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Anisotropic Nanomaterial Liquid Crystals: From Fiber Spinning to Additive Manufacturing

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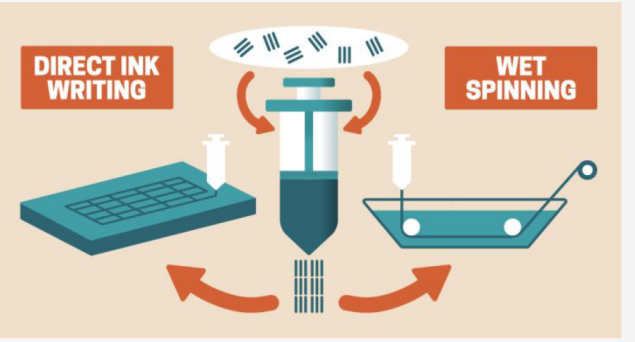
ABSTRACT: There have long been synergistic relationships among the discovery of new anisotropic materials, advancements in liquid crystal science, and the production of manufactured goods with exciting new properties. Ongoing progress in understanding the phase behavior and shear response of lyotropic liquid crystals comprised of one-dimensional and two-dimensional nanomaterials, coupled with advancements in extrusion-based manufacturing methods, promises to enable the scalable production of solid materials with outstanding properties and controlled order across multiple length scales. This Perspective highlights progress in using anisotropic nanomaterial liquid crystals in two extrusion-based manufacturing methods: solution spinning and direct ink writing. It also describes current challenges and opportunities at the interface of nanotechnology, liquid crystalline science, and manufacturing. The intent is to inspire additional transdisciplinary research that will enable nanotechnology to fulfill its potential for producing advanced materials with precisely controlled morphologies and properties.



I. INTRODUCTION

The ultimate goal of nanotechnology is to port the remarkable set of material properties that can be obtained by nanoscience into advanced materials that can aid in solving some of society's greatest challenges, including those related to energy, the environment, and human health. For anisotropic nanomaterials such as one-dimensional (1D) nanocylinders and two-dimensional (2D) nanosheets, the potential for lyotropic liquid crystalline phase formation facilitates the production of aligned materials with anisotropic properties. In lyotropic liquid crystals, the transition from an isotropic dispersion to a liquid crystalline one is driven by changes in concentration. This is in contrast to thermotropic liquid crystals, comprised of small molecules with rigid cores, whose phase behavior is driven by changes in temperature. While thermotropic liquid crystals are well-known for their use in liquid crystal displays and colorful temperature sensors, the most commonly known application of lyotropic liquid crystals is the wet spinning of high-strength polymer fibers such as Kevlar. More broadly, lyotropic liquid crystals are used to produce materials for the transportation, biotechnology, energy, and defense industries; their global market value was 1.4 billion USD in 2021 with an expected compound annual growth rate of 5.5% through 2030.[1] Ongoing research on the phase behavior and manufacturing of anisotropic nanomaterial dispersions will further increase the commercial and societal impacts of lyotropic liquid crystals. Although they were invented a century apart and produce materials of dramatically different sizes, wet spinning and direct ink writing (DIW) are two particularly exciting manufacturing methods for exploiting the liquid crystalline phase behavior of anisotropic nanomaterials. The shear inherent in these extrusion-based methods can be used to further enhance liquid crystalline alignment and facilitate manufacturing products with controlled morphologies at the nano-, micro-, and macroscales. This Perspective provides an overview of the history of anisotropic nanomaterials in liquid crystal science, wet spinning, and DIW. It also describes opportunities for further advancement that will enable nanotechnology to fulfill its promise of enabling precise control of the morphology and properties across multiple length scales.

