MIT Open Access Articles

Advanced Polymer Fibers: High Performance and Ultrafine

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Park, Jay Hoon and Gregory C. Rutledge. "50th Anniversary Perspective: Advanced Polymer Fibers: High Performance and Ultrafine." *Macromolecules* 50, 15 (July 2017): 5627–5642 © 2017 American Chemical Society

As Published: <http://dx.doi.org/10.1021/acs.macromol.7b00864>

Publisher: American Chemical Society (ACS)

Persistent URL: <https://hdl.handle.net/1721.1/125818>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of Use: Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.

Advanced Polymer Fibers: High Performance and Ultrafine

*Jay Hoon Park, Gregory C. Rutledge**

Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA, 02139

KEYWORDS

Aramid, UHMWPE, Tenacity, Nanofiber, Electrospinning

ABSTRACT

As *Macromolecules* celebrates its 50th anniversary, we reflect on the impact of polymer chemistry and engineering on the advancement of synthetic polymer fibers. In this Perspective, we focus on two exemplary cases: i) high performance fibers and ii) ultrafine electrospun fibers. High performance in this context refers to fibers like Kevlar[®] and Spectra[®], which emerged as a consequence of novel chemistry and processing innovations to convert synthetic polymers into fibers with exceptional specific stiffness and strength. More recently, the development of “ultrafine” (i.e. submicron diameter) fibers by technologies such as electrospinning has advanced dramatically, resulting in interesting, emergent structures and properties, such as surface and internal morphologies, electrical and mechanical properties, and growth applications like tissue engineering and sensors, which are subjects of current research. In both cases, challenges and

opportunities exist in the development of polymer processes to advance the current state of these synthetic polymer fibers.

1. Introduction

For millenia, natural polymers and polymeric fibers, ranging from animal fibers such as hair and wool, to plant fibers such as cotton, flax and hemp, have served mankind as one of the most abundant and useful forms of matter.^[1] From apparel to building materials, fibers are ubiquitous, and their scope of use has grown with the progress of technology through the centuries. Man-made fiber was first proposed in 1664 by Robert Hooke, who suggested the concept of synthetic fabrication of a fiber that would be “if not fully as good, nay better” than silk.^[2] However, commercially important man-made fibers only became a reality with the introduction of cellulose dinitrate, called “Chardonnet silk”, by Hilaire Bernigaud, Comte de Chardonnet de Grange, at the 1889 Worlds Fair.^[3] This was soon followed by the invention of the viscose process by Cross and Bevan in 1892 ^[3] to produce regenerated cellulose (also called “Rayon”), which subsequently came to dominate the fiber industry for several decades. As chemists learned to modify natural materials and to synthesize new ones, man-made polymer fibers became widely used, with applications ranging from mundane yet essential uses such as apparel, furnishings and building materials to more advanced materials applications.^[4,5] The first truly synthetic fiber, Nylon 66, was discovered by Wallace Carothers in the 1930’s^[6] and achieved its widespread success as sewing thread, hosiery and parachute fabric during World War II. DuPont followed up on such success with development of synthetic fibers such as Orlon acrylic, Dacron® polyester, Lycra® spandex, Teflon® fluorocarbon, and Nomex® high temperature fibers by the 1950’s.^[7] Since that time, the family of synthetic polymer fibers has grown to include a variety of

polyamides, polyesters, acrylics and polyolefins; demand for synthetic polymer fibers over the last century has grown to match.^[8] In 2013, the percentage of synthetic polymer fiber in the global textile market was 59%, followed by cotton at 35%.^[8]

By and large, modern-day applications of polymer fibers are still highly represented in the apparel industry and home furnishings, where they have served to replace their natural fiber predecessors. However, innovations in polymer science and fiber engineering in recent years have reshaped the way fibers are used, especially over the last several decades. For instance, manufactured fibers are now used as super-absorbent diapers, artificial organs, and construction materials for moon-based space stations.^[9] Fibers with novel structures and functionalities ranging from thermal regulation to energy harvesting have been developed.^[10] Simply put, the modern advancement of manufactured fibers have opened up new applications that go far beyond the mundane. Polymer science is now responsible for fibers that exceed the performance limits of the best natural fibers drawn from spiders, grown in the fields, or spun from the fleece of animals.

The most recent developments of synthetic polymer fibers were made possible, in large part, by discoveries of new chemical functionalities and material properties that stemmed from both the chemistries of the fiber constituents and the physics of fiber formation. Reflecting these developments, the goal of this Perspective is thus several fold: i) to highlight areas of application for advanced fibers that surpass those originally served by natural fibers, ii) to discuss the current state-of-the-art in such areas of use, and iii) to identify challenges and opportunities for future synthetic polymer fiber development. To accomplish this goal, we focus on two groups of

advanced polymer fibers where their unique material properties have been quintessential to the expansion of application. The first group is the high performance fibers, whose remarkable mechanical properties (notably, stiffness and strength) combined with light weight led to application of polymer fibers in such innovative areas as automotive and aircraft composites, body armor and sports equipment. The second group is the ultrafine or submicron fibers, sometimes called “nanofibers”, which are remarkable for their small diameters (less than 1 micrometer) and high specific surface areas. Synthetic fibers in this size range fill a broad gap in dimensions between conventional fibers, which are typically several to hundreds of micrometers in diameter, and the supramolecular objects called multiwalled nanotubes, whose diameters typically range from several to tens of nanometers. Such fibers offer the prospect for “fiber nanotechnology”, where chemical and physical behaviors are altered from those of the same material in bulk, or even in conventional fibers, and where new, emergent properties and behaviors become apparent with the reduction of diameter to nanometer dimension. In the following sections, these two classes of polymer fibers are discussed in more detail.

2. High Performance Fibers

High performance fibers are known to have mechanical properties (e.g. stiffness, strength, and toughness) ^[11,12] that are remarkable in combination with their light weight. Although there exists no universal definition for such types of fibers, they typically have Young’s moduli (E) on the order of 100 GPa or more, and thus can be used in mechanically-demanding applications such as protective clothing for soldiers. Their specific moduli, or E/ρ where ρ is the material density, are typically on the order of 100 to 200 N/tex, which is 5-10 times stiffer than steel, on a

per weight basis. Specific modulus has the units of force per unit of linear density, which in the fiber industry is widely reported in N/tex, tex being the mass in grams of 1000 m of fiber. Similarly, in the fiber industry “tenacity” refers to the specific strength of a fiber, or σ/ρ , which is also typically 5-10 times greater than that of steel (*c.f.* **Figure 1**). In addition, as a result of their exceptional heat and chemical resistances,^[11] these fibers can be engineered for use in extreme environments.

Figure 1. Specific strength plotted against the specific stiffness for different types of high performance fibers. Reprinted with permission from ref. [14]. Copyright: American Association for the Advancement of Science, 2007.

2.1. Polymer Precursor Fibers

Carbon fibers have been in existence since 1860, but a true high-performance carbon fiber was not manufactured until 1958 when Roger Bacon thermally carbonized rayon.^[15] High performance carbon fibers are specifically engineered to meet the needs of more mechanically demanding applications, such as military and aerospace applications.^[16] The mechanical, electrical, and thermal properties of carbon fibers are governed by their degree of carbonization, carbon orientation, and the degree of crystallization.^[17]

The precursor materials used to fabricate carbon fibers are polymers such as rayon, pitch, and acrylics. Most commercial carbon fibers are fabricated by extrusion of such organic precursor materials, followed by a process of stabilization and carbonization to turn the precursor filaments into carbon fibers. Polyacrylonitrile (PAN) is the most common polymeric precursor used to fabricate carbon fibers; around 90 percent of carbon fibers are fabricated through some type of thermal conversion of PAN.^[18] The microstructure of PAN-based carbon fibers is disordered, which confers high tensile and compressive strengths. By contrast, pitch-based carbon fibers generally have higher tensile modulus and thermal conductivity. These structure-property differences have led to the specialization of carbon fibers for applications that take advantage of the strengths of each type of carbon fiber. Hence, the majority of PAN-based fibers have found applications where strength is critical, while pitch-based fibers have dominated applications where heat transfer or stiffness is important (e.g. spacecraft components). The relatively low tensile strength and higher cost associated with rayon-based carbon fibers have led to their decline when compared to the other two precursors.^[19]

2.2 Aramid Fibers

High performance polymer fibers were first realized through the pioneering work of Stephanie Kwolek and co-workers at DuPont, who invented the first aromatic polyamides, or “aramids” in the 1960’s^[20,21]; for this work Dr. Kwolek received the National Medal of Technology in 1996. By definition, aramids are synthetic long chain molecules containing amide moieties wherein at least 85% of the amide linkages are attached directly to two aromatic rings.^[22] Foremost among these aramids are the *p*-aramids like poly(*p*-benzamide) (PBA) and poly(*p*-phenylene terephthalamide) (PPTA, or Kevlar[®]) and the *m*-aramids like poly(*m*-phenylene isophthalamide) (MPIA, or Nomex[®]), developed extensively in the literature in the 1970’s.^[23-26]

Being amides, aramids are closely related to aliphatic polyamides, or nylons. Hence, the knowledge of both synthesis and processing of nylons contributed greatly to their advancement. Whereas nylons are semi-flexible polymers and are routinely spun into fibers from solution (“wet spinning”) or melts (“melt spinning”), aramids exhibit highly extended molecular conformations. The *p*-aramids in particular are rigid rod-like polymers, with persistence lengths in solution on the order of 15 to 20 nm.^[27,28] In many cases, they decompose at high temperature before melting, and dissolve only in aggressive solvents such as 100% sulfuric acid. However, once in solution, these remarkable polymers exhibit the novel (at the time) property of lyotropic liquid crystallinity, resulting in the formation of domains of high molecular level order even in quiescent solutions. During processing, the imposition of an external field (e.g flow or magnetic) induces co-alignment of these liquid crystal domains with minimal entanglement of molecules. This reduction in entanglement is important to achieving high orientation in conventional fiber-forming processes.^[22] As the flow stresses on these solutions increase, their

viscosity first increases, then decreases again as the nematic directors of the liquid crystal domains become co-oriented with the flow, resulting in exceptionally high levels of molecular alignment in fiber spinning operations. The formation of high performance fibers from lyotropic solutions of *p*-aramids benefitted remarkably from the invention of “dry-jet wet spinning”, in which a solution is first drawn in air to induce uniformly high molecular orientation before coagulating in a nonsolvent bath.^[29,30] Without pre-orientation within the domains of the liquid crystalline solution, the long relaxation time for polymer motions would preclude the attainment of high molecular orientation within the time frame of the spinning process.^[31] Thus, a crucial step in the formation of high performance polymer fibers is the mechanical drawing of a liquid crystalline polymer solution (lyotropic liquid crystals) or melt (thermotropic liquid crystals).

Aramids display higher tensile strength and thermal resistance than nylons due to their molecular rigidity, orientation, and stability of the aromatic rings and amide linkages. Of the two main types of aramids, *p*-aramids exhibit higher strength and thermal resistance than *m*-aramids, due to the difference in stereochemistry. It had long been hypothesized that fibers would exhibit high stiffness and strength when the polymer chains were fully extended and highly oriented.^[32] The high performance tensile properties of these aramid fibers were thus attributed to the unusually stiff extended conformational characteristics of the molecules and the relative ease with which these macromolecular chains could be aligned along the fiber axis during fiber formation. The resulting fibers and yarns are conjectured to bear tensile loads almost entirely along the molecular axis, which, being extended, cannot elongate significantly without bond scission. Tensile strength (tenacity) and stiffness (modulus) both increase with decreases in orientation angle, a measure of crystallite alignment that can be obtained through X-ray diffraction analysis.

2.3 Commercialized High Performance Polymer Fibers

Subsequent to the development and commercialization of aramid fibers, other types of high performance polymer fibers were discovered and commercialized. Among the more important fibers are those developed from the aromatic copolyesters, which are notable for their thermotropic liquid crystallinity, or formation of ordered domains within the quiescent melt. Also important are poly(*p*-phenylene-2,6-benzobisoxazole) (PBO), poly(phenylene benzobisthiazole) (PBZT), and gel-spun ultrahigh molecular weight polyethylene (UHMWPE). The development of these polymer fiber technologies began in earnest in the 1970s, with the example of *p*-aramids and the drive for more lightweight materials for military and commercial applications. Being more diverse in composition, the family of high performance polymer fibers offers greater range of material properties than carbon fibers, which allows for tailored combinations of mechanical, thermal, flame-resistant, and other properties. These properties are functions of both the chemistry and the microstructure of the polymers. Such flexibility to tailor these properties to specific needs has enabled a range of applications. **Table 1** summarizes the chemical structures of several currently available high performance polymer fibers. In the subsequent sections, the different chemistries and physics involved with each type of polymeric high performance fiber are reviewed.

