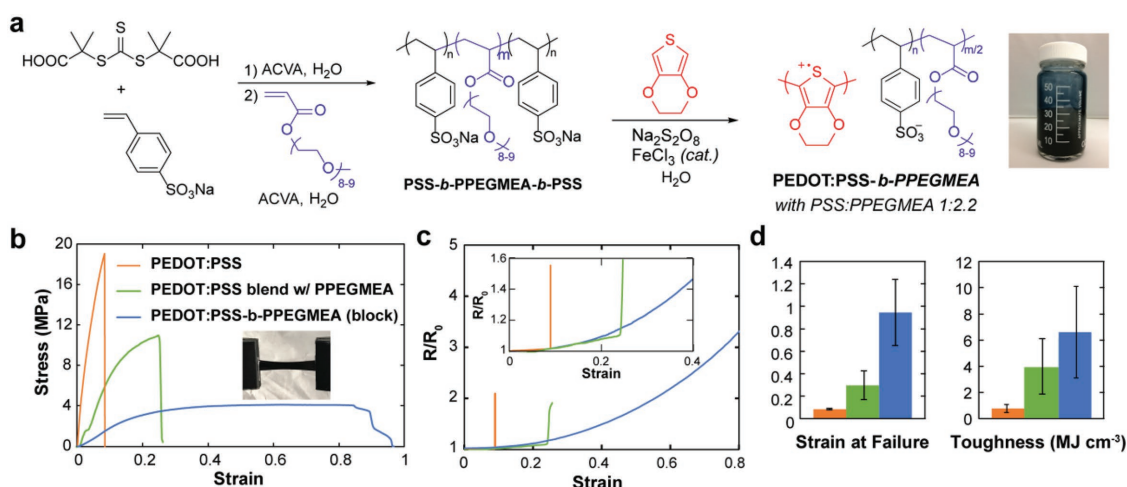


Figure 8. Intrinsically stretchable PSS-*b*-PPEGMEA block copolymer matrix for PEDOT. a) Synthesis via RAFT polymerization of the block copolymer followed by oxidative polymerization of PEDOT. b) Stress–strain curves of PEDOT:PSS (orange), PEDOT:PSS blend w/ PPEGMEA (green), and PEDOT:PSS-*b*-PPEGMEA (blue). c) Change in resistance versus strain. d) Strain at failure and toughness. Adapted with permission.^[159] Copyright 2018, American Chemical Society.

8. Conclusions and Outlook

Several innovative approaches have been proposed to address the stiffness and brittleness of PEDOT and PEDOT:PSS in their native forms. These methods include the use of physical approaches such as the patterning of strain-relief microstructures or embedding in stretchable matrices, the development of conductive hydrogels and textiles, and the synthesis of intrinsically stretchable molecular scaffolds. Nevertheless, there are several challenges that remain to be addressed. 1) There is currently no technique to obtain high conductivity and stretchable PEDOT without using small molecule additives. 2) Nonhydrogel-based PEDOT will need to have a larger elastic range for a truly reversible stretchability. 3) The effects of humidity, temperature, stretching rate, and morphology should be taken into account when studying the mechanical and electronic properties of new stretchable materials. In particular, experimental conditions need to be precisely defined, and reporting the “stretchability” simply as an engineering strain should not be used as a substitute for the mechanical properties (especially modulus, toughness, and strength, when it is possible to measure these quantities). Time-dependent mechanical properties of π -conjugated materials, including PEDOT and its derivatives, have received limited attention. 4) Finally, applications which require direct contact with biological systems should be tested for toxicity, biocompatibility, biodegradability, and in some cases stability in vivo.

This progress report highlights the need and interest for stretchable conductive materials for applications in wearable and implantable electronics. The strategies that have been employed to enhance the stretchability of PEDOT and PEDOT:PSS could be used to design new types of organic electronics which combine high conductivity and mechanical compliance. We anticipate that the development of new stretchable conductors will lead to discoveries in neuroscience, will offer new wearable and implantable biosensing platforms, and will provide solution-processable and transportable energy alternatives.