II. COMPARISON OF FIBER SPINNING AND ADDITIVE MANUFACTURING

Ancient methods of fiber spinning involved processes for combing and twisting flax and other plant fibers. More recently developed methods include the melt spinning of thermoplastic polymers such as nylon and the solution spinning of polymeric

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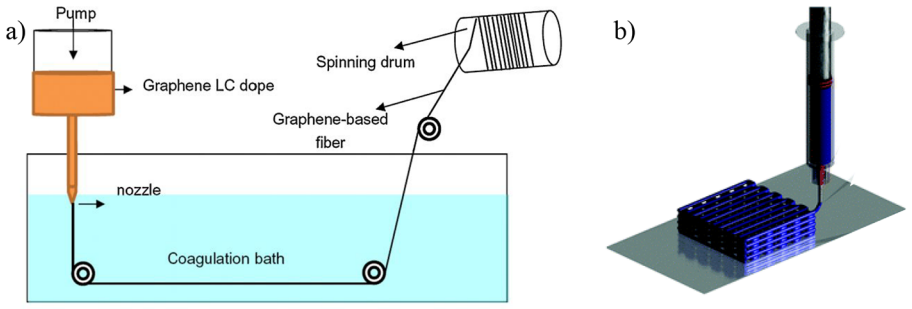

Figure 1. Schematics of (a) wet spinning of a lyotropic nanomaterial liquid crystal. Adapted with permission from ref 3. Copyright 2015 Elsevier. (b) Direct ink writing. Adapted with permission from ref 4. Copyright 2021 Royal Society of Chemistry.

or nanomaterial dispersions. In solution spinning, the fiber-forming material is dispersed in a solvent to create a homogeneous dispersion commonly called a "dope". The dope is pressurized through a vessel such as a syringe and exists through a smaller diameter needle or orifice known as a spinneret (Figure 1a). Volatile, low-surface tension solvents can be removed by evaporation in a process known as dry spinning. However, dry spinning is rarely used for nanomaterial dispersions; few anisotropic nanomaterials can be dispersed in solvents suitable for dry spinning at concentrations sufficient for achieving liquid crystal phase formation. An exception is graphene oxide (GO), but dry spinning GO has resulted in poor properties due to rapid solvent evaporation creating voids in the fiber microstructure.[2] For these reasons, most nanomaterial fibers are produced via wet spinning; in this process, the material exiting the nozzle, or spinneret, is fed into a coagulation bath that partially or fully solidifies the fiber through a competitive diffusion process. The coagulation bath is chosen such that it is miscible with the spinning dope solvent, but not the fiber-forming solute. The coagulation bath composition, residence time, and the use of drawing rolls to stretch the solidifying fiber have significant impacts on fiber alignment, density, microstructure, and cross-sectional shape. Final fiber properties are also influenced by whether there is an air gap between the spinneret and the coagulation bath (dry jet wet spinning) or the spinneret is immersed in the bath (wet jet wet spinning). At the laboratory scale, fibers are typically produced via batch processes using lab syringes and stagnant or rotating coagulation baths. However, commercial systems extrude through thousands of orifices simultaneously at production rates of thousands of meters per hour.

The more recently invented extrusion-based method of DIW, also known as robocasting and extrusion printing, was patented in 1997 for printing ceramic dispersions to form complex solid structures. In contrast to continuous high-speed fiber spinning, DIW is essentially a batch process that produces multilayered structures in complex patterns (Figure 1b) at typical printing speeds on the order of tens of millimeters per second (~100 m/h). Except for the large format printers used in construction, print areas are typically <100 cm^2. Interest in DIW has grown exponentially in the past 20 years alongside interest in emerging nanomaterials and additive manufacturing in general.[5] Similar to wet spinning, DIW starts with a complex fluid, known as an ink, comprised of the solute that will form the printed pattern and a solvent. Instead of being extruded into a coagulation bath and spooled onto rollers, the material is extruded via a path dictated by a computer-aided design (CAD) file that controls the motion of the syringe and stage (Figure 1b). DIW can be subdivided into continuous filament writing, where the ink is expelled in a continuous stream, and ink jetting, where the ink is expelled drop by drop. This Perspective focuses on filament writing, sometimes called F-DIW, because of its direct analogy to wet spinning.