Table 1. Properties of several common high performance fibers^[33]

Type	Lyotropic Liquid Crystal			Thermotropic Liquid Crystal	Polyolefin
Trade name	Kevlar®	Zylon®	M5	Vectran®	Spectra®
Monomer structure
Polymer	PPTA	PBO	PIP	Vectra	UHMWPE
Solvent	sulfuric acid	polyphosphoric acid	polyphosphoric acid	N/A (Melt)	decalin
Fiber density (g/cm ³)	1.44 - 1.47	1.56	1.7	1.4	0.97
Young's modulus (GPa)	130-185	270	330	65	100-130
Tensile strength (GPa)	3.6-4.1	5.8	3.5-4.5	2.9	2.4-3.5
T _{melt} < T _{decompose} ?	No	No	No	No	Yes (T _{melt} = 140 °C)
Decomposition temp. (°C)	550	650	500	400	350-510

2.3.1 Lyotropic Liquid Crystal Polymers

A lyotropic liquid crystal forms ordered structures at sufficiently high concentration in a solvent. As described above, the *p*-aramids are the best-known and most widely used of lyotropic liquid crystals. Upon alignment of the highly extended molecular conformations during fiber spinning and removal of solvent, the formation of intermolecular hydrogen bonds and stacking of rings results in fiber with tensile stiffness (*E*) of 130-185 GPa and tensile strength (σ) of 3.4-4.1 GPa.^[33] In addition, the dimensional stability due to the high rigidity translates to improved thermal properties. Kevlar® and Twaron® are the two leading commercial fibers based on PPTA. Technora® is a copolymer of 3,4'-diaminodiphenyl ether and *p*-phenylenediamine reacted with terephthaloyl chloride, resulting in a noncrystalline fiber that can be processed by conventional fiber drawing from organic solvents. Kevlar is used in both defense and commercial applications that take advantage of its excellent mechanical properties and thermal resistance. These applications include but are not limited to protective gear, asbestos replacement, tire

reinforcement, ropes, and sporting goods.^[18] Most famous for its high impact resistance, Kevlar is the fabric of choice for bullet-proof soft body armor. However, PPTA fibers are susceptible to humidity and ultraviolet radiation.^[9]

Efforts to improve upon these first generation liquid crystalline-based fibers led to the more recent development of even more rigid polymers such as PBO and PBZT, originally developed by Wolfe *et al.*^[34] PBO was eventually commercialized by Toyobo as Zylon[®] in the 1990s.^[35] As with other lyotropic liquid crystal polymers, PBO is processed as an anisotropic solution. With the elimination of amide bonds, the PBO crystal has higher rigidity than its aramid counterparts, which translates into improved mechanical and thermal properties ($E = 270$ GPa, $\sigma = 5.8$ GPa, $\rho = 1.56$ g/cm³, decomposition temperature = 650 °C).^[35] Though demonstration of these superior material properties led to its first use in protective vests in the early 2000's, economic and technical issues prevented more extensive use. The higher costs associated with synthesis of the polymer, use of a highly aggressive solvent (polyphosphoric acid), and difficulty in processing due to high viscosities are all issues that have prevented deeper market penetration.^[18] In addition, the PBO chemistry exhibits poor adhesion to resin, UV instability, and hydrolytic instability.^[36]

The most recently developed rigid rod polymer, poly(hydroquinone-diimidazopyridine) (PIPD), is the raw material for high performance M5 fibers, developed originally by Sikeema and co-workers for Akzo Nobel.^[37] It was first produced on a pilot scale by Magellan Systems, which was then acquired by DuPont.^[18] M5 is also spun from an anisotropic solution with polyphosphoric acid. The Young's modulus is around 271 GPa, tensile strength is 3.9 GPa,

decomposition temperature = 500 °C, and $\rho = 1.7 \text{ g/cm}^3$ [33] which are similar to those of PBO. The compressive strength of M5, however, ranges from two to four times higher than those of other high performance polymer fibers.[18] The distinct mechanical properties of the M5 fiber derive from its ability to hydrogen bond in two dimensions lateral to the axis of molecular extension.[18] In addition, these fibers exhibit higher flame resistivity than MPIA and improved stability under UV light and humidity due to the presence of imidazole rings.[9] M5 fibers present great opportunities for the future, especially in protective textiles applications, though the extra steps required to process the fiber currently present a barrier to cost-effective commercialization of the fiber. The polymer fibers often require extensive washing with water, heating, and exposure to controlled stress to enhance molecular alignment and favorable configuration for tensile and compressive strength.

2.3.2 Thermotropic Liquid Crystal Polymers

In contrast to lyotropic liquid crystals, thermotropic liquid crystals can be processed from liquid crystalline melts, and do not require any solvent removal or recovery. The aromatic polyester Vectra[®], for example, is a thermotropic liquid crystal statistical copolymer of 1,4-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid. The incommensurate distribution of ester groups along the chain backbone due to the random sequencing of differently sized phenyl and naphthyl moieties lowers the enthalpy of solidification, and thus the melt temperature for this group of polymers. The resulting melt-spun fiber, Vectran[®], has mechanical and thermal properties of $E = 65 \text{ GPa}$, $\sigma = 2.85 \text{ GPa}$ ($\rho = 1.4 \text{ g/cm}^3$), and decomposition temperature of 400 °C, [33] which are comparable to the properties of low modulus Kevlar fibers. Vectran fibers are primarily used as reinforcing fibers for tow ropes, cargo tie-downs, and cables. Vectran fibers

played a role in space exploration, with their notable application as the fabric used for the landing airbags on the Mars Pathfinder in 1997.^[38] Although Vectran fills a niche in the tradeoff between stiffness and toughness, they too are susceptible to UV radiation.

2.3.3 Gel-Forming Polymers

A somewhat different case is that exemplified by the high performance fibers of gel-spun ultra high molecular weight polyethylene (UHMWPE). UHMWPE is an extremely long chain of polyethylene, with a degree of polymerization on the order of 10^6 or more. First synthesized in 1950's by Karl Ziegler,^[39] the reaction utilized a highly reactive organotitanate catalyst to polymerize the ethylene gas.^[39,40] The chains of UHMWPE are polymerized to greater lengths prior to its termination when compared to high density polyethylene (HDPE), which results in remarkably linear chains with less than 3% branching.^[41] Unlike the liquid crystalline polymers, polyethylene is a relatively flexible chain that does not spontaneously align within liquid crystalline domains in the solution or melt. Despite its flexibility, the preferred conformation in the crystal phase is a 2_1 helix, or fully extended zig-zag conformation, with a cross-sectional area of only 0.18 nm^2 per chain. As a result, theoretical estimates of the modulus of crystalline PE at finite temperature are surprisingly high, with typical values ranging from 230 to 350 GPa.^[42] Coaxing such flexible molecules to form high performance, highly crystalline fibers again relies on first realizing a processable liquid state with minimal entanglement of molecules, followed by subsequent drawing to extend and align molecules prior to solidification into a para-crystalline fiber. This remarkable feat is accomplished by the gel-spinning method, first developed by Smith and Lemstra in the 1980's.^[43] This process begins with the formation of a gel filament by extrusion of a solution comprising as little as 0.1 – 1.0 wt% polymer. These gel filaments are subsequently drawn at elevated temperature to 40 or 50 times their original length at strain rates

around 1 s^{-1} , resulting in very high levels of molecular orientation and crystallinity. Although the thermal stability is weak (melt temperature = 140°C), tensile moduli and ultimate tensile strengths of these lightweight materials are typically around $E = 100\text{-}130 \text{ GPa}$ and $\sigma = 2.4\text{-}3.5 \text{ GPa}$,^[33] respectively. With a fiber density of 0.97 g/cm^3 , these polyolefin fibers exhibit exceptional performance on a per unit weight basis.

The high drawability of UHMWPE in solution is a consequence of the process step that creates the low density of entanglements between polymer chains in the intermediate gel-like fiber. The overlap concentration c^* that distinguishes an entangled from unentangled solution is given approximately by the relation $c^* = \rho M_c / M$, where ρ is the density of the polymer in the melt state, M_c is the molecular weight of chain segments between entanglements in the melt state, and M is the polymer molecular weight.^[44] Thus, high molecular weight is the key to attaining a low overlap concentration and a highly drawable viscoelastic filament. When drawn to high extension, high levels of molecular orientation and crystallinity are obtained. The fibers are then woven or laid down as a mesh with high fiber density and orientation, and the meshes are then laminated or impregnated to form a flexible or rigid composite. Gel-spun UHMWPE fibers have been commercialized as Spectra® by Honeywell in the US and Dyneema® by DSM in the Netherlands. Primary applications of these fibers are ballistic vests, helmets, and sailing ropes.

2.4. Current State and Challenges of High Performance Fiber

Since the first commercialization of Nomex in the 1960s, high performance polymer fibers have enjoyed significant increases in demand over the years. As was the case for carbon fibers, polymer fiber technology advancement in the 1970s and 1980s made possible the development

of lightweight polymer-matrix composites. In contrast to carbon fibers, however, the growth in high performance polymer fibers has been more stable, driven by both high value-added military and high volume civilian applications. In addition, the flexibility the researcher has in fine-tuning material properties to meet a broader range of applications has resulted in broad and sustained demand for high performance polymer fibers. Currently, aramids account for approximately 90% of worldwide demand for high performance polymer fibers, which exceeds the demand for PAN-based carbon fibers.^[45] In order to meet the rise in demand, both DuPont and Honeywell (or their successors) continue to increase their fiber production capacity, while new suppliers continue to appear^[46] and invest in further development of processing-structure-property interactions to enhance material properties.^[18]

Despite such growth in commercialization, there are several challenges that should be addressed in order to improve upon these materials in the upcoming years. We begin by noting that many of the current high-performance fibers have yet to reach their theoretical maximum stiffnesses or strengths. For instance, the tensile moduli reported for Kevlar, Spectra, PBO (Zylon), and PIPD (M5) to date are still well below their theoretical values (*c.f.* **Figure 2**). Fiber tensile strengths are also estimated to be around 40-50% of their theoretical values.^[47-49] This unrealized potential suggests some opportunity exists for further development of high performance polymer fibers.

Figure 2. Measured fiber modulus^[33] for several high performance polymer fibers plotted against the theoretical crystal modulus of the polymer.^{[42], [50]}

In general, high performance fiber technologies have matured over the course of several decades. Therefore, it seems likely that incremental improvements are largely exhausted, and that the field is ripe for something transformative. Synthesis of new materials comes at the expense of considerable time and cost. The exploration of new fiber-forming chemistries was a very active area of research in the 1970's and 80's, but only a small fraction of those chemistries were ultimately commercialized, largely due to the high cost of synthesis. It is telling that the last major new chemistry (M5) was introduced nearly 20 years ago. We believe the greater opportunity lies in manipulating polymer architecture and processing. Developments in the

1990's in metallocene catalysts, for example, have led to polymers from inexpensive feed stocks with new thermodynamic and viscoelastic properties. By controlling the number, length and distribution of branching across the molecular weight range in polyolefins, for example, a remarkable diversity in material properties has been found to exist just within this single class of chemistries. Most of the progress in architectural control has been through improved formulations for blown films and injection molded parts; nevertheless, one can speculate whether advancements in control of architecture and entanglement density could lead to greater processability in fiber operations or higher performing fibers.^[51] In what follows, we highlight several recent studies that illustrate other opportunities for further improvements in high performance polymer fibers through processing.

Some recent studies have demonstrated the potential of using the gel-spinning process to enhance the mechanical properties of other polymers besides the polyolefins.^[52-54] A particularly notable example is a gel-spun poly(acrylonitrile-co-methacrylic acid) (PAN-co-MAA) copolymer fiber, which was subsequently carbonized in a continuous fashion.^[54] Tensile strength in the range of 5.5-5.8 GPa and tensile modulus in the range of 354-375 GPa were observed, which is a vast improvement even among carbon fibers. As these recent studies have shown, process development or modification can drastically improve the mechanical properties with existing polymer fibers.

Apart from improving the performance of the fibers themselves, opportunities exist to make the fabrication processes less expensive and more environmentally benign. As noted in Table 1, processing of high performance polymer fibers often requires the use of solvents that pose

environmental and health hazards. For instance, gel-spinning of UHMWPE requires the recovery of large amounts of a flammable solvent (e.g. 9 kg solvent per 1 kg fiber), by evaporation in the case of decalin^[55] or extraction with hexane or fluorocarbon compounds, in the case of mineral oil.^[56] Recovery of such solvents in large volume can present potentially serious health concerns.^[57] Recently, however, Schaller *et al.* reported gel-spinning of UHMWPE using olive oil, peanut oil, stearic acid, and lauric acid as solvents, which yielded enhanced productivity and properties, as shown in **Figure 3**.^[58] These solvents were extracted using isopropanol and diethyl ether.^[58] The advantage of using these alternative solvents is that they are environmental-friendly and pose less of a health hazard for workers. To the best of our knowledge, this work is the only recent study to promote environmentally-benign processing of high performance fibers, but it may be only the vanguard of more to come.