Acknowledgements

This work was supported by the National Institutes of Health Director's New Innovator Award under Grant No. 1DP2EB022358. Some of the original work by the authors' laboratory cited in this article was supported by the Air Force Office of Scientific Research, Grant Number FA9550-16-1-0220.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioelectronics, conductive hydrogels, conductive textiles, PEDOT:PSS, stretchable electronics

Received: September 20, 2018

Revised: October 23, 2018

Published online:

- [1] A. Elschner, S. Kirchmeyer, W. Lovenich, U. Merker, K. Reuter, *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*, CRC Press, Boca Raton, FL **2010**.
- [2] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481.
- [3] S. Kirchmeyer, K. Reuter, *J. Mater. Chem.* **2005**, *15*, 2077.
- [4] H. Shi, C. Liu, Q. Jiang, J. Xu, *Adv. Electron. Mater.* **2015**, *1*, 1500017.
- [5] W. Yangping, X. Jingkun, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 1121.
- [6] J. Zhao, Z. Chi, Z. Yang, X. Chen, M. S. Arnold, Y. Zhang, J. Xu, Z. Chi, M. P. Aldred, *Nanoscale* **2018**, *10*, 5764.
- [7] S. E. Root, S. Savagatrup, A. D. Printz, D. Rodriguez, D. J. Lipomi, *Chem. Rev.* **2017**, *117*, 6467.
- [8] D. J. Lipomi, Z. Bao, *MRS Bull.* **2017**, *42*, 93.
- [9] T. Q. Trung, N. E. Lee, *Adv. Mater.* **2017**, *29*, 1603167.
- [10] D. J. Lipomi, *Adv. Mater.* **2016**, *28*, 4180.
- [11] T. Sekitani, T. Someya, *Adv. Mater.* **2010**, *22*, 2228.
- [12] K. J. Yu, Z. Yan, M. Han, J. A. Rogers, *npj Flexible Electron.* **2017**, *1*, 4.
- [13] S. Yao, Y. Zhu, *Adv. Mater.* **2015**, *27*, 1480.
- [14] S. Inal, J. Rivnay, A.-O. Sui, G. G. Malliaras, I. McCulloch, *Acc. Chem. Res.* **2018**, *51*, 1368.
- [15] G. J. N. Wang, A. Gasperini, Z. Bao, *Adv. Electron. Mater.* **2018**, *4*, 1700429.
- [16] Y. Qian, X. Zhang, L. Xie, D. Qi, B. K. Chandran, X. Chen, W. Huang, *Adv. Mater.* **2016**, *28*, 9243.
- [17] A. K. Sen, S. Roy, V. A. Juvekar, *Polym. Int.* **2007**, *56*, 167.
- [18] J. Rivnay, S. Inal, B. A. Collins, M. Sessolo, E. Stavridou, X. Strakosas, C. Tassone, D. M. Delongchamp, G. G. Malliaras, *Nat. Commun.* **2016**, *7*, 11287.
- [19] U. Lang, E. Müller, N. Naujoks, J. Dual, *Adv. Funct. Mater.* **2009**, *19*, 1215.
- [20] A. Aleshin, R. Kiebooms, R. Menon, F. Wudl, A. J. Heeger, *Phys. Rev. B* **1997**, *56*, 3659.
- [21] R. Kiebooms, A. Aleshin, K. Hutchison, F. Wudl, A. Heeger, *Synth. Met.* **1999**, *101*, 436.
- [22] L. Stepien, A. Roch, R. Tkachov, B. Leupolt, L. Han, N. van Ngo, C. Leyens, *Synth. Met.* **2017**, *225*, 49.
- [23] J. Liu, X. Wang, D. Li, N. E. Coates, R. A. Segalman, D. G. Cahill, *Macromolecules* **2015**, *48*, 585.
- [24] E. Vitoratos, S. Sakkopoulos, E. Dalas, N. Paliatsas, D. Karageorgopoulos, F. Petraki, S. Kennou, S. A. Choulis, *Org. Electron.* **2009**, *10*, 61.
- [25] E. Vitoratos, S. Sakkopoulos, N. Paliatsas, K. Emmanouil, S. A. Choulis, *Open J. Org. Polym. Mater.* **2012**, *2*, 5.