In both fiber spinning and DIW, the shear experienced when exiting the needle can serve to align anisotropic solutes such as 1D and 2D nanomaterials. This alignment will be greater if some alignment was already present in the initial dispersion as a result of liquid crystalline phase formation. In both processes, continuous flow should occur on demand; therefore, it is important to understand the dispersion's rheological behavior as a function of shear rate. The dispersion's yield stress should be high enough that the material does not flow prematurely but low enough that it can be overcome by the applied processing pressure. To achieve uniform flow, the dispersion should also be shear thinning so that the viscosity is higher at the low shear rates experienced in the syringe and significantly lower at the high shear rates experienced in the nozzle (or spinneret). For both processes, enough extensional viscosity is needed to retard filament breakup and the dispersion should possess a storage modulus G' that is greater than the loss modulus G'' ($\tan\delta < 1$), particularly at low frequencies.

There are, however, several distinctions in the dispersion design requirements for wet spinning and DIW. Wet spinning is a steady state process where the goal is typically to retain a continuous discrete cylindrical structure that uniformly decreases in diameter from the moment the dispersion exits the needle until the fiber is fully solidified. However, DIW is a more dynamic process. The ink filament must follow a complex path; it experiences stretching and bending forces between exiting the nozzle and being deposited onto the print bed. These forces are primarily a function of the ratio between extrusion rate and print speed,[4] but they vary as the ink filament follows straight paths and bends in the pattern. The deposited ink must also retain its shape while bearing the weight of subsequent layers. These requirements suggest the need for a high storage modulus and yield stress, but enough fluidity (large enough G'') is also needed to enable interlayer coalescence and prevent delamination. Some researchers have defined processing windows for DIW, fiber spinning, and other fluid phase manufacturing methods in terms of the ratio of $G'/G'' = 1/\tan\delta$. Spinnable dispersions typically have $1.8 < G'/G'' < 6.4$,[6] while $G'/G'' > 2$ is generally sufficient for DIW. Since DIW inks must quickly undergo a transition from a flowing liquid exiting the nozzle to a nearly stationary viscoelastic solid upon deposition, understanding the inks' time-dependent (thixotropic) properties is particularly important. For this reason, a three-interval thixotropy test (3ITT) is often used in addition to standard steady shear and small-amplitude

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oscillatory rheology tests to characterize an ink's thixotropic behavior; this sequence is typically conducted using oscillatory rheology to avoid the issues with slip that can be encountered using steady shear rheology.[7] The first interval is a low-frequency test in the linear viscoelastic region to mimic the ink moving slowly in the syringe. This is followed by a very high frequency to mimic extrusion through the nozzle and, finally, another low-frequency test to mimic the material's recovery. This series provides information about whether the ink will flow at a steady rate through the nozzle and if its recovery to a solid-like state is fast enough for the printing speed.

There are also distinctions between wet spinning and DIW with respect to the solidification process. Most nanomaterial fibers are produced using wet spinning due to their low dispersibility in volatile solvents, the ability to obtain more uniform fiber cross sections, and the ability to tune thermodynamic interactions and fiber properties through the inclusion of additives in the coagulation bath. Because the forming fiber is continuous and has a nearly uniform (albeit time-dependent) diameter, the competitive diffusion process that results in solidification[8] is uniform and can easily be modeled using a cylindrical geometry. In contrast, most patterns printed by DIW are currently dried in air (analogous to dry spinning). This limits the range of solutes and solvents that can be used and reduces the opportunities for tuning morphology, interactions, and other properties during solidification. Also, the prints have a much longer vertical diffusion path, and complex shapes can result in different sections solidifying at different rates. To address the limitations of printing in air, there is increasing interest in printing onto a cold plate followed by lyophilization, printing into a coagulation bath, or immersing a print in a bath after completion. However, outside of the field of biomaterials, research on techniques such as fluid bath-assisted printing is at a relatively early stage.[9]