Figure 3. (a) Strands of gel filaments consisting of 20% v/v UHMWPE crystallized from olive oil, nicknamed UHMWPE "Al Dente"; the filaments were produced by 10 min mixing

UHMWPE in olive oil at 230 °C, followed by extrusion and cooling in air to room temperature.

(b) Maximum draw ratio with corresponding tensile strength and Young's modulus of UHMWPE gel filaments, processed from different solvents, as functions of polymer volume fraction: (black ●) neat UHMWPE; (green ▲) peanut oil; (green ◆) olive oil; (blue ▲) decalin; (green ◇) peanut oil–stearic acid (1:1 w/w); (green ●) stearic acid; (green ○) lauric acid. Reprinted with permission from ref. [58]. Copyright: American Chemical Society, 2015.

3. Ultrafine Fibers

Most synthetic polymer fibers commercialized to date have diameters on the order of 10 to 100 μm . With the revival of electrostatic fiber formation technology, or “electrospinning” in the 1990's,^[59] ultrafine fibers having diameters less than 1 μm (commonly called “nanofibers”) have become widely available. Though the formation of very fine fibers by electrostatic forces was described as early as the late 19th century,^[60] the term “electrospinning” did not appear until later.^[59] Other fiber-forming technologies such as melt-blowing^[61] pre-date this revival or, like centrifugal spinning^[62] and electroblowing^[63], have been discovered and popularized since. Nevertheless, the ease of implementation of electrospinning in the lab, the uniformity and control over fiber diameter and morphology that have been demonstrated with this technology, and the timeliness of its re-discovery just as “nanotechnology” was coming into its own,^[64] have contributed to the strong association between electrospinning and the ultrafine polymer fibers that it produces. Electrospinning is a relatively straightforward, “top-down” process that does not exhibit the same delicacy that molecular assembly processes “from the bottom up” often do.^[65,66] While our discussion in this Perspective draws largely upon the electrospinning literature, it is implied that the remarkable properties and applications of the ultrafine fibers highlighted here

are consequences primarily of their size and structure, regardless of the process by which they were formed.

The mechanism of electrospinning has been thoroughly investigated over the years, and has been shown to reflect a complex interplay of viscoelastic rheology, inertial, capillary and aerodynamic forces, heat and mass transfer, and phase behavior, in addition to dielectric and Coulombic effects. From the seminal studies by G.I. Taylor^[67], D.A. Saville^[68] and A. Gañan-Calvo^[69], to the more applied modeling efforts by Brenner, Rutledge and co-workers^[70,71], Joo and co-workers^[72,73], and Reneker, Yarin and co-workers,^[74] a more or less compelling description of the electrospinning process has emerged. The process comprises three stages: i) the steady cone-jet, ii) the whipping instability, and iii) solidification. Both the cone-jet and the whipping instability are characterized by unusually high extensional strain rates ($\sim 1000 \text{ s}^{-1}$), which result in reduction of fiber diameter to tens or hundreds of nanometers.^[74] The number of publications and patents involving ultrafine fibers has grown dramatically since 2000, and report applications in areas as varied as filtration, drug delivery and tissue engineering, energy, and sensors. ^[75-80] In the sections that follow, we highlight several properties of ultrafine polymer fibers where their combinations of composition, diameter and continuous fibrous nature impart these polymeric fibers with unique opportunities. The selection of topics is influenced by personal taste and is by no means exhaustive; we regret the omission of many promising examples that could not be discussed here.

3.1 Emergent Properties

3.1.1 Surface Properties of Ultrafine fibers

Synthetic nanofiber meshes are known to exhibit surface morphologies similar to the hydrophobic surfaces of certain leaves found in nature. Many plants from nature ^[81] produce textured leaves that repel water and cause rain droplets to roll off, carrying other contaminants away from the surface.^[82] The contact angle of a droplet of liquid, like water, placed on the surface of such a mesh is known to depend sensitively on not only the chemical affinity of water for polymer, but also the roughness of the surface and any trapped heterogeneities such as air. The combined effects of surface chemistry and morphology can be understood starting with the classical models of Wenzel ^[83] and of Cassie and Baxter.^[84] The water contact angle (WCA) of polystyrene (PS), a mildly hydrophobic polymer, was found to increase from 95°, when in the form of a smooth film, to as much as 160° ^[85] when electrospun into a mesh of ultrafine fibers. Ma *et al.* electrospun fibrous materials from solutions of poly(styrene-*b*-dimethylsiloxane) blended with PS, which exhibited a WCA of 163° and a contact angle hysteresis of 15°. ^[86] Other electrospun hydrophobic polymer fiber meshes have also exhibited similar increases of hydrophobicity when compared to their bulk counterparts.^[87-89]

The small diameter of the ultrafine fibers plays a crucial role in the liquid repellency of these meshes. According to the Cassie-Baxter model, the WCA of a fiber mesh depends on the surface porosity of the mesh, which is length scale-independent. However, resistance of the mesh to forced intrusion of the liquid depends on the size of the pores relative to the capillary length scale of the liquid.^[90] The property, denoted “robustness” by Tuteja *et al.* ^[91,92], depends sensitively on fiber diameter, with which the effective pore size of an electrospun mesh scales. The smaller the fiber diameter, the smaller the gaps between the fibers compared to the capillary length of the liquid, and the greater the robustness against intrusion.

The high specific surface areas of nanofiber mats make them good candidates for surface modification. Ma *et al.* combined electrospinning with initiated chemical vapor deposition (*i*-CVD) to fabricate meshes of poly(ϵ -caprolactone) (PCL) with the beads-on-a-string morphology (~ 100 nm fiber diameter and ~ 2 μm bead diameter) with a ~ 70 nm conformal layer of poly(perfluoroalkyl ethyl methacrylate) (PPFEMA) polymerized from the vapor.^[93] The combination of the low surface energy of the PPFEMA coating (~ 9.3 mJ/m²) and the high porosity of the fiber mats yielded a high WCA of 175° , with contact angle hysteresis less than 2° (c.f. **Figure 4** a-c). A recent study by Guo *et al.* using similar meshes of electrospun poly(trimethyl hexamethylene terephthalamide) (PA6(3)T) surface-modified with a fluoropolymer by *i*-CVD showed that the liquid entry pressure (a measure of robustness) increased by over an order of magnitude, from about 20 kPa to more than 370 kPa, as the fiber diameter was decreased from 1.8 μm to 250 nm.^[94] These fiber mats performed well as desalination membranes, with salt rejections above 99.9% and permeate fluxes up to 10 kg/m²/hr. Hardman *et al.* demonstrated in-situ surface modification by electrospinning polystyrene with end-functionalized with 1–3 fluoroalkyl groups, which also exhibited superhydrophobicity.^[95]

Figure 4. (a) SEM image of electrospun beaded (PCL) fiber. (b) The molecular structure of PPFEMA. (c) A water droplet with WCA of 175° , indicative of superhydrophobicity, observed on a mesh of electrospun PCL fibers modified by i-CVD with a conformal coating of PPFEMA. Reproduced with permission from ref. [93]. Copyright: American Chemical Society, 2005. (d) An SEM image of nanofiber shish-kebab structure fabricated by surface crystallization of a block copolymer on electrospun PEO nanofibers. Reproduced with permission from ref. [105] Copyright: American Chemical Society, 2010.

In addition to chemical modification, the surfaces of ultrafine fibers can be modified topographically, with pores, wrinkles or beads. Megelski *et al.* observed that pores varying in size from nanometers to micrometers could be formed on the surfaces of electrospun nanofibers; the formation of these structures was found to be sensitive to the volatility of the solvent and the spinning conditions.^[96] They attributed the observed structure formation to thermally induced phase separation (TIPS). Similarly, Pai *et al.* observed the formation of wrinkled surfaces, which they explained in terms of a rapidly formed skin layer that buckles when the fluid core continues to shrink during solidification.^[97,98] Such observed structure formation was attributed to vapor induced phase separation (VIPS)^[99] as humidity in the surrounding environment diffused into the jet and caused phase separation. Ma *et al.* combined the formation of surface pores on electrospun PMMA fibers and surface modification with PPFEMA to create superhydrophobic fabrics with contact angles of 160-163 degrees ^[100] In a similar way, ultrafine fibers can be decorated with inorganic nanoparticles for added functionality and surface texture. The layer-by-layer (LbL) method was used to coat electrospun fibers with SiO₂ nanoparticles, resulting in a chemically hydrophobic layer with added physical texture that displayed superhydrophobicity with low hysteresis for longer than 25 minutes.^[100] Other groups have reported an increase in

hydrophobicity using the same technique for various polymers and inorganic nanoparticles.^[101-103] Lee *et al.* coated TiO₂ nanoparticles on electrospun poly(dimethylsiloxane-b-etherimide) (PSEI) fibers, which exhibited high photocatalytic activity.^[104]

More complex structures such as “shish-kebabs” have been fabricated. Chen *et al.* crystallized block copolymer oligomers on electrospun polyethylene oxide (PEO) nanofibers, which formed a “nanofiber shish-kebab” (NFSK); examples of these shish-kebabs are shown in Figure 4d.^[105] The texture of the NFSK was controlled by adjusting the rate of crystallization.^[105] Similarly, Jing *et al.* combined electrospinning and self-induced crystallization of PCL to fabricate NFSKs.^[102] This structure was made to mimic the topography of collagen fibrils in extracellular matrix (ECM). When immobilized with Matrigel[®], the PCL NFSKs showed increased cell compatibility due to the introduction of binding sites on the surface.^[106]

3.1.2 Internal Structural Assembly in Ultrafine fibers

Ultrafine polymer fibers have been fabricated with a variety of interesting internal structures. Such internal structures include highly porous morphologies^[107] and modulation of molecular orientation and crystallinity under confinement^[108]. Nanoparticles^[109] and carbon nanotubes^[110-112] have also been added to the spin dopes, resulting in their inclusion within the internal structure of the nanofibers. However, the most dramatic demonstration of emergent behavior in internal structures of ultrafine fibers is the appearance of entirely new, self-assembled microphase separated morphologies of block copolymers upon confinement in nanofibers, as described next.

In bulk, diblock copolymers self-assemble into spheres, cylinders, gyroids, or lamellae, depending on composition and strength of incompatibility of the blocks, in a process known as “microphase separation”. These morphologies are illustrated in **Figure 5a**,^[113] and can be explained by the thermodynamic theory of Liebler.^[114] However, when block copolymers are electrospun into fibers, their approach to thermodynamic equilibrium is usually incomplete; the internal structures are not well-ordered, presumably due to the high extensional strain rate and rapid solidification.^[115, 116] However, when coaxially spun with an outer fluid that forms a thermally stable shell layer of, e.g., *tetra*-ethyl *ortho*-silicate (TEOS)^[117] or poly(methacrylic acid) (PMAA)^[118,119], the block copolymer in the core can be thermally annealed without losing the cylindrical fiber geometry. This annealing results in the microphase separation of the block copolymer under cylindrical confinement (the fiber shell), leading to the formation of various new morphologies not observed in the bulk. For example, lamellae-forming copolymers change to either a stacked disk or concentric cylinder morphology under cylindrical confinement within the nanofibers.^[120] Sphere- and cylinder-forming morphologies give rise to an equally rich variety of new morphologies when the length scale of cylindrical confinement decreases to within an order of magnitude of the long period of the block copolymer morphology, and surface forces become significant.^[121, 122] The concentric cylinder morphology is illustrated in Figure 5b.^[119] This particular internal structural assembly proved to be an excellent template for manipulating the spatial distribution of functional nanoparticles.^[123,124] Recent studies that exhibited internal self-assembly of a block copolymer included functional inorganic components, which are used to form ordered inorganic structures.^[125-128] Going forward, further investigations

are expected to concentrate on the enhanced functionalities that can be realized through such by structural assembly.

Figure 5. (a) Block copolymer phase diagram and idealized microphase-separated morphologies in bulk. Reproduced with permission from ref. [113]. Copyright: American Chemical Society, 1996. (b) Block copolymers are shown to self-assemble into concentric cylinders under cylindrical confinement on the length scale of the microphase-separated morphology (10's of nanometers). Reproduced with permission from ref. [119]. Copyright: American Chemical Society, 2009.