- [26] J. Huang, P. F. Miller, J. C. de Mello, A. J. de Mello, D. D. C. Bradley, *Synth. Met.* **2003**, *139*, 569.
- [27] A. M. Nardes, M. Kemerink, M. M. de Kok, E. Vinken, K. Maturova, R. A. J. Janssen, *Org. Electron.* **2008**, *9*, 727.
- [28] G. H. Kim, L. Shao, K. Zhang, K. P. Pipe, *Nat. Mater.* **2013**, *12*, 719.
- [29] J. Chung, K.-H. Kim, J. C. Lee, M. K. Kim, H. J. Shin, *Org. Electron.* **2008**, *9*, 869.
- [30] Y. Kim, A. M. Ballantyne, J. Nelson, D. D. C. Bradley, *Org. Electron.* **2009**, *10*, 205.
- [31] M. Girtan, M. Rusu, *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 446.
- [32] F. Zhang, M. Johansson, M. R. Andersson, J. C. Hummelen, O. Inganäs, *Adv. Mater.* **2002**, *14*, 662.
- [33] T. F. O'Connor, A. V. Zaretski, S. Savagatrup, A. D. Printz, C. D. Wilkes, M. I. Diaz, E. J. Sawyer, D. J. Lipomi, *Sol. Energy Mater. Sol. Cells* **2016**, *144*, 438.

- [34] Z. Li, G. Ma, R. Ge, F. Qin, X. Dong, W. Meng, T. Liu, J. Tong, F. Jiang, Y. Zhou, K. Li, X. Min, K. Huo, Y. Zhou, *Angew. Chem., Int. Ed.* **2016**, 55, 979.
- [35] S. Gouse Peera, K. K. Tintula, A. K. Sahu, S. Shanmugam, P. Sridhar, S. Pitchumani, *Electrochim. Acta* **2013**, 108, 95.
- [36] A. S. M. I. Uddin, U. Yaqoob, G.-S. Chung, *ACS Appl. Mater. Interfaces* **2016**, 8, 30079.
- [37] J. Jo, I. Oh, M.-J. Jin, J. Park, J. S. Son, K.-S. An, J.-W. Yoo, *Org. Electron.* **2017**, 50, 367.
- [38] H. Kai, W. Suda, Y. Ogawa, K. Nagamine, M. Nishizawa, *ACS Appl. Mater. Interfaces* **2017**, 9, 19513.
- [39] M. S. White, M. Kaltenbrunner, E. D. Głowacki, K. Gutnichenko, G. Kettlgruber, I. Graz, S. Aazou, C. Ulbricht, D. A. M. Egbe, M. C. Miron, Z. Major, M. C. Scharber, T. Sekitani, T. Someya, S. Bauer, N. S. Sariciftci, *Nat. Photonics* **2013**, 7, 811.
- [40] K. Sun, S. Zhang, P. Li, Y. Xia, X. Zhang, D. Du, F. H. Isikgor, J. Ouyang, *J. Mater. Sci.: Mater. Electron.* **2015**, 26, 4438.
- [41] M. Bharti, A. Singh, S. Samanta, D. K. Aswal, *Prog. Mater. Sci.* **2018**, 93, 270.
- [42] J. G. Ibanez, M. E. Rincón, S. Gutierrez-Granados, M. h. Chahma, O. A. Jaramillo-Quintero, B. A. Frontana-Urbe, *Chem. Rev.* **2018**, 118, 4731.
- [43] D. Chen, Q. Pei, *Chem. Rev.* **2017**, 117, 11239.
- [44] S. Savagatrup, E. Chan, S. M. Renteria-Garcia, A. D. Printz, A. V. Zaretski, T. F. O'Connor, D. Rodriguez, E. Valle, D. J. Lipomi, *Adv. Funct. Mater.* **2015**, 25, 427.
- [45] B. Mazzolai, V. Mattoli, L. Beccai, E. Sinibaldi, in *Bioinspired Approaches for Human-Centric Technologies* (Ed: R. Cingolani), Springer, Berlin **2014**, p. 111.
- [46] J. Wang, M.-F. Lin, S. Park, P. S. Lee, *Mater. Today* **2018**, 21, 508.