III. FUNDAMENTALS OF LYOTROPIC LIQUID CRYSTALS

Liquid crystal science is usually said to have begun in 1888 as a result of Friedrich Reinitzer's observation of two melting points in the cholesteryl benzoate he had extracted from carrots combined with Otto Lehmann's observations of this material using his newly invented hot stage polarizing microscope.[8] Cholesteryl benzoate and other small molecules with rigid cores that undergo isotropic to liquid crystalline phase transitions as a result of temperature changes are now known as thermotropic liquid crystals. However, Lehmann's idea that a material could flow like a liquid while maintaining the optical properties of a crystal was controversial for approximately 20 years.[8] Early 20th century observations of birefringence in 1D vanadium pentoxide (V_2O_5) sols by Freundlich, Zocher, Langmuir, and others initially added to the controversy[8,10,11] but are now recognized as the first investigations of lyotropic liquid crystals, the class of liquid crystals in which changes in concentration drive the phase transitions. Friedel's over 200-page 1922 *Annales de Physique* paper provided details about many liquid crystalline systems along with the classification scheme for types of positional and orientational liquid crystalline ordering (Figure 2).[8] Nematic liquid crystals possess long-range positional order but lack orientational order. This is the phase obtained in most nanomaterial liquid crystals; retaining this aligned structure after solidification can enable anisotropic mechanical, electrical, and thermal properties. Chiral nematic, also known as cholesteric, liquid crystals are similar to nematics except the

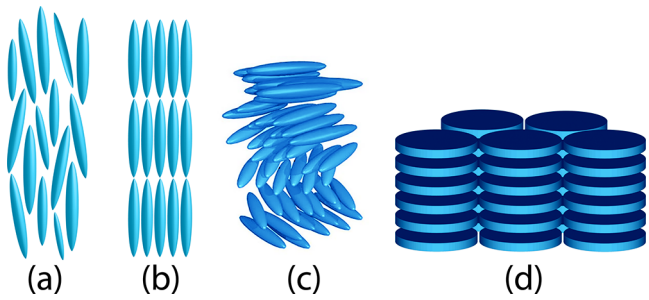

Figure 2. Schematic diagram representing the orientation of nanorods in (a) nematic, (b) chiral nematic (cholesteric), (c) smectic A, and (d) discotic liquid crystalline phases. Modified with permission from ref 13. Copyright 2021 MDPI.

orientational director rotates over a distance known as the pitch. In the case of planar alignment, sometimes termed standing helices, the wavelength of maximum reflectance under circularly polarized light with the same handedness is $\lambda_{max} = n_{av}P \sin \theta$, where n_{av} is the average refractive index, P is the helical pitch, and θ is the angle of incidence with respect to the film surface.[12] Natural materials such as pollia fruit and several types of beetles owe their iridescence to the chiral nematic ordering of biomaterials on their surface. This has inspired considerable research on casting chiral nematic films of cellulose nanocrystals to produce polarizers, color filters, sensors, and security documents. However, the shear involved in extrusion-based manufacturing methods generally causes a chiral nematic to nematic transition. As a result, there are relatively few investigations of trying to achieve chirality after DIW or fiber spinning. Smectic liquid crystals are highly ordered phases that possess both orientational order and positional order. Historically, the polydispersity inherent in most nanomaterial systems has been viewed as an inhibitor to smectic phase formation. As discussed in Progress and Future Opportunities, this is not always the case, and polydispersity has the potential to be used as a tool for achieving both ordering and improved manufacturability. All three of the aforementioned phases can be formed by 1D or 2D materials; 2D materials can also order into stacks or columnar phases as well as layered structures known as lamellar phases.

Modern nanotechnology has reinvigorated lyotropic liquid crystal research,[14−16] but even before nanotechnology became a word and we had the techniques to image individual nanomaterials, the ability of anisotropic nanomaterials to form birefringent liquid crystalline dispersions was well established. By the end of the 1930s, V_2O_5, several 2D nanoclays, tobacco mosaic virus (TMV), and even "graphite oxide colloids"[17] were all found to exhibit some liquid crystalline properties. In fact, tobacco mosaic virus, an approximately 300 nm long, 20 nm diameter cylindrical biomolecule, inspired Onsager's seminal 1949 theory for lyotropic liquid crystal phase formation.[18] According to Onsager theory, lyotropic liquid crystals form as a result of the competition between rotational and translational entropy; the alignment of rods (or sheets) in a dispersion is the more favorable thermodynamic state because the increase in translational entropy is greater than the loss of rotational entropy.[18] For infinitely long, monodisperse spherocylinders that could not interpenetrate each other, Onsager found that a biphasic dispersion (consisting of an isotropic phase and a liquid crystalline phase in equilibrium with each other) forms at volume fraction $\phi_I = 3.34/(L/D)$, where L is the rod length and