3.1.3 Electrically Conductive Ultrafine Fibers

Combined with their high specific surface area, electrically conductive nanofibers have promising applications as multifunctional textiles, sensors, and for electrochemical storage. [129-

^{132]} Electrical conductivity can be increased by various methods, such as including conductive nanoparticles or nanotubes within the ultrafine fibers during fabrication^[133], converting the as-spun fibers to ultrafine carbon fibers^[134], or by forming the nanofibers directly from intrinsically conductive polymers (ICP). ^[135] Polyaniline (PAni) is one such ICP; its electrical conductivity changes many orders of magnitude when doped with an electron-acceptor like (+)-camphor-10-sulfonic acid (HCSA). However, PAni is difficult to process on its own, due to a combination of low molecular weight and poor solubility in common solvents, resulting in inadequate viscoelasticity. Zhang *et al.* fabricated ultrafine fibers by blending PAni with other polymers;^[136] the electrical conductivities of the fibers increased exponentially with the weight percent of doped PAni in the fibers. Using coaxial electrospinning, they also fabricated fibers comprising a doped PAni core with a PMMA shell. Electrical conductivity as high as 50 ± 30 S/cm was observed for the as-electrospun fibers, and 130 ± 40 S/cm for the same fiber after solid state drawing.^[136] As seen in **Figure 6**, these high electrical conductivities were attributed to the enhanced molecular orientation arising from extensional deformation in the electrospinning process and afterward during solid state drawing. When fabricated as ultrafine fibers, these electrically conductive threads proved to be excellent chemiresistive gas sensors, due to the high specific surface area and small diffusive length scale afforded by the fiber diameter. Doped PAni fibers exhibit high sensitivity to ammonia vapor, which serves to de-dope the PAni, while the undoped PAni fibers exhibit very high sensitivity to nitrogen dioxide, an electron acceptor.^[137]

Figure 6. (a) Illustration of PANi molecular orientation within a fiber (b) Electrical conductivity of as-electrospun polyaniline fibers as a function of the weight fraction of PANi in the blended fibers; the pure PANi fiber was obtained after dissolving the shell component (PMMA) of the core-shell. Reproduced with permission from ref. [136]. Copyright: American Chemical Society, 2012.

For electrochemical applications such as supercapacitors and lithium-ion batteries, carbon precursor polymers (e.g. PAN, PAA or cellulose acetate) are formed into ultrafine fibers and thermally treated to create ultrafine carbon fibers. In general, the electrochemical and mechanical properties of ultrafine carbon fibers are controlled by i) the choice of carbon precursor, ii) fiber processing and subsequent thermal treatment conditions, and iii) incorporation of electrically conductive nanofillers.^[138] Recent investigations have shown that electrospun carbon nanofibers are promising as electrochemically active materials.^[139-145] To date, electrospun carbon nanofibers generally exhibit lower electrical conductivities than carbon nanotubes and graphenes, due to the lower degree of graphitization obtained by thermal processing.^[138]

Although inclusion of electrically conductive nanofillers can compensate somewhat for the lower electrical conductivity, the inclusion comes at the expense of increased complexity in processing.

3.1.4 Ultrafine Fibers in Biomedical Applications

In recent years, ultrafine fibers have received a lot of interest from the biomedical field, especially for application as tissue engineering scaffolds. In its Global Research Report on Materials Science and Technology^[146], Thomson Reuters ranked “electrospun nanofibrous scaffolds” tenth among the fastest growing research specialties that “offer great potential for the 21st century”, alongside graphene and solar cells. In particular, electrospun nanofibrous scaffolds for tissue engineering was singled out as one of three specialties of exceptional current interest, for its potential to revolutionize biomedical engineering. The ultrafine diameter of the fibers places them on the same scale as naturally occurring collagen fibrils in the extracellular matrix of many common types of living tissue. The versatile nature of electrospinning allows fine-tuning of mechanical and biological properties by varying the composition of a mixture.^[147] In general, biomimetic materials seek to replicate both the structure and function of the natural material. For example, an arterial wall is composed of three concentric layers, each with different physical characteristics. The wall of the artery must be able to withstand pressures up to 260 kPa without bursting, to prevent rupture during blood flow. The ability to tune the surface structure, mechanical property, and biocompatibility with electrospinning makes the technology attractive for such mimicry. Tubular scaffolds have been fabricated by combining electrospinning with hydrogel fabrication on a mandrel.^[147] Many studies involved electrospinning elastomers such as polyurethane (PU), PCL, collagen, and gelatin.^[148-153] Though most of the subsequent cell

viability studies were performed *in vitro*, a few studies have successfully demonstrated success *in vivo*.^[154-156] Illustrative of the latter, He *et al.*^[156] fabricated tubular poly(L-lactic acid-co-ε-caprolactone) (PLL-CL) scaffolds of 3 mm diameter and implanted them in rabbits to replace the inferior superficial epigastric veins. Various images of the tubular scaffold are shown in Figure 7.^[156] These scaffolds maintained their structural integrity for up to 7 weeks *in vivo*, illustrated in **Figure 7g**.

Figure 7. Macroscopic and microscopic structures of the P(LLA-CL) tubular nanofiber scaffold. (a, b) macroscopic structures, (c, d, e, f) microscopic structures shown by SEM photographs: (c) 3-D structure; (d) cross-section; (e) outer lumen; (f) inner lumen. (g) H&E staining image of the oblique-section of the explanted scaffold after 7-week implantation into the rabbit model. The scale bar in (c) is 100 μm . Reproduced with permission from ref. [156]. Copyright: Wiley Interscience, 2009.

These preclinical studies are very encouraging. However, the full potential of these grafts has not yet been tested in clinical applications. Although many of these grafts show mechanical properties similar to the target structure, often the match is limited to the uniaxial tensile mechanical properties. However, other measures of mechanical properties can potentially be more important, such as the burst strength of blood vessel walls. In such cases, a direct measurement with a burst pressure is desirable, as demonstrated by Thomas *et al.*^[157] More rigorous investigations of these nanofibrous scaffolds are necessary to examine other mechanical properties and functionalities. In the case of blood vessels, the functionalities where electrospun fibers have not particularly excelled are the cell viability, bioreactivity, and cell adhesion.^[147] Cell viability and adhesion, in particular, are common issues that need to be resolved for other biomedical applications, such as wound dressings, bone, skin, neural stem cells, connective tissue, and cell encapsulation.^[158] Surface modification of these polymers, whether *in situ* or *ex situ*, needs to be examined for improved compatibility with cells. Recent studies attempted to resolve the cell compatibility *in situ* by combining electrospinning with electrospraying.^[159] Stankus *et al.* electrosprayed vascular cells and simultaneously electrospun poly(ester urethane) urea (PEUU) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) solvent.^[160] Their method showed

that cell viability improved, though the mechanical integrity of PEUU was sacrificed due to gelation within the fiber network.^[160] Although this problem has not yet been fully addressed, this progress in processing clearly shows promise, offering clinical viability of nanofiber scaffolds in the future.

3.1.5 Mechanical Properties of Ultrafine fibers

In this last example, we bring together the topics of high performance and ultrafine diameter in synthetic polymer fibers. Several studies have shown that reduction in the diameter of fibers below about 500 nm is accompanied by improvements in tensile stiffness.^[161-164] To the extent that such reduction in diameter is achieved through high levels of extensional deformation, improvements in stiffness and strength can be traced to higher levels of molecular orientation and crystallinity,^[165-167] in accord with the lessons learned from other high performance fibers. In one striking example, Li *et al* fabricated individual UHMWPE nanofibers with diameters on the order of 100 nm, using a hot tip-drawing process with a gel of UHMWPE and a micromanipulator; these fibers exhibited tensile moduli on the order of 300 GPa,^[168] Though the process does not lend itself well to scale-up, it confirms in a dramatic way the principle of improved mechanical properties with reduction of fiber diameter to nanometer dimensions.

Increases in yield strength and toughness have also been noted to occur with decreases in fiber diameter; such increases are not always reflected by the high performance fibers discussed earlier. One explanation links the increase in strength and toughness to reduction of diameter below a characteristic length for flaws, in accordance with Griffith's theory.^[169] To illustrate this idea, **Figure 8**^[170] shows a cartoon of fiber microstructure as a function of fiber diameter. It has

been argued that a fiber with a diameter on the order of 100 nm or less (e.g. carbon nanotubes, polymer nanofibers) would have fewer defects, resulting in higher strength and toughness.^[170, 171]

Figure 8. Schematic of transverse sections of fibers. Textile fibers are large diameter ($\sim 100\ \mu\text{m}$)^[171] with a partially crystalline structure (left); high-performance fibers are around $10\ \mu\text{m}$ ^[171] in diameter and feature more extended chains, leading to higher strength and modulus, but still contain many defects (center), whereas the ideal fiber would have a much smaller diameter ($\sim 100\ \text{nm}$)^[171] and be essentially defect free (right). Reproduced with permission from ref. [170]. Copyright: American Association for the Advancement of Science, 2008.

Electrospun fibers typically exhibit Young's moduli of 0.1 GPa to 10 GPa, and strengths well below 1.0 GPa, far below those of high performance polymers discussed above.^[172-174] As mentioned above, recent studies have shown a 3- to 5-fold increase of the fiber modulus with decreasing diameter below about 500 nm,^[161-164] the improvements in stiffness being related to higher levels of molecular orientation within the thinner fibers.^[175] The origin of this molecular

orientation has been explained in terms of a surface oriented layer,^[163] core-shell geometry,^[176] or confined supramolecular orientation.^[164] Greenfield *et al.* recently proposed a modeling scheme to relate the increased modulus to the extensional flow of an entangled solution via the flow-induced molecular orientation (*c.f.* **Figure 9**).^[177]

Figure 9. Relationships of modulus with respect to fiber diameter among electrospun fibers. A comparison between theoretical prediction and experimental values. Reproduced with permission from ref. [177]. Copyright: American Chemical Society, 2016.

Despite these recent improvements, electrospun fibers still fall significantly short of the state of the art in high performance fibers. Boland and co-workers electrospun single-walled carbon nanotube/polyvinyl alcohol composite fibers with Young's moduli up to 85 GPa.^[178] Other groups have attempted to electrospin the base materials used in high performance fibers such as

Kevlar and UHMWPE. Reneker and co-workers were the first to electrospin PPTA^[179], but only produced short fibers with a wide distribution of diameters. More recently, Yao *et al.* reported a modulus of 59 GPa for a short filament of electrospun *p*-aramid fiber.^[180] They also electrospun co-polyimide fiber bundles with a Young's modulus of 38 GPa and strength of 1.6 GPa.^[181] Dzenis and co-workers electrospun ultrafine PAN fibers ($d \sim 250$ nm) with Young's modulus, true strength, and toughness as high as 48 GPa, 1.75 GPa, and 0.6 GPa, respectively.^[182] There have also been several efforts in the past to electrospin PE of various forms, but all of them faced difficulties in achieving thin, monodisperse PE fibers with high mechanical strength.^[183-187] In general, electrospinning of PE is complicated by the necessity to elevate and control process temperatures, and its low solubility in polar solvents commonly used for electrospinning. Despite such complications, a recent paper describing “gel-electrospinning” applied to UHMWPE^[188] reports submicron diameter fibers with Young's moduli of 73 ± 13 GPa, yield strengths of 3.5 ± 0.6 GPa, and toughnesses of 1.8 ± 0.3 GPa. Among the smallest fibers examined, one with a diameter of 490 ± 50 nm showed a Young's modulus of 110 ± 16 GPa, ultimate tensile strength of 6.3 ± 0.9 GPa, and toughness of 2.1 ± 0.3 GPa, a combination of mechanical properties that is unparalleled among polymer nanofibers to date. The correlation of stiffness, strength, and toughness with fiber diameter is attributed to increased crystallinity and crystallite orientation, and to surface-enhanced molecular slip processes.