- [47] P. J. Taroni, G. Santagiuliana, K. Wan, P. Calado, M. Qiu, H. Zhang, N. M. Pugno, M. Palma, N. Stingelin-Stutzman, M. Heeney, O. Fenwick, M. Baxendale, E. Bilotti, *Adv. Funct. Mater.* **2018**, 28, 1704285.
- [48] F. Zhang, Y. Zhang, D. Huang, C.-a. Di, D. Zhu, *Nat. Commun.* **2015**, 6, 8356.
- [49] A. Lund, N. M. van der Velden, N.-K. Persson, M. M. Hamed, C. Müller, *Mater. Sci. Eng., R* **2018**, 126, 1.
- [50] J. S. Heo, J. Eom, Y.-H. Kim, S. K. Park, *Small* **2018**, 14, 1703034.
- [51] R. T. Hassarati, J. A. Goding, S. Baek, A. J. Patton, L. A. Poole-Warren, R. A. Green, *J. Polym. Sci., Part B: Polym. Phys.* **2014**, 52, 666.
- [52] D. Prodanov, J. Delbeke, *Front. Neurosci.* **2016**, 10, 11.
- [53] R. M. Miriani, M. R. Abidian, D. R. Kipke, in *30th Annual Int. Conf. of the IEEE Engineering in Medicine and Biology Society*, IEEE, Piscataway, NJ **2008**.
- [54] S. Inal, G. G. Malliaras, J. Rivnay, *Nat. Commun.* **2017**, 8, 1767.
- [55] X. T. Cui, D. D. Zhou, *IEEE Trans. Neural Syst. Rehabil. Eng.* **2007**, 15, 502.
- [56] S.-C. Luo, E. Mohamed Ali, N. C. Tansil, H.-h. Yu, S. Gao, E. A. B. Kantchev, J. Y. Ying, *Langmuir* **2008**, 24, 8071.
- [57] Kenry, B. Liu, *Biomacromolecules* **2018**, 19, 1783.
- [58] E. Bihar, T. Roberts, E. Ismailova, M. Saadaoui, M. Isik, A. Sanchez-Sanchez, D. Mecerreyes, T. Hervé, J. B. De Graaf, G. G. Malliaras, *Adv. Mater. Technol.* **2017**, 2, 1600251.
- [59] Kenry, J. C. Yeo, C. T. Lim, *Microsyst. Nanoeng.* **2016**, 2, 16043.
- [60] J. Isaksson, P. Kjäll, D. Nilsson, N. Robinson, M. Berggren, A. Richter-Dahlfors, *Nat. Mater.* **2007**, 6, 673.
- [61] J. Rivnay, S. Inal, A. Salleo, R. M. Owens, M. Berggren, G. G. Malliaras, *Nat. Rev. Mater.* **2018**, 3, 17086.
- [62] B. Guo, P. X. Ma, *Biomacromolecules* **2018**, 19, 1764.
- [63] M. Sasaki, B. C. Karikkineth, K. Nagamine, H. Kaji, K. Torimitsu, M. Nishizawa, *Adv. Healthcare Mater.* **2014**, 3, 1919.
- [64] I. Bernardeschi, F. Greco, G. Ciofani, A. Marino, V. Mattoli, B. Mazzolai, L. Beccai, *Biomed. Microdevices* **2015**, 17, 46.
- [65] J. A. Goding, A. D. Gilmour, U. A. Aregueta-Robles, E. A. Hasan, R. A. Green, *Adv. Funct. Mater.* **2018**, 28, 1702969.
- [66] A. J. Shoffstall, J. R. Capadona, *Curr. Opin. Biomed. Eng.* **2018**, 6, 110.
- [67] R. Green, M. R. Abidian, *Adv. Mater.* **2015**, 27, 7620.
- [68] M. R. Abidian, D. C. Martin, *Adv. Funct. Mater.* **2009**, 19, 573.
- [69] D. T. Simon, S. Kurup, K. C. Larsson, R. Hori, K. Tybrandt, M. Gojny, E. W. H. Jager, M. Berggren, B. Canlon, A. Richter-Dahlfors, *Nat. Mater.* **2009**, 8, 742.