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D is the rod diameter. Further increasing the concentration increases the fraction of the liquid crystalline phase until the entire system becomes liquid crystalline at $\phi_{LC} = 4.49/(L/D)$. Onsager's initial theory also considered the case of a bimodal mixture of lengths, and numerous subsequent refinements have been developed to account for thermodynamic interactions as well as continuous length distributions. Because a disk is geometrically a short cylinder, the same thermodynamic principles generally apply to the ordering of 2D materials; however, there are inconsistencies in the nomenclature used for the long and short dimensions. In this work, the larger, lateral dimension of the disk will be termed D_{lat} and the shorter, thickness dimension will be termed t. Figure 3 shows that for a

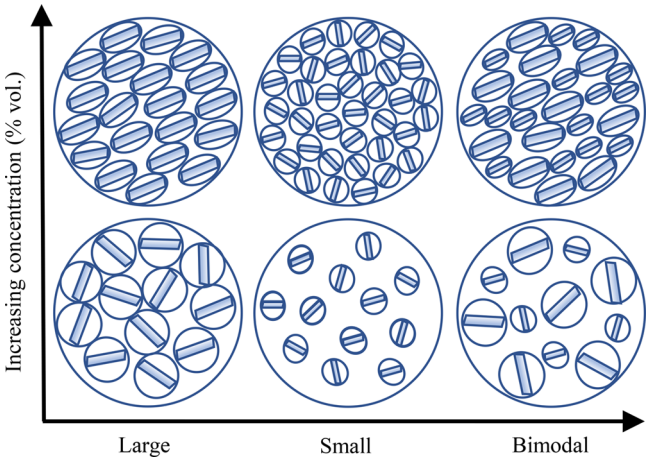

Figure 3. Effects of sheet (or rod) size on liquid crystalline phase behavior. Each sheet has an excluded volume within which it can rotate. For larger sheets, an increase in concentration results in alignment and an increase in translational entropy. For small sheets, alignment does not occur. For mixtures of large and smaller sheets, such as the binomial mixture shown, the excluded volume of the large sheets enables alignment of the small sheets and the small sheets fill voids between large sheets.

fixed thickness, sheets with a larger lateral size have larger excluded volumes. With an increase in concentration, alignment reduces the excluded volume of each sheet and increases the overall entropy, resulting in the formation of a nematic liquid crystalline phase. In contrast, smaller sheets do not have enough excluded volume to align even at very high concentrations.[19] In mixtures of different-sized sheets, the phase behavior and morphology depend on the relative concentrations and sheet dimensions. The excluded volume of large sheets can cause the alignment of smaller sheets, and small sheets can intercalate between the large sheets.