3.2 Challenges and Opportunities

Although electrospun fibers have shown great promise in many diverse materials applications, one major obstacle that prevents their widespread commercial development is the low production rate of the process. On average, a single-nozzle electrospinning process can fabricate 1-100 mg

of nanofibers per hour^[189-191] Over the last decade, productivity of electrospinning technologies has increased significantly with the introduction of production prototypes at a semi-industrial scale. For instance, the Nanospider[®] technology of Elmarco, Inc. (Liberec, CZ), uses free surface electrospinning from wire electrodes to fabricate 200 nm poly(vinyl alcohol) (PVA) at a production rate of 200 g/h.^[192] Employing 250 pins of 20 nozzles each, Fintex Inc. (Lebanon, PA) demonstrated the fabrication of 100 nm diameter fibers of Nylon 6 at a production rate of 0.7 kg/h.^[193] Other possible modifications include employing gas-assisted electrospinning, or “electroblowing”, which can increase productivity up to one order of magnitude higher than for a single nozzle.^[63]

Alternatively, other methods for fabricating ultrafine fibers may help to meet the needs of industrial-scale productivity. Melt blowing, for instance, is already widely used in industry to fabricate fibers with diameters around 1 μm .^[194] However, the choice of materials are often limited to a few polymers, such as polypropylene (PP), PS, or polybutylene terephthalate (PBT), and the dispersity of fiber diameter tends to be large.^[195] Some other methods are also limited in the range of materials that they can process into ultrafine fibers.^[196,197] “Touch spinning”^[198] and “pull spinning”^[199] are among the newest methods reported for production of ultrafine fibers. However, centrifugal spinning has gained perhaps the most attention to date, due to its high productivity and capacity to work with a wide-range of polymers.^[194] Although the technology dates back over 50 years^[62] centrifugal spinning as a means to fabricate ultrafine fibers has grown significantly in popularity over the last decade. Weitz *et al.* reported fabrication of PMMA nanofibers with average diameter small as 25 nm.^[200] Lozano and Sakar developed a three-plate spinning head system to fabricate PEO nanofibers.^[201] The reported production rate

was around 50 g/h, significantly higher than that of a typical lab-scale electrospinning process. In addition, centrifugal spinning can produce fibers with diameters similar to those obtained by electrospinning, but using more concentrated polymer solutions; this results in less solvent waste and increased mass production rate. Despite these promising reports, centrifugal spinning has gained less academic interest due to the cost barrier associated with initial setup when compared to electrospinning.^[194]

4. Conclusion

The synthetic polymer fiber industry has come a long way from Nylon stockings in the 1930's. Many of these technologies have been around now for decades, and have seemingly exhausted opportunities for improvement. However, the demand for better high performance fibers remains strong, in both civilian and defense applications. Opportunities are identified with recent innovations in architectural control of the polymers, application of advanced processes to other known polymer types, and substitution of more environmentally benign solvents. Meanwhile, ultrafine fibers and technologies for their fabrication are both relatively new compared to more conventional fibers and processes, and would appear ripe for exploitation. The unique properties that arise from the sub-micon length-scale have attracted applications that span over multiple disciplines of engineering and science over the last two decades. Rigorous investigation of process-structure-property relationships has led to control over both internal and external structures of these fibers, which are used to make hierarchically-ordered structures, enhance material properties, and provide for functionalities therein. Both high performance and ultrafine polymer fibers are quintessential to the modern polymer enterprise. As polymer science and

industry have been for the last hundred years or so, these materials and the associated technologies will constantly be challenged to meet the unmet needs.

AUTHOR INFORMATION

Corresponding Author

Gregory C. Rutledge* rutledge@mit.edu*

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Funding for this work was provided by the U.S. Army through the Natick Soldier Research, Development and Engineering Center (NSRDEC).

ORCID Identifiers

Jay H. Park: 0000-0002-3302-2068

Gregory C. Rutledge: 0000-0001-8137-1732

REFERENCES

- [1] Flory, P.J. *Principles of Polymer Chemistry* Cornell University Press, Ithaca, NY, **1953**
- [2] Hooke, R. *Micrographia: or some physiological descriptions of minute bodies made by magnifying glasses: with observations and inquiries thereupon*, Royal Society, London, **1667**, 6-10.
- [3] F. Aftalion, *A History of the International Chemical Industry*, Ch 3, Chemical Heritage Press: Philadelphia, 2001.
- [4] Corbman, B. P. *Textiles:Ffiber to Fabrics*; McGraw-Hill, New York, **1983**.
- [5] Bai, J. *Advanced fibre-reinforced polymer (FRP) composites for structural applications*; Woodhead Publ. Oxford, **2013**.
- [6] Carothers, W. H.; Hill, J. W. Studies of Polymerization and Ring Formation. XII. Linear Superpolyesters *J. Am.Chem. Soc.* **1932**, 54, 1559-1587.
- [7] Hounshell, D.; Smith, J. K. *Science and Corporate Strategy: Du Pont R&D 1902-1980*, Cambridge University Press, **1989**.
- [8] Rauschendorfer, L. *The Industrial Association of Chemical Fibers*. Wiley-VCH, Weinheim, **2013**
- [9] Afshari, M.; Kotek, R.; Chen, P. *High Performance Polymers and Engineering Plastics* **2011**, 269–340.
- [10] Chung, H.; Luo, J.; Gulgunje, P. J.; Kumar, S. Structural and Functional Fibers, *Annu. Rev. Mater. Res.*, **2017**, 47, 336-359.

- [11] Adams, W. W.; Eby, R. K. High-Performance Polymer Fibers *MRS Bulletin*, **1987**, *12*, 22-26.
- [12] Jiang, H.; Adams, W. W.; Eby, R. K. High Performance Polymer Fibers *Materials Science and Technology* **2006**
- [13] Gabara, V. *High performance fibers 1: aramid fibers. Synthetic Fibre Materials*, H. Brody, ed. New York. Longman Publishing Group, New York. **1994**.
- [14] Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cunniff, P.; Sennett, M.; Windle, A. High-Performance Carbon Nanotube Fiber *Science* **2007**, *318*, 1892–1895.
- [15] Bacon, R. U.S. Patent 2957756, March 18, **1958**.
- [16] Fitzer, E. *Carbon Fibers Filaments and Composites* **1990**, 169–219.
- [17] Chand, S. *J. Mater. Sci.* Carbon Fibers for Composites **2000**, *35*, 1303–1313.
- [18] Committee on High-Performance Structural Fibers for Advanced Polymer Matrix Composites, National Research Council. In *High-Performance Structural Fibers for Advanced Polymer Matrix Composites*; The National Academies Press: Washington, DC, **2005**.
- [19] Chemical Economics Handbook. Menlo Park, CA, SRI Consulting. **1999**.
- [20] Hill, E. H. W.; Kwolek, S. L.; Morgan, P. W. U.S. Patent 3006899, Oct. 31 1961.
- [21] Kwolek, S. L.; Morgan, P. W.; Sorenson, W. R. U.S. Patent 3063966, Nov. 13 1962
- [22] Preston, J. “Polyamides, Aromatic” in *Encyclopedia of Polymer Science and Engineering*, Wiley-Interscience: New York, 1987, 381.

- [23] Kwolek, S. L. U.S. Patent 3671542, June 20, 1972.
- [24] Morgan, P.W., Synthesis and Properties of Aromatic and Extended Chain Polyamides *Macromolecules* **1977**, *10*, 6, 1381-1390.
- [25] Kwolek, S.L., Morgan, P.W., Schaefgen, J.R., Gulrich, L.W. Synthesis, Anisotropic Solutions, and Fibers of Poly(1,4-benzamide) *Macromolecules* **1977**, *10*, 6, 1390-1396.
- [26] Bair, T.I.; Morgan, P.W.; Killian, F.L. Poly(1,4-phenyleneterephthalamides). Polymerization and Novel Liquid-Crystalline Solutions *Macromolecules* **1977**, *10*, 6, 1396-1400.
- [27] Arpin, M.; Strazielle, C. Characterization and Conformation of Aromatic Polyamides: Poly(1,4-phenylene terephthalamide) and Poly(p-benzamide) in Sulphuric Acid *Polymer* **1977**, *18*, 591-598.
- [28] Zero, K.; Aharoni, S.M. Depolarization Ratios and Rigidity of Aromatic Polyamides *Macromolecules* **1987**, *20*, 1957-1960.
- [29] Blades, H. U.S. Patent 3767756, Oct 23 1973.
- [30] Blades, H. U.S. Patent 3869430, Mar. 4 1975.
- [31] Chung, T. The Recent Developments of Thermotropic Liquid Crystalline Polymers *J. Polym. Eng. Sci.* **1986**, *26*, 901-919.
- [32] Bigg, D. M. A Review of Techniques for Processing Ultra-High Modulus Polymers *Polym. Eng. Sci.* **1976**, *16*, 725-734.

- [33] Chae, H. G.; Kumar, S. Rigid-Rod Polymeric Fibers *J. App. Poly. Sci.* **2006**, *100*, 791–802.
- [34] Wolfe, J. F.; Loo, B. H.; Arnold, F. E. Rigid-Rod Polymers. 2. Synthesis and Thermal Properties of Para-Aromatic Polymers with 2,6-Benzobisthiazole Units in the Main Chain *Macromolecules* **1981**, *14*, 915-920.
- [35] Toyobo Zylon ®. <http://www.toyobo-global.com/seihin/kc/pbo/>. Accessed March 3rd, 2017.
- [36] Teramoto, Y.; Kubota, F. Zylon®: Super Fiber from Lyotropic Liquid Crystal of the Most Rigid Polymer *High-Performance and Specialty Fibers* **2016**, 191–216.
- [37] Reichwein, A.M.; Sikkema, D.J. U.S. Patent 5939553, Aug. 17,1999.
- [38] Cadogan, D.; Sandy, C.; Grahne, M. Development and Evaluation of The Mars Pathfinder Inflatable Airbag Landing System *Acta Astronautica* **2002**, *50*, 633–640.
- [39] Ziegler, K. in *Organometallic Chemistry*, H. Zeiss, Ed.; ACS Monograph 147; Reinhold Publishing Corp.: New York, 1960.
- [40] Kelly, J. M. Ultra-High Molecular Weight Polyethylene *J. Macromol. Sci. Part C: Polymer Reviews* **2002**, *42*, 355–371.
- [41] Chauh, H.H.; Kanamoto, T.; Porter, R.S. *Measures for Polymer Chain Extension, in High Modulus Polymers: Approaches to Design and Development.* Zachariades, A.E.;Porter, R.S. Eds. Marcel Dekker, New York, Marcel Dekker 1988.

- [42] Rutledge, G.C., “Modeling of Polymer Crystals”, in *Simulation Methods for Polymers*, M. Kotelyanskii and D.N. Theodorou, Eds., Ch. 7, Dekker: New York, 2004.
- [43] Smith, P.; Lemstra, P. J. Ultra-High-Strength Polyethylene Filaments by Solution Spinning/Drawing *J. Mater. Sci.* **1980**, *15*, 505-514.
- [44] Graessley, W. M. Polymer Chain Dimensions and the Dependence of Viscoelastic Properties on Concentrations, Molecular Weight, and Solvent Power *Polymer* **1980**, *21*, 258-262.
- [45] DeLong, D. J. *Carbon fiber cost analysis and trends, presentation at the Global Outlook for Carbon Fiber*, Raleigh, NC, **2002**.
- [46] MirAcle, www.ropes.co.kr/MirAcle/, accessed March 29th, 2017.
- [47] Kelly, A.; Macmillan, N. H. *Strong Solids*, Oxford University Press, Oxford, U.K., **1986**.
- [48] Boudreaux, D. S. Calculations of the Strength of the Polyethylene Molecule *J. Polym. Sci.: Polym. Phys.* **1973**, *11*, 1285–1292.
- [49] O’Connor, T. C.; Robbins, M. O. Chain Ends and The Ultimate Strength of Polyethylene Fibers *ACS Macro Letters* **2016**, *5*, 263–267.
- [50] Kitagawa, T.; Ishitobi, M.; Yabuki, K. An analysis of deformation process on poly-p-phenylenebenzobisoxazole fiber and a structural study of the new high-modulus type PBO HM+ fiber *J Polym Sci Part B: Polym Phys* **2000**, *38*, 1605-1611.

- [51] Bartczak, Z.; Beris, P. F. M.; Wasilewski, K.; Galeski, A.; Lemstra, P. J. Deformation of The Ultra-High Molecular Weight Polyethylene Melt in The Plane-Strain Compression *J. Appl. Polym. Sci.* **2012**, *125*, 4155–4168.
- [52] Lu, C.; Blackwell, C.; Ren, Q.; Ford, E. Effect of the Coagulation Bath on the Structure and Mechanical Properties of Gel-Spun Lignin/Poly(vinyl alcohol) Fibers *ACS Sustainable Chem. Eng.* **2017**, *5*, 2949-2959.
- [53] Minus, M. L.; Chae, H. G.; Kumar, S. Interfacial Crystallization in Gel-Spun Poly (vinyl alcohol)/Single-Wall Carbon Nanotube Composite Fibers *Macromol. Chem. Phys.* **2009**, *210*, 1799–1808.
- [54] Chae, H. G.; Newcomb, B. A.; Gulgunje, P. V.; Liu, Y.; Gupta, K. K.; Kamath, M. G.; Lyons, K. M.; Ghoshal, S.; Pramanik, C.; Giannuzzi, L.; Şahin, K.; Chasiotis, I.; Kumar, S. High Strength and High Modulus Carbon Fibers *Carbon* **2015**, *93*, 81–87.
- [55] Smith, P.; Lemstra, P. J. U.S. Patent 4344908, Aug 17, 1982.
- [56] Prevorsek, D. C.; Kavesh, S. U.S. Patent 4413110, Nov 1, 1983.
- [57] Rajput, A. W.; Aleem, A. u.; Arain, F. A. An Environmentally Friendly Process for the Preparation of UHMWPE As-Spun Fibres *Int. J. Polym. Sci.* **2014**, 1–5.
- [58] Schaller, R.; Feldman, K.; Smith, P.; Tervoort, T. A. High-Performance Polyethylene Fibers “Al Dente”: Improved Gel-Spinning of Ultrahigh Molecular Weight Polyethylene using Vegetable Oils *Macromolecules* **2015**, *48*, 8877–8884.
- [59] Doshi, J.; Reneker, D. H. Electrospinning Process and Applications of Electrospun Fibers *J. Electrostat.* **1995**, *35*, 151–160.