- [70] U. Lang, N. Naujoks, J. Dual, *Synth. Met.* **2009**, 159, 473.
- [71] J. Zhou, D. H. Anjum, L. Chen, X. Xu, I. A. Ventura, L. Jiang, G. Lubineau, *J. Mater. Chem. C* **2014**, 2, 9903.
- [72] J. M. G. Cowie, V. Arrighi, *Polymers: Chemistry and Physics of Modern Materials*, 3rd ed., CRC Press, Boca Raton, FL **2007**.
- [73] D. Tahk, H. H. Lee, D.-Y. Khang, *Macromolecules* **2009**, 42, 7079.
- [74] J. Yang, D. C. Martin, *J. Mater. Res.* **2006**, 21, 1124.
- [75] J. Qu, L. Ouyang, C.-c. Kuo, D. C. Martin, *Acta Biomater.* **2016**, 31, 114.
- [76] L. Yuechen, T. Ryo, O. Hidenori, *Smart Mater. Struct.* **2014**, 23, 074010.
- [77] S. Ichikawa, N. Toshima, *Polym. J.* **2015**, 47, 522.
- [78] J. Zhou, E. Q. Li, R. Li, X. Xu, I. A. Ventura, A. Moussawi, D. H. Anjum, M. N. Hedhili, D.-M. Smilgies, G. Lubineau, S. T. Thoroddsen, *J. Mater. Chem. C* **2015**, 3, 2528.
- [79] J. Y. Oh, S. Kim, H.-K. Baik, U. Jeong, *Adv. Mater.* **2016**, 28, 4455.
- [80] J. Y. Oh, M. Shin, J. B. Lee, J.-H. Ahn, H. K. Baik, U. Jeong, *ACS Appl. Mater. Interfaces* **2014**, 6, 6954.
- [81] M. Y. Teo, N. Kim, S. Kee, B. S. Kim, G. Kim, S. Hong, S. Jung, K. Lee, *ACS Appl. Mater. Interfaces* **2017**, 9, 819.
- [82] Y. Wang, C. Zhu, R. Pfattner, H. Yan, L. Jin, S. Chen, F. Molina-Lopez, F. Lissel, J. Liu, N. I. Rabiah, Z. Chen, J. W. Chung, C. Linder, M. F. Toney, B. Murmann, Z. Bao, *Sci. Adv.* **2017**, 3, e1602076.
- [83] K. S. Egorova, E. G. Gordeev, V. P. Ananikov, *Chem. Rev.* **2017**, 117, 7132.
- [84] P. Li, K. Sun, J. Ouyang, *ACS Appl. Mater. Interfaces* **2015**, 7, 18415.
- [85] J. H. Lee, Y. R. Jeong, G. Lee, S. W. Jin, Y. H. Lee, S. Y. Hong, H. Park, J. W. Kim, S.-S. Lee, J. S. Ha, *ACS Appl. Mater. Interfaces* **2018**, 10, 28027.
- [86] C.-h. Chen, A. Torrents, L. Kulinsky, R. D. Nelson, M. J. Madou, L. Valdevit, J. C. LaRue, *Synth. Met.* **2011**, 161, 2259.
- [87] C. Chwee-Lin, S. Mun-Bo, L. Byoung-Sun, J. Sanghun, K. Dong-Su, K. Tae-Hyung, B. Jihyun, L. S. Hoon, B. Kyung-Eun, I. Jungkyun, J. Y. Jin, P. C. Eon, P. Jong-Jin, C. U-In, *Adv. Mater.* **2014**, 26, 3451.
- [88] P. Li, D. Du, L. Guo, Y. Guo, J. Ouyang, *J. Mater. Chem. C* **2016**, 4, 6525.
- [89] M. Z. Seyedin, J. M. Razal, P. C. Innis, G. G. Wallace, *Adv. Funct. Mater.* **2014**, 24, 2957.
- [90] C. Teng, X. Lu, Y. Zhu, M. Wan, L. Jiang, *RSC Adv.* **2013**, 3, 7219.
- [91] J.-S. Noh, *RSC Adv.* **2014**, 4, 1857.