IV. LIQUID CRYSTALS AND FIBER SPINNING

In 1965, Stephanie Kwolek discovered *p*-polyphenylene terephthalamide (PPTA). This discovery coupled with the ability of this rod-like polymer to form liquid crystals in sulfuric acid and be wet spun into a high-strength fiber resulted in the commercialization of Kevlar in 1971.[20] These events spurred significant research into rod-like polymer molecules, their lyotropic liquid crystalline phase behavior, and wet spinning. Decades later, scientists were inspired to wet spin fibers from another high-strength cylindrical macromolecule, single-walled carbon nanotubes (SWNTs), and their multilayered analogues, MWNTs. Like Kevlar, SWNTs, MWNTs, and other carbon nanotubes (CNTs) owe their strength to their aromaticity. Perfect CNTs consist of only sp^2-hybridized carbon, which imparts greater strength as well as outstanding thermal and electrical properties. The earliest wet-spun SWNT fibers were produced by Poulin and co-workers by spinning aqueous low-concentration dispersions of SWNTs stabilized by sodium dodecyl sulfate into a rotating aqueous poly(vinyl alcohol) coagulation bath.[21] In the same time frame, a large collaborative effort led by Richard E. Smalley and Matteo Pasquali of Rice University, of which the author was a part, focused on wet spinning additive-free SWNT fibers. Even in the early stages, SWNTs were perceived as the ultimate rigid rod, and it was anticipated that they could be wet spun in a process analogous to that used for lyotropic polymer liquid crystals. However, trying to find a solvent that could disperse high concentrations of SWNTs was frustrating. Surfactants and organic compounds such as *n*-methyl pyrrolidone (NMP) enabled only low-concentration dispersions and were difficult to remove after processing. Oxidation enabled dispersion in water but deteriorated the SWNTs' mechanical and electrical properties. In the summer of 2001, we discovered that similar to PPTA, pristine SWNTs could be dispersed in fuming sulfuric acid at concentrations that were orders of magnitude higher than that of any other solvent known at that time. We then conducted the first SWNT/H_2SO_4 fiber spinning experiments, using a diethyl ether coagulation bath. Similar to V_2O_5 more than 100 years before, the idea that SWNTs could form liquid crystals was initially controversial. The dispersions lacked the extensional viscosity associated with lyotropic polymer liquid crystals, and changing the temperature had no impact on the phase boundaries. However, their birefringence and rheological characteristics confirmed their liquid crystalline phase behavior.[22] Within a few years, we discovered that we could tune the phase boundaries by changing the protonating ability of the solvent.[23,24] This resulted in a phase diagram in which the experimentally determined biphasic-liquid crystalline phase transitions matched the results from an Onsager-based model.[25] Moreover, we showed that this phase behavior was not only scientifically interesting but also important for manufacturing. The most protonating solvent, chlorosulfonic acid, resulted in a smoother microstructure with larger liquid crystal domain sizes, which resulted in more uniform fiber structure and better fiber properties.[25] Twenty years of ongoing advancements, including the use of longer CNTs, have enabled an impressive 26% per year increase in electrical conductivity and a 23% per year increase in tensile strength leading to the current values of 10 MS/m and 5 GPa, respectively (Figure 4).[26] In addition, sewable fibers are now commercially available from DexMat High Performance CNT Products (Houston, TX).

Given the chemical similarity to SWNTs, and commercial interest in carbon fiber, it is not surprising that there has been significant research on producing neat graphene and GO fibers from their liquid crystalline dispersions.[2,27] Publications on GO fiber spinning increased from a few studies in 2011 to nearly 300 per year by 2018.[2] Many of these studies involve the post-process reduction of GO to reduced graphene oxide (RGO) to recover much of graphene's intrinsic properties. Similar to CNTs, ongoing refinements in tuning the GO size distribution, liquid crystalline microstructure, rheological properties, and fiber spinning process have resulted in rapid gains in mechanical, electrical, and electrochemical properties.

The understanding developed through research on 1D and 2D carbon materials has provided a template for assessing the