- [60] Boys, C. V. On the Production, Properties, and Some Suggested Uses of The Finest Threads *Proceedings of the Physical Society of London* **1887**, 9, 8–19.
- [61] Harding, J.; Keller, J.; Buntin, R. U.S. Patent 3825380, July 7 1974.
- [62] Jiri, Havlas; Karel, Valasek; Miloslav, Pavek U.S. Patent 3328949, July 4 1967.
- [63] Um, I. C.; Fang, D.; Hsiao, B. S.; Okamoto, A.; Chu, B. Electro-spinning and Electro-blowing of Hyaluronic Acid *Biomacromolecules* **2004**, 5, 1428–1436.
- [64] “National Nanotechnology Initiative: Leading to the Next Industrial Revolution”, White House press release, Jan. 21, 2000.
- [65] S. A. Edwards *The nanotech pioneers: where are they taking us?* Wiley-VCH Verlag Gmbh & Co. Weinheim, Germany, **2006**.
- [66] Y. Dzenis, Spinning Continuous Fibers for Nanotechnology *Science* **2004**, 304, 1917-1919.
- [67] Taylor, G. I. Disintegration of Water Drops in An Electric Field *Proc. R. Soc.* A280 **1964**, 383-397.
- [68] Saville, D. A. Electrohydrodynamic Stability: Fluid Cylinders in Longitudinal Electric Fields *Phys. Fluids* **1970**, 13, 2987-2994.
- [69] Ganan-Calvo, A. M. Cone-Jet Analytical Extension of Taylor's Electrostatic Solution and The Asymptotic Universal Scaling Laws in Electrospraying *Phys. Rev. Lett.* **1997**, 79, 217-220.
- [70] Hohman, M. M.; Shin, Y. M.; Rutledge, G. C.; Brenner, M. P. Electrospinning and Electrically Forced Jets. I. Stability Theory *Phys. Fluids* **2001**, 13, 2201–2220.

- [71] Fridrikh, S. V.; Yu, J. H.; Brenner, M. P.; Rutledge, G. C. Controlling The Fiber Diameter During Electrospinning *Phys. Rev. Lett.* **2003**, *90*, 144502.
- [72] Carroll, C.P.; Joo, Y. L. Electrospinning of Viscoelastic Boger Fluids: Modeling and Experiments *Phys. Fluids* **2006**, *18*, 053102.
- [73] Carroll, C. P.; Joo, Y. L. Axisymmetric Instabilities of Electrically Driven Viscoelastic Jets *J. Non-Newtonian Fluid Mech.* **2008**, *153*, 130–148.
- [74] Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. Bending Instability of Electrically Charged Liquid Jets of Polymer Solutions in Electrospinning *J. Appl. Phys.* **2000**, *87*, 4531-4547.
- [75] Li, D.; Xia, Y. Electrospinning of Nanofibers: Reinventing the Wheel? *Adv. Mat.* **2004**, *16*, 1151–1170.
- [76] Long, Y.; Chen, H.; Yang, Y.; Wang, H.; Yang, Y.; Li, N.; Li, K.; Pei, J.; Liu, F. Electrospun Nanofibrous Film Doped With A Conjugated Polymer for DNT Fluorescence Sensor *Macromolecules* **2009**, *42*, 6501–6509.
- [77] Choong, L.T.; Khan, Z.; Rutledge, G.C. Permeability of Electrospun Fiber Mats under Hydraulic Flow *J. Membr. Sci.* **2014**, *451*, 111-116.
- [78] Hwang, T. H.; Lee, Y. M.; Kong, B.-S.; Seo, J.-S.; Choi, J. W. Electrospun Core–Shell Fibers for Robust Silicon Nanoparticle-based Lithium Ion Battery Anodes *Nano Lett.* **2012**, *12*, 802–807.

- [79] Park, J. H.; Joo, Y. L. Tailoring Nanorod Alignment in a Polymer Matrix by Elongational Flow Under Confinement: Simulation, Experiments, and Surface Enhanced Raman Scattering *Soft Matter* **2014**, *10*, 3494-3505.
- [80] Bhardwaj, N.; Kundu, S. C. Electrospinning: A Fascinating Fiber Fabrication Technique *Biotechnol. Adv.* **2010**, *28*, 325–347.
- [81] W. Barthlott, C. Heinhuis, D. Cutler, F. Ditsch, I. Meusel, I. Theisen, H. Wilhelm, Classification and Terminology of Plant Epicuticular Waxes *Botanical J. Linnean Soc.*, **1998**, *126*, 237-260.
- [82] Ma, M.; Hill, R.H.; Rutledge, G.C. A Review of Recent Results on Superhydrophobic Materials Based on Micro- and Nanofibers *J. Adh. Sci. Technol.* **2008**, *22*, 1799-1817.
- [83] Wenzel, R.N. Resistance of Solid Surfaces to Wetting by Water *Ind. Eng. Chem.* **1936**, *28*, 988-994.
- [84] Cassie, A.B.D.; Baxter, S. Wettability of Porous Surfaces *Trans Farad. Soc.* **1944**, *40*, 546-551.
- [85] Rijke, A.M. Wettability and Phylogenetic Development of Feather Structure in Water Birds *J. Exp. Biol.*, **1970**, *52*, 469-479.
- [86] Ma, M.; Hill, R. M.; Lowery, J. L.; Fridrikh, S. V.; Rutledge, G. C. Electrospun Poly (styrene-block-dimethylsiloxane) Block Copolymer Fibers Exhibiting Superhydrophobicity *Langmuir* **2005**, *21*, 5549–5554.

- [87] Acatay, K.; Simsek, E.; Ow-Yang, C.; Menciloglu, Y. Z. Tunable, Superhydrophobically Stable Polymeric Surfaces by Electrospinning *Angew. Chem. Int. Ed.* **2004**, *43*, 5210-5213.
- [88] Singh, A.; Steely, L.; Allcock, H. R. Poly [bis (2, 2, 2-trifluoroethoxy) phosphazene] Superhydrophobic Nanofibers *Langmuir* **2005**, *21*, 11604-11607.
- [89] Agarwal, S.; Horst, S.; Bognitzki, M. Electrospinning of Fluorinated Polymers: Formation of Superhydrophobic Surfaces *Macromol. Mater. Eng.* **2006**, *291*, 592-601.
- [90] Gu, Z.-Z.; Wei, H.-M.; Zhang, R.-Q.; Han, G.-Z.; Pan, C.; Zhang, H.; Tian, X.-J.; Chen, Z.-M. Artificial Silver Ragwort Surface *App. Phys. Lett.* **2005**, *86*, 201915.
- [91] Tuteja, A., Choi, W., Ma, M., Mabry, J.M., Mazzella, S.A., Rutledge, G.C., McKinley, G.H., Cohen, R.E. *Science* **2007**, *318*, 1618-1622.
- [92] Tuteja, A., Choi, W., Mabry, J.M., McKinley, G.H., Cohen, R.E. Robust Omniphobic Surfaces *Proc. Natl. Acad. Sci. U.S.A.*, **2008**, *105*, 18200.
- [93] Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. Superhydrophobic Fabrics Produced by Electrospinning and Chemical Vapor Deposition *Macromolecules* **2005**, *38*, 9742–9748.
- [94] Guo, F.; Servi, A.; Liu, A.; Gleason, K. K.; Rutledge, G. C. Desalination by Membrane Distillation using Electrospun Polyamide Fiber Membranes with Surface Fluorination by Chemical Vapor Deposition *ACS Appl. Mater. Int.* **2015**, *7*, 8225–8232.

- [95] Hardman, S. J.; Muhamad-Sarih, N.; Riggs, H. J.; Thompson, R. L.; Rigby, J.; Bergius, W. N. A.; Hutchings, L. R. Electrospinning Superhydrophobic Fibers using Surface Segregating end-Functionalized Polymer Additives *Macromolecules* **2011**, *44*, 6461–6470.
- [96] Megelski, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F. Micro-and Nanostructured Surface Morphology on Electrospun Polymer Fibers *Macromolecules* **2002**, *35*, 8456–8466.
- [97] Pai, C. L.; Boyce, M. C.; Rutledge, G. C. Morphology of Porous and Wrinkled Fibers of Polystyrene Electrospun from Dimethylformamide *Macromolecules* **2009**, *42*, 2102-2114.
- [98] Wang, L.; Pai, C. L.; Boyce, M.C.; Rutledge, G. C. Wrinkled Surface Topographies of Electrospun Polymer Fibers *Appl. Phys. Lett.* **2009**, *94*, 151916
- [99] Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. Controlling Surface Morphology of Electrospun Polystyrene Fibers: Effect of Humidity and Molecular Weight in the Electrospinning Process *Macromolecules* **2004**, *37*, 573-578.
- [100] Ma, M.; Gupta, M.; Li, Z.; Zhai, L.; Gleason, K. K.; Cohen, R. E.; Rubner, M. F.; Rutledge, G. C. Decorated Electrospun Fibers Exhibiting Superhydrophobicity *Adv. Mat.* **2007**, *19*, 255–259.
- [101] Zheng, J.; He, A.; Li, J.; Xu, J.; Han, C. C. Studies on the Controlled Morphology and Wettability of Polystyrene Surfaces by Electrospinning or Electrospraying *Polymer* **2006**, *47*, 7095–7102.
- [102] Koo, W.-T.; Choi, S.-J.; Kim, N.-H.; Jang, J.-S.; Kim, I.-D. Catalyst-decorated Hollow WO₃ Nanotubes using Layer-by-Layer Self-Assembly on Polymeric Nanofiber Templates and

Their Application in Exhaled Breath Sensor *Sensors and Actuators B: Chemical* **2016**, 223, 301–310.

[103] Cheng, H.-H.; Chen, F.; Yu, J.; Guo, Z.-X. Gold-nanoparticle-decorated thermoplastic polyurethane electrospun fibers prepared through a chitosan linkage for catalytic applications *J. Appl. Polym. Sci.* **2017**, 1, 44336.

[104] Lee, J. A.; Krogman, K. C.; Ma, M.; Hill, R. M.; Hammond, P. T.; Rutledge, G. C. Highly Reactive Multilayer-Assembled TiO₂ Coating on Electrospun Polymer Nanofibers *Adv. Mater.* **2009**, 21, 1252–1256.

[105] Chen, X.; Dong, B.; Wang, B.; Shah, R.; Li, C. Y. Crystalline Block Copolymer Decorated, Hierarchically Ordered Polymer Nanofibers *Macromolecules* **2010**, 43, 9918–9927.

[106] Jing, X.; Mi, H.-Y.; Cordie, T. M.; Salick, M. R.; Peng, X.-F.; Turng, L.-S. Fabrication of Shish-kebab Structured Poly (ϵ -caprolactone) Electrospun Nanofibers that Mimic Collagen Fibrils: Effect of Solvents and Matrigel Functionalization *Polymer* **2014**, 55, 5396–5406.

[107] Yang, Y.; Centrone, A.; Chen, L.; Simeon, F.; Hatton, T. A.; Rutledge, G. C. Highly porous electrospun polyvinylidene fluoride (PVDF)-based carbon fiber *Carbon* **2011**, 49, 3395–3403.

[108] Dersch, R.; Liu, T.; Schaper, A. K.; Greiner, A.; Wendorff, J. H. Electrospun nanofibers: Internal structure and intrinsic orientation *J. Polym. Sci. A. Polym. Chem.* **2003**, 41, 545–553.

[109] Si, Y.; Ren, T.; Li, Y.; Ding, B.; Yu, J. Fabrication of magnetic polybenzoxazine-based carbon nanofibers with Fe₃O₄ inclusions with a hierarchical porous structure for water treatment *Carbon* **2012**, 50, 5176–5185.