- [92] H.-E. Yin, C.-H. Wu, K.-S. Kuo, W.-Y. Chiu, H.-J. Tai, *J. Mater. Chem.* **2012**, 22, 3800.
- [93] D.-H. Kim, J. Xiao, J. Song, Y. Huang, J. A. Rogers, *Adv. Mater.* **2010**, 22, 2108.
- [94] T.-H. Kim, A. Carlson, J.-H. Ahn, S. M. Won, S. Wang, Y. Huang, J. A. Rogers, *Appl. Phys. Lett.* **2009**, 94, 113502.
- [95] B. Sarkar, D. K. Satapathy, M. Jaiswal, *Soft Matter* **2017**, 13, 5437.
- [96] I. M. Graz, D. P. J. Cotton, S. P. Lacour, *Appl. Phys. Lett.* **2009**, 94, 071902.
- [97] M. Vosgueritchian, D. J. Lipomi, Z. Bao, *Adv. Funct. Mater.* **2012**, 22, 421.
- [98] D. J. Lipomi, J. A. Lee, M. Vosgueritchian, B. C. K. Tee, J. A. Bolander, Z. Bao, *Chem. Mater.* **2012**, 24, 373.
- [99] F. Xi, X. Bingang, W. Naixiang, W. Jinzhao, L. Shenghua, W. Hao, Y. Feng, *Adv. Electron. Mater.* **2017**, 3, 1600471.

- [100] Z. Zhu, G. Yang, R. Li, T. Pan, *Microsyst. Nanoeng.* **2017**, 3, 17004.
- [101] N. Srivastava, V. Venugopalan, M. S. Divya, V. A. Rasheed, J. James, K. S. Narayan, *Tissue Eng., Part A* **2013**, 19, 1984.
- [102] V. Vijay, A. D. Rao, K. S. Narayan, *J. Appl. Phys.* **2011**, 109, 084525.
- [103] J. G. Tait, B. J. Worfolk, S. A. Maloney, T. C. Hauger, A. L. Elias, J. M. Buriak, K. D. Harris, *Sol. Energy Mater. Sol. Cells* **2013**, 110, 98.
- [104] L. Yoo-Yong, L. Ji-Hoon, C. Ju-Young, K. Na-Rae, N. Dae-Hyun, C. In-Suk, N. K. Tae, J. Young-Chang, *Adv. Funct. Mater.* **2013**, 23, 4020.
- [105] E. J. Sawyer, A. V. Zaretski, A. D. Printz, N. V. de los Santos, A. Bautista-Gutierrez, D. J. Lipomi, *Extreme Mech. Lett.* **2016**, 8, 78.
- [106] X. Fan, N. Wang, J. Wang, B. Xu, F. Yan, *Mater. Chem. Front.* **2018**, 2, 355.
- [107] D. J. Lipomi, B. C. K. Tee, M. Vosgueritchian, Z. Bao, *Adv. Mater.* **2011**, 23, 1771.
- [108] M. Drack, I. Graz, T. Sekitani, T. Someya, M. Kaltenbrunner, S. Bauer, *Adv. Mater.* **2015**, 27, 34.
- [109] S. Zhang, E. Hubis, G. Tomasello, G. Soliveri, P. Kumar, F. Ciccoira, *Chem. Mater.* **2017**, 29, 3126.
- [110] M. Mehdi, K. H. Cho, K. H. Choi, *J. Appl. Polym. Sci.* **2015**, 132, 41235.
- [111] M. S. Murtuza, J. Jeongda, D. Y. Hoi, D. H. Woo, C. K. Hyun, *J. Polym. Sci., Part B: Polym. Phys.* **2015**, 53, 226.
- [112] A. J. Bandodkar, R. Nuñez-Flores, W. Jia, J. Wang, *Adv. Mater.* **2015**, 27, 3060.
- [113] Y. Lee, H. Zhou, T.-W. Lee, *J. Mater. Chem. C* **2018**, 6, 3538.
- [114] J. T. Kim, J. Pyo, J. Rho, J.-H. Ahn, J. H. Je, G. Margaritondo, *ACS Macro Lett.* **2012**, 1, 375.