- [110] Ko, F.; Gogotsi, Y.; Ali, A.; Naguib, N.; Ye, H.; Yang, G.; Li, C.; Willis, P. Electrospinning of continuous carbon nanotube-filled nanofiber yarns *Adv. Mater.* **2003**, *15*, 1161–1165.
- [111] Hou, H.; Ge, J. J.; Zeng, J.; Li, Q.; Reneker, D. H.; Greiner, A.; Cheng, S. Z. D. Electrospun polyacrylonitrile nanofibers containing a high concentration of well-aligned multiwall carbon nanotubes *Chem.Mater.* **2005**, *17*, 967–973.
- [112] Dror, Y.; Salalha, W.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. Carbon Nanotubes Embedded in Oriented Polymer Nanofibers by Electrospinning *Langmuir* **2003**, *19*, 7012–7020.
- [113] Matsen, M. W.; Bates, F. S. Unifying Weak-and Strong-Segregation Block Copolymer Theories *Macromolecules* **1996**, *29*, 1091-1098.
- [114] Leibler, L. Theory of Microphase Separation in Block Copolymers *Macromolecules* **1980**, *13*, 1602–1617.
- [115] Ruotsalainen, T.; Turku, J.; Heikkilä, P.; Ruokolainen, J.; Nykänen, A.; Laitinen, T.; Torkkeli, M.; Serimaa, R.; Ten Brinke, G.; Harlin, A.; Ikkala, O. Towards Internal Structuring of Electrospun Fibers by Hierarchical Self-assembly of Polymeric Comb-Shaped Supramolecules *Adv. Mater.* **2005**, *17*, 1048–1052.
- [116] Kalra, V.; Kakad, P. A.; Mendez, S.; Ivannikov, T.; Kamperman, M.; Joo, Y. L. Self-Assembled Structures in Electrospun Poly (styrene-*b* lock-isoprene) Fibers *Macromolecules* **2006**, *39*, 5453-5457.

- [117] Kalra, V.; Mendez, S.; Lee, J. H.; Nguyen, H.; Marquez, M.; Joo, Y. L. Confined Assembly in Coaxially Electrospun Block Copolymer Fibers *Adv. Mater.* **2006**, *18*, 3299–3303.
- [118] Ma, M.; Krikorian, V.; Yu, J. H.; Thomas, E. L.; Rutledge, G. C. Electrospun Polymer Nanofibers with Internal Periodic Structure Obtained by Microphase Separation of Cylindrically Confined Block Copolymers *Nano Lett.* **2006**, *6*, 2969–2972.
- [119] Ma, M.; Titievsky, K.; Thomas, E. L.; Rutledge, G. C. Continuous Concentric Lamellar Block Copolymer Nanofibers with Long Range Order *Nano Lett.* **2009**, *9*, 1678–1683.
- [120] Shin, K.; Xiang, H.; Moon, S. I.; Kim, T.; McCarthy, T. J.; Russell, T. P. Curving and Frustrating Flatland *Science* **2004**, *306*, 76.
- [121] Wu, Y.; Cheng, G.; Katsov, K.; Sides, S. W.; Wang, J.; Tang, J.; Fredrickson, G. H.; Moskovits, M.; Stucky, G. D. Composite Mesosstructures by Nano-Confinement *Nat. Mater.* **2004**, *3*, 816–822.
- [122] Xiang, H.; Shin, K.; Kim, T.; Moon, S. I.; McCarthy, T. J.; Russell, T. P. Block Copolymers under Cylindrical Confinement *Macromolecules* **2004**, *37*, 5660–5664.
- [123] Kalra, V.; Lee, J.; Lee, J. H.; Lee, S. G.; Marquez, M.; Wiesner, U.; Joo, Y. L. Controlling Nanoparticle Location via Confined Assembly in Electrospun Block Copolymer Nanofibers *Small* **2008**, *4*, 2067–2073.
- [124] Kalra, V.; Lee, J. H.; Park, J. H.; Marquez, M.; Joo, Y. L. Confined Assembly of Asymmetric Block-Copolymer Nanofibers via Multiaxial Jet Electrospinning *Small* **2009**, *5*, 2323–2332.

- [125] Brezesinski, K.; Ostermann, R.; Hartmann, P.; Perlich, J.; Brezesinski, T. Exceptional photocatalytic activity of ordered mesoporous β -Bi₂O₃ thin films and electrospun nanofiber mats *Chem. Mater.* **2010**, *22*, 3079–3085.
- [126] Zhan, S.; Chen, D.; Jiao, X.; Tao, C. Long TiO₂ Hollow Fibers with Mesoporous Walls: Sol–Gel Combined Electrospun Fabrication and Photocatalytic Properties *J. Phys. Chem. B.* **2006**, *110*, 11199–11204.
- [127] Nguyen, T.-A.; Jun, T.-S.; Rasd, M.; Kim, Y. S. Synthesis of Mesoporous Tungsten Oxide Nanofibers using the Electrospinning Method *Mater. Lett.* **2011**, *65*, 2823–2825.
- [128] Teng, M.; Wang, H.; Li, F.; Zhang, B. Thioether-Functionalized Mesoporous Fiber Membranes: Sol–Gel Combined Electrospun Fabrication and Their Applications for Hg²⁺ Removal *J. Colloid Int. Sci.* **2011**, *355*, 23–28.
- [129] Shao, S.; Zhou, S.; Li, L.; Li, J.; Luo, C.; Wang, J.; Li, X.; Weng, J. Osteoblast Function on Electrically Conductive Electrospun PLA/MWCNTs Nanofibers *Biomater.* **2011**, *32*, 2821–2833.
- [130] Chronakis, I. S. *Nanostructured Conductive Polymers* **2010**, 161–207.
- [131] Kidd, B. E.; Forbey, S. J.; Steuber, F. W.; Moore, R. B.; Madsen, L. A. Multiscale Lithium And Counterion Transport In An Electrospun Polymer-Gel Electrolyte *Macromolecules* **2015**, *48*, 4481–4490.
- [132] Reneker, D. H.; Yarin, A. L.; Zussman, E.; Xu, H. Electrospinning of Nanofibers From Polymer Solutions And Melts *Adv. Appl. Mech.* **2007**, *41*, 43–195.

- [133] Ra, E. J.; An, K. H.; Kim, K. K.; Jeong, S. Y.; Lee, Y. H. Anisotropic Electrical Conductivity of MWCNT/PAN Nanofiber Paper *Chem. Phys. Lett.* **2005**, *413*, 188–193.
- [134] Luo, X.; Mather, P. T. Conductive Shape Memory Nanocomposites for High Speed Electrical Actuation *Soft Matter* **2010**, *6*, 2146-2149.
- [135] Laforgue, A.; Robitaille, L. Production of Conductive PEDOT Nanofibers by The Combination of Electrospinning And Vapor-Phase Polymerization *Macromolecules* **2010**, *43*, 4194–4200.
- [136] Zhang, Y.; Rutledge, G. C. Electrical Conductivity of Electrospun Polyaniline And Polyaniline-Blend Fibers And Mats *Macromolecules* **2012**, *45*, 4238-4246.
- [137] Zhang, Y.; Kim, J. J.; Chen, D.; Tuller, H. L.; Rutledge, G. C. Electrospun Polyaniline Fibers as Highly Sensitive Room Temperature Chemiresistive Sensors for Ammonia And Nitrogen Dioxide Gases *Adv. Funct. Mater.* **2014**, *24*, 4005–4014.
- [138] Mao, X.; Hatton, T. A.; Rutledge, G. C. A Review of Electrospun Carbon Fibers as Electrode Materials For Energy Storage *Curr. Org. Chem.* **2013**, *17*, 1390–1401.
- [139] Niu, H. T.; Zhang, J.; Xie, Z. L.; Wang, X. G.; Lin, T. Preparation, Structure and Supercapacitance of Bonded Carbon Nanofiber Electrode Materials *Carbon* **2011**, *49*, 2380-2388.
- [140] Kim, B. H.; Yang, K. S.; Woo, H. G. Preparation and Electrochemical Properties of Carbon Nanofiber Composite Dispersed with Silver Nanoparticles Using Polyacrylonitrile and β -Cyclodextrin *J. Nanosci. Nanotechnol.* **2011**, *11*, 7193-7197.

- [141] Wang, L.; Yu, Y.; Chen, P. C.; Zhang, D. W.; Chen, C. H. Electrospinning Synthesis of C/Fe₃O₄ Composite Nanofibers and Their Application For High Performance Lithium-Ion Batteries *J Power Sources* **2008**, *183*, 717-723.
- [142] Ji, L. W.; Medford, A. J.; Zhang, X. W. Porous Carbon Nanofibers Loaded With Manganese Oxide Particles: Formation Mechanism And Electrochemical Performance as Energy-Storage Materials *Journal of Materials Chemistry* **2009**, *19*, 5593-5601.
- [143] Yu, Y.; Gu, L.; Wang, C. L.; Dhanabalan, A.; van Aken, P. A.; Maier, J. Encapsulation of Sn@carbon Nanoparticles in Bamboo-like Hollow Carbon Nanofibers as an Anode Material in Lithium-based Batteries. *Angew Chem Int Ed* **2009**, *48*, 6485-6489.
- [144] Kim, Y. S.; Shoorideh, G.; Zhmayev, Y.; Lee, J.; Li, Z.; Patel, B.; Chakrapani, S.; Park, J. H.; Lee, S.; Joo, Y. L. The Critical Contribution of Unzipped Graphene Nanoribbons to Scalable Silicon–Carbon Fiber Anodes in Rechargeable Li-ion Batteries *Nano Energy* **2015**, *16*, 446-457.
- [145] Ji, L. W.; Zhang, X. W. Electrospun Carbon Nanofibers Containing Silicon Particles as An Energy-Storage Medium *Carbon* **2009**, *47*, 3219-3226.
- [146] Adams, J.; Pendlebury, D. *Global Research Report Materials Science and Technology*, Thomson Reuters, June 2011.
- [147] Hasan, A.; Memic, A.; Annabi, N.; Hossain, M.; Paul, A.; Dokmeci, M. R.; Dehghani, F.; Khademhosseini, A. Electrospun Scaffolds for Tissue Engineering of Vascular Grafts *Acta Biomater.* **2014**, *10*, 11–25.

- [148] Sato, M.; Nakazawa, Y.; Takahashi, R.; Tanaka, K.; Sata, M.; Aytemiz, D., *et al.* Small-Diameter Vascular Grafts of Bombyx Mori Silk Fibroin Prepared by A Combination of Electrospinning and Sponge Coating *Mater. Lett.* **2010**, *64*, 1786-1788.
- [149] Uttayarat, P.; Perets, A.; Li, M. Y.; Pimton, P.; Stachelek, S. J.; Alferiev, I. *et al.* Micropatterning of Three-Dimensional Electrospun Polyurethane Vascular Grafts *Acta Biomater.* **2010**, *6*, 4229–4237.
- [150] McClure, M. J.; Wolfe, P. S.; Simpson, D. G.; Sell, S. A.; Bowlin, G. L. The Use of Air-Flow Impedance to Control Fiber Deposition Patterns During Electrospinning *Biomaterials* **2009**, *33*, 771–779.
- [151] Zhu, Y. B.; Cao, Y.; Pan, J.; Liu, Y. X. Macro-Alignment of Electrospun Fibers For Vascular Tissue Engineering *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2010**, *92B*, 508–516.
- [152] Soletti, L.; Hong, Y.; Guan, J.; Stankus, J. J.; El-Kurdi, M. S.; Wagner, W. R. *et al.* A Bilayered Elastomeric Scaffold For Tissue Engineering of Small Diameter Vascular Grafts. *Acta Biomater.* **2009**, *6*, 110–122.
- [153] Zander, N. E.; Orlicki, J. A.; Rawlett, A. M.; Beebe, T. P. Quantification of Protein Incorporated into Electrospun Polycaprolactone Tissue Engineering Scaffolds *ACS Appl Mater Interfaces* **2012**, *4*, 2074–2081.
- [154] Wise, S. G.; Byrom, M. J.; Waterhouse, A.; Bannon, P. G.; Ng, M. K. C.; Weiss, A. S. A Multilayered Synthetic Human Elastin/polycaprolactone Hybrid Vascular Graft with Tailored Mechanical Properties *Acta Biomater.* **2011**, *7*, 295–303.

- [155]Soletti, L.; Nieponice, A.; Hong, Y.; Ye, S. H.; Stankus, J. J.; Wagner, W. R.; Vorp, D. A. In Vivo Performance of A Phospholipid-Coated Bioerodable Elastomeric Graft for Small-Diameter Vascular Applications *J. Biomed. Mater. Res. Part A* **2011**, *96A*, 436–448.
- [156]He, W.; Ma, Z. W.; Teo, W. E.; Dong, Y. X.; Robless, P. A.; Lim, T. C.; Ramakrishna, S. Tubular Nanofiber Scaffolds for Tissue Engineered Small-Diameter Vascular Grafts *J. Biomed. Mater. Res. Part A* **2009**, *90A*, 205–216.
- [157]Thomas, V.; Donahoe, T.; Nyairo, E.; Dean, D. R.; Vohra, Y. K. Electrospinning of Biosyn®-based Tubular Conduits: Structural, Morphological, and Mechanical Characterizations *Acta Biomater* **2011**, *7*, 2070–2079.
- [158]Cheng, J.; Jun, Y.; Qin, J.; Lee, S.-H. Electrospinning Versus Microfluidic Spinning of Functional Fibers for Biomedical Applications *Biomaterials* **2017**, *114*, 121–143.
- [159]Ekaputra, A. K.; Prestwich, G. D.; Cool, S. M.; Hutmacher, D. W. Combining Electrospun Scaffolds with Electrosprayed Hydrogels Leads to Three-Dimensional Cellularization of Hybrid Constructs *Biomacromolecules* **2008**, *9*, 2097–2103.
- [160]Stankus, J. J.; Guan, J. J.; Fujimoto, K.; Wagner, W. R. Microintegrating Smooth Muscle Cells into A Biodegradable, Elastomeric Fiber Matrix *Biomaterials* **2006**, *27*, 735–744.
- [161]Pai, C.L.; Boyce, M.C.; Rutledge, G.C. Mechanical Properties of Individual Electrospun PA 6 (3) T Fibers and Their Variation With Fiber Diameter *Polymer* **2011**, *52*, 2295-2301.
- [162]Pai, C.L.; Boyce, M.C.; Rutledge, G.C. On the Importance of Fiber Curvature to the Elastic Moduli of Electrospun Nonwoven Fiber Meshes *Polymer* **2011**, *52*, 6126-6133.

- [163]Ji, Y.; Li, B.; Ge, S.; Sokolov, J. C.; Rafailovich, M. H. Structure and nanomechanical characterization of electrospun PS/clay nanocomposite fibers *Langmuir* **2006**, *22*, 1321-1328.
- [164]Arinstein, A.; Burman, M.; Gendelman, O.; Zussman, E. Effect of supramolecular structure on polymer nanofibre elasticity *Nat. Nanotechnol.* **2007**, *2*, 59-62.
- [165]Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; Brinke, G. T.; Zugenmaier, P. Crystal structure, conformation and morphology of solution-spun poly (L-lactide) fibers *Macromolecules* **1990**, *23*, 634–642.
- [166]Liivak, O.; Blye, A.; Shah, N.; Jelinski, L. W. A Microfabricated Wet-Spinning Apparatus To Spin Fibers of Silk Proteins. Structure– Property Correlations *Macromolecules* **1998**, *31*, 2947–2951.
- [167]Seidel, A.; Liivak, O.; Calve, S.; Adaska, J.; Ji, G.; Yang, Z.; Grubb, D.; Zax, D. B.; Jelinski, L. W. Regenerated spider silk: Processing, properties, and structure *Macromolecules* **2000**, *33*, 775–780.
- [168]Li, P.; Hu, L.; McGaughey, A. J. H.; Shen, S. Crystalline Polyethylene Nanofibers with the Theoretical Limit of Young's Modulus *Adv. Mater.* **2014**, *26*, 1065-1070.
- [169]Griffith, A. A. The Phenomena of Rupture and Flow in Solids *Philos. Trans. R. Soc. A* **1921**, *221*, 163–198.
- [170]Chae, H. G.; Kumar, S. Making Strong Fibers *Science* **2008**, *319*, 908–909.
- [171]Committee on Opportunities in Protection Materials Science and Technology for Future Army Applications In *Opportunities in Protection Materials Science and Technology for Future Army Applications*; The National Academies Press: Washington, DC, **2011**.

- [172]Chew, S. Y.; Hufnagel, T. C.; Lim, C. T.; Leong, K. W. Mechanical properties of single electrospun drug-encapsulated nanofibres *Nanotechnology* **2006**, *17*, 3880-3891.
- [173]Wong, S. C.; Baji, A.; Leng, S. Effect of fiber diameter on tensile properties of electrospun poly (ϵ -caprolactone) *Polymer* **2008**, *49*, 4713-4722.
- [174]Naraghi, M.; Chasiotis, I.; Kahn, H.; Wen, Y.; Dzenis, Y. Novel method for mechanical characterization of polymeric nanofibers *Rev. Sci. Instrum.* **2007**, *78*, 085108.
- [175]Richard-Lacroix, M.; Pellerin, C. Molecular orientation in electrospun fibers: from mats to single fibers *Macromolecules* **2013**, *46*, 9473-9493.
- [176]Reneker, D. H.; Yarin, A. L.; Zussman, E.; Xu, H. in *Advances in Applied Mechanics*; Hassan, A., van der Erik, G., Eds. Elsevier. Amsterdam, **2007**, *41*, 43–346.
- [177] Greenfeld, I.; Sui, X. M.; Wagner, H. D. Stiffness, Strength, and Toughness of Electrospun Nanofibers: Effect of Flow-Induced Molecular Orientation *Macromolecules*, **2016**, *49*, 6518-6530.
- [178] Almecija, D.; Blond, D.; Sader, J. E.; Coleman, J. N.; Boland, J. J. Mechanical Properties of Individual Electrospun Polymer-Nanotube Composite Nanofibers *Carbon* **2009**, *47*, 2253-2258.
- [179] Srinivasan, G.; Reneker, D. H. Structure and Morphology of Small Diameter Electrospun Aramid Fibers *Polymer Int.* **1995**, *36*, 195–201.
- [180] Yao, J.; Jin, J. ; Lepore, E.; Pugno, N. M.; Bastiaansen, C. W. M.; Peijs, T. Electrospinning of p-Aramid Fibers *Macro. Mater. Eng.* **2015**, *12*, 1238-1245.

- [181] Yao, J.; Pantano, M. F.; Pugno, N. M.; Bastiaansen, C. W. M.; Peijs, T. High-performance electrospun co-polyimide nanofibers *Polymer* **2015**, *76*, 105-112.
- [182] Papkov, D.; Zou, Y.; Andalib, M. N.; Goponenko, A.; Cheng, S. Z. D.; Dzenis, Y. A. Simultaneously strong and tough ultrafine continuous nanofibers *ACS Nano* **2013**, *7*, 3324-3331.
- [183] Larrondo, L.; St. John Manley, R. Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties *J. Polym. Sci.-Phys.* **1981**, *19*, 909-920.
- [184] Givens, S.R.; Gardner, K.H.; Rabolt, J.F.; Chase, D.B. High-temperature electrospinning of polyethylene microfibers from solution *Macromolecules* **2007**, *40*, 608-610.
- [185] Yoshioka, T.; Dersch, R.; Greiner, A.; Tsuji, M.; Schaper, A.K. Highly Oriented Crystalline PE Nanofibrils Produced by Electric-Field-Induced Stretching of Electrospun Wet Fibers *Macromol. Mater. Eng.* **2010**, *295*, 1082-1089.
- [186] Rein, D.M.; Shavit-Hadar, L.; Khalfin, R.L.; Cohen, Y.; Shuster, K.; Zussman, E. Electrospinning of ultrahigh-molecular-weight polyethylene nanofibers *J. Polym. Sci.-Phys.* **2007**, *45*, 766-773.
- [187] Rein, D. M.; Cohen, Y.; Ronen, A.; Shuster, K.; Zussman, E. Application of gentle annular gas veil for electrospinning of polymer solutions and melts *Polym. Eng. Sci.* **2009**, *49*, 774-782.
- [188] Park, J. H.; Rutledge, G. C. High Performance Polyethylene Fibers by Gel-Electrospinning **2017** (in preparation).

- [189]Demir, M. M.; Yilgor, E.; Erman, B. Electrospinning of polyurethane fibers *Polymer*, **2002**, *43*, 3303-3309.
- [190]Kessick, R.; Fenn, J.; Tepper, G. The use of AC potentials in electrospraying and electrospinning processes *Polymer*. **2004**, *45*, 2981–2984.
- [191]Ji, L.; Lin, Z.; Li, Y. Formation and characterization of core-sheath nanofibers through electrospinning and surface-initiated polymerization *Polymer* **2010**, *51*, 4368–4374.
- [192]Petras, D.; Maly, M.; Pozner, J.; Trdlicka, J.; Kovac, M., U. S. Patent Application 20100034914, 2010.
- [193]Kim, H.-Y. U. S. Patent 7332050, Feb. 19 2008.
- [194]Zhang, X.; Lu, Y. Centrifugal spinning: an alternative approach to fabricate nanofibers at high speed and low cost *Polym. Rev.* **2014**, *54*, 677–701.
- [195]Ellison, C. J.; Phatak, A.; Giles, D. W.; Macosko, C. W.; Bates, F. S. Melt blown nanofibers: fiber diameter distributions and onset of fiber breakup *Polymer*. **2007**, *48*, 3306–3316.
- [196]Ma, P X.; Zhang, R. Y. Synthetic nano-scale fibrous extracellular matrix *J. Biomed. Mater. Res.* **1999**, *46*, 60–72.
- [197]Yang, Z.; Xu, B. Supramolecular hydrogels based on biofunctional nanofibers of self-assembled small molecules *J. Mater. Chem.* **2007**, *17*, 2385–2393.
- [198]Tokarev, A.; Asheghali, D.; Griffiths, I. M.; Trotsenko, O.; Gruzd, A.; Lin, X.; Stone, H. A.; Minko, S. Touch- and Brush-Spinning of Nanofibers *Adv. Mater.* **2015**, *27*, 6526–6532.

- [199]Deravi, L. F.; Sinatra, N. R.; Chantre, C. O.; Nesmith, A. P.; Yuan, H.; Deravi, S. K.; Goss, J. A.; Macqueen, L. A.; Badrossamy, M. R.; Gonzalez, G. M.; Phillips, M. D.; Parker, K. K. Design and Fabrication of Fibrous Nanomaterials Using Pull Spinning *Macromol. Mater. Eng.* **2017**, 302, 1600404.
- [200]Weitz, R. T.; Harnau, L.; Rauschenbach, S.; Burghard, M.; Kern, K. Polymer nanofibers via nozzle-free centrifugal spinning *Nano Lett.* **2008**, 8, 1187–1191.
- [201]Sarkar, K.; Gomez, C.; Zambrano, S.; Ramirez, M.; Hoyos, E.; Vasquez, H.; Lozano, K. Electrospinning to forcespinning™ *Mater. Today.* **2010**, 13, 12–14.

About the Cover: High performance fibers, characterized by their excellent mechanical properties, and ultrafine fibers, characterized by their submicron diameters, represent two exemplary case studies in fiber science over the last 50 years where macromolecular chemistry and engineering have joined to produce advanced materials with exceptional properties.

Dr. Jay Hoon Park is a postdoctoral associate in Department of Chemical Engineering at Massachusetts Institute of Technology. He received his B.S. in chemical engineering from Johns Hopkins University in 2004, an M.S. in chemical engineering from Cornell University in 2009, and a Ph.D. in chemical engineering from Cornell University in 2013. During his years at Cornell, he had studied the self-assembly of polymer/nanoparticle composites under flow and confinement, where he examined the correlation between the meso-scale structure and its functionality. As a postdoctoral associate in MIT, he has been developing a process to fabricate high performance polymer nanofibers that can rival commercial ones.

Gregory C. Rutledge is the Lamont du Pont Professor in the Department of Chemical Engineering at the Massachusetts Institute of Technology (MIT). He holds B.S. and Ph.D. degrees in chemical engineering from the University of Virginia and MIT, respectively. He

served as Director of the Program in Polymer Science and Technology and as Executive Officer in the Department of Chemical Engineering at MIT. He is a Fellow of the American Institute of Chemical Engineers, the American Physical Society, and the Polymer Materials Science and Engineering (PMSE) Division of the American Chemical Society, and he is a recipient of The Founders Award of the Fiber Society. Prof. Rutledge's research on molecular engineering of soft matter focuses on the relationships between processing, structure and properties of engineered polymers, using statistical mechanics and knowledge of their chemistry and molecular level architecture. His expertise includes both computations and experiments. Since 2001 he and his coworkers have published extensively on the fabrication, properties and applications of ultrafine polymer fibers and nonwoven membranes formed by the electrospinning technology. (Photo – David Sella)