- [115] F. Boubée de Gramont, S. Zhang, G. Tomasello, P. Kumar, A. Sarkissian, F. Ciccoira, *Appl. Phys. Lett.* **2017**, 111, 093701.
- [116] Z. Wang, J. Cheng, Q. Guan, H. Huang, Y. Li, J. Zhou, W. Ni, B. Wang, S. He, H. Peng, *Nano Energy* **2018**, 45, 210.
- [117] M. R. Abidian, K. A. Ludwig, T. C. Marzullo, D. C. Martin, D. R. Kipke, *Adv. Mater.* **2009**, 21, 3764.
- [118] M. Tassarolo, I. Gualandi, B. Fraboni, *Adv. Mater. Technol.* **2018**, 3, 1700310.
- [119] Y. Ding, M. A. Invernale, G. A. Sotzing, *ACS Appl. Mater. Interfaces* **2010**, 2, 1588.
- [120] Y. Ding, W. Xu, W. Wang, H. Fong, Z. Zhu, *ACS Appl. Mater. Interfaces* **2017**, 9, 30014.
- [121] M. J. Kye, J. Cho, J. C. Yu, Y.-W. Chang, J. Han, E. Lee, H. S. Lim, J. A. Lim, *Dyes Pigm.* **2018**, 155, 150.
- [122] S. Seyedin, J. M. Razal, P. C. Innis, A. Jeiranikhameneh, S. Beirne, G. G. Wallace, *ACS Appl. Mater. Interfaces* **2015**, 7, 21150.
- [123] N. Cheng, L. Zhang, J. Joon Kim, T. L. Andrew, *J. Mater. Chem. C* **2017**, 5, 5787.
- [124] L. Zhang, M. Fairbanks, T. L. Andrew, *Adv. Funct. Mater.* **2017**, 27, 1700415.
- [125] P. Kovacic, G. d. Hierro, W. Livernois, K. K. Gleason, *Mater. Horiz.* **2015**, 2, 221.
- [126] M. Asplund, T. Nyberg, O. Inganäs, *Polym. Chem.* **2010**, 1, 1374.
- [127] S. M. Richardson-Burns, J. L. Hendricks, D. C. Martin, *J. Neural Eng.* **2007**, 4, L6.
- [128] J. M. Murbach, S. Currlin, A. Widener, Y. Tong, S. Chhatre, V. Subramanian, D. C. Martin, B. N. Johnson, K. J. Otto, *MRS Commun.* **2018**, 8, 1043.
- [129] D. Mawad, A. Lauto, G. G. Wallace, in *Polymeric Hydrogels as Smart Biomaterials* (Ed: S. Kalia), Springer International Publishing, Cham **2016**, p. 19.
- [130] R. A. Green, S. Baek, L. A. Poole-Warren, P. J. Martens, *Sci. Technol. Adv. Mater.* **2010**, 11, 014107.
- [131] A. Guiseppi-Elie, *Biomaterials* **2010**, 31, 2701.
- [132] U. A. Aregueta-Robles, A. J. Woolley, L. A. Poole-Warren, N. H. Lovell, R. A. Green, *Front. Neuroeng.* **2014**, 7, 15.
- [133] Y. Shi, J. Zhang, L. Pan, Y. Shi, G. Yu, *Nano Today* **2016**, 11, 738.
- [134] Y. Zhao, B. Liu, L. Pan, G. Yu, *Energy Environ. Sci.* **2013**, 6, 2856.
- [135] F. Zhao, Y. Shi, L. Pan, G. Yu, *Acc. Chem. Res.* **2017**, 50, 1734.
- [136] S. Ghosh, J. Rasmussen, O. Inganäs, *Adv. Mater.* **1998**, 10, 1097.
- [137] M. A. Leaf, M. Muthukumar, *Macromolecules* **2016**, 49, 4286.
- [138] M. Vázquez, P. Danielsson, J. Bobacka, A. Lewenstam, A. Ivaska, *Sens. Actuators, B* **2004**, 97, 182.
- [139] T. Dai, X. Jiang, S. Hua, X. Wang, Y. Lu, *Chem. Commun.* **2008**, 4279.
- [140] Y. Bowen, W. Haiyan, Z. Qinqin, W. Mingmao, Z. Miao, L. Chun, S. Gaoquan, *Adv. Mater.* **2017**, 29, 1700974.
- [141] T. Dai, X. Qing, H. Zhou, C. Shen, J. Wang, Y. Lu, *Synth. Met.* **2010**, 160, 791.
- [142] S. Naficy, J. M. Razal, G. M. Spinks, G. G. Wallace, P. G. Whitten, *Chem. Mater.* **2012**, 24, 3425.
- [143] J. Goding, A. Gilmour, P. Martens, L. Poole-Warren, R. Green, *Adv. Healthcare Mater.* **2017**, 6, 1601177.
- [144] V. R. Feig, H. Tran, M. Lee, Z. Bao, *Nat. Commun.* **2018**, 9, 2740.
- [145] S. Wang, G. Guo, X. Lu, S. Ji, G. Tan, L. Gao, *ACS Appl. Mater. Interfaces* **2018**, 10, 19133.
- [146] Q. Wu, J. Wei, B. Xu, X. Liu, H. Wang, W. Wang, Q. Wang, W. Liu, *Sci. Rep.* **2017**, 7, 41566.
- [147] Y. Xu, X. Yang, A. K. Thomas, P. A. Patsis, T. Kurth, M. Kräter, K. Eckert, M. Bornhäuser, Y. Zhang, *ACS Appl. Mater. Interfaces* **2018**, 10, 14418.
- [148] A. R. Spencer, A. Primbetova, A. N. Koppes, R. A. Koppes, H. Fenniri, N. Annabi, *ACS Biomater. Sci. Eng.* **2018**, 4, 1558.
- [149] T. Tetsuhiko, N. Hiroshi, K. Nahoko, S. Satoshi, T. Aya, T. Shingo, S. Koji, *Adv. Funct. Mater.* **2016**, 26, 8185.
- [150] M. C. G. Saborío, S. Lanza-laco, G. Fabregat, J. Puiggali, F. Estrany, C. Alemán, *J. Phys. Chem. C* **2018**, 122, 1078.
- [151] C. Xu, S. Guan, S. Wang, W. Gong, T. Liu, X. Ma, C. Sun, *Mater. Sci. Eng., C* **2018**, 84, 32.
- [152] D. Mawad, A. Artzy-Schnirman, J. Tonkin, J. Ramos, S. Inal, M. M. Mahat, N. Darwish, L. Zwi-Dantsis, G. G. Malliaras, J. J. Gooding, A. Lauto, M. M. Stevens, *Chem. Mater.* **2016**, 28, 6080.
- [153] L. Jiang, C. Gentile, A. Lauto, C. Cui, Y. Song, T. Romeo, S. M. Silva, O. Tang, P. Sharma, G. Figtree, J. J. Gooding, D. Mawad, *ACS Appl. Mater. Interfaces* **2017**, 9, 44124.
- [154] Y.-Y. Lee, H.-Y. Kang, S. H. Gwon, G. M. Choi, S.-M. Lim, J.-Y. Sun, Y.-C. Joo, *Adv. Mater.* **2016**, 28, 1636.
- [155] Z. U. Khan, J. Edberg, M. M. Hamedi, R. Gabrielsson, H. Granberg, L. Wägberg, I. Engquist, M. Berggren, X. Crispin, *Adv. Mater.* **2016**, 28, 4556.
- [156] T. S. Hansen, K. West, O. Hassager, N. B. Larsen, *Adv. Funct. Mater.* **2007**, 17, 3069.
- [157] S. Duan, Z. Wang, L. Zhang, J. Liu, C. Li, *ACS Appl. Mater. Interfaces* **2017**, 9, 30772.
- [158] S. J. Kwon, T. Y. Kim, B. S. Lee, T. H. Lee, J. E. Kim, K. S. Suh, *Synth. Met.* **2010**, 160, 1092.
- [159] L. V. Kayser, M. D. Russell, D. Rodriguez, S. N. Abuhamdieh, C. Dhong, S. Khan, A. N. Stein, J. Ramirez, D. J. Lipomi, *Chem. Mater.* **2018**, 30, 4459.