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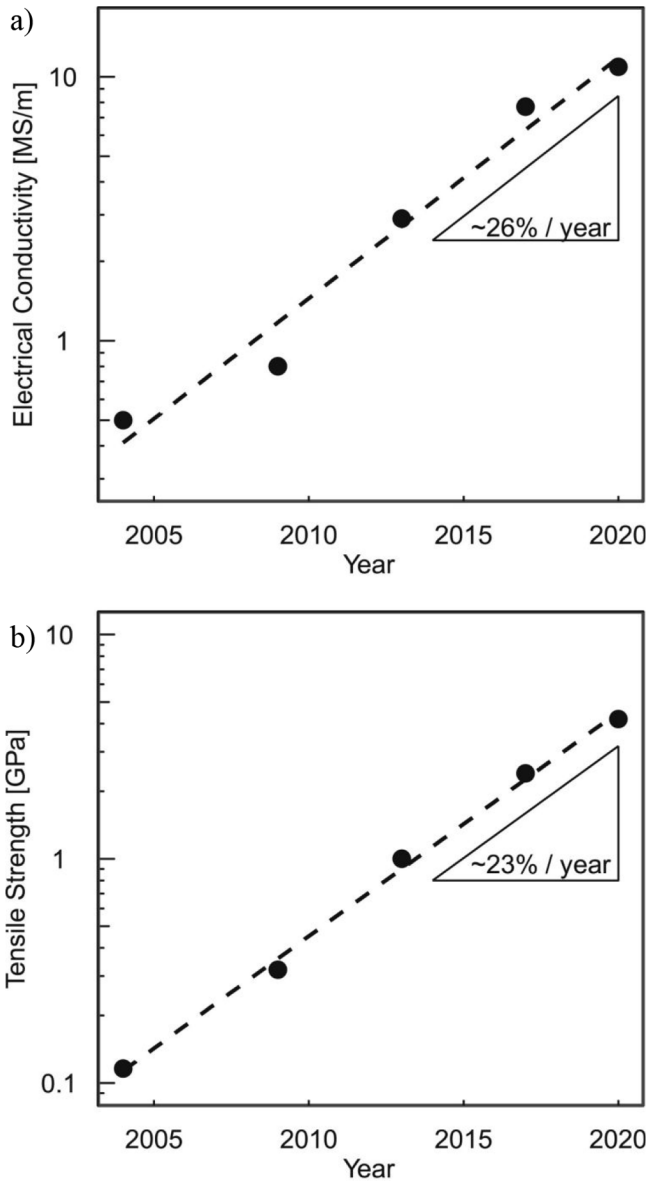

Figure 4. Rate of improvement in (a) electrical conductivity and (b) tensile strength of fibers spun from CNT/acid liquid crystals at Rice University. Reproduced with permission from ref 26. Copyright 2021 Elsevier.

individual liquid crystalline phase behavior and fiber spinning of more recently discovered nanomaterials. For example, although MXenes were discovered only 11 years ago, and synthesis schemes still produce relatively limited quantities, their liquid crystalline phase behavior is already established and several research groups have produced additive-free MXene fibers. While MXene fibers lack the high specific strength of CNT and graphene fibers, they are very attractive for use as electrodes, smart textiles, sensors, and electromagnetic shielding.[6,28]

The next frontier in anisotropic nanomaterial liquid crystal fiber spinning is to move beyond single-nanomaterial systems. Different shapes of chemically similar materials can be used to tailor nano- to microstructural arrangements and packing, and materials with different chemistries can enhance properties. For example, Xu et al. showed that guest-host fibers of reduced graphene oxide (RGO) and silver nanowires had more than twice the electrical conductivity of their neat RGO fibers.[29] Similarly, Yang et al. found that combining MXene dispersions with an LC of 5−8 μm GO resulted in synergistic electrical and mechanical properties.[30] The larger GO sheets facilitated liquid crystal phase formation and intersheet interactions, while the MXenes served to fill gaps between the GO sheets; this resulted in high-performance flexible supercapacitors. A broad range of other active materials and binders in a range of shapes and sizes have also been included in nanomaterial fibers, but of these studies, few have explored the complex relationships among dispersion composition, phase behavior, rheological properties, the fiber spinning process, and fiber properties. A holistic approach to understanding and optimizing both the colloid science and manufacturing of anisotropic nanomaterial dispersions will enable improved properties for existing systems as well as the rational design of new systems with targeted multifunctional properties.

V. LIQUID CRYSTALS AND ADDITIVE MANUFACTURING

Advancements in additive manufacturing have been occurring in parallel to those in nanotechnology and attracted significant attention from academia and industry in the past 10 years. Much of the early emphasis for DIW and other additive manufacturing methods was on the computer control and equipment aspects, but it is now widely understood that fully realizing DIW's potential requires a colloid science approach to understanding the dispersion behavior of the materials being printed and the inks' rheological properties.[31] DIW of lyotropic nanomaterial liquid crystals provides the opportunity to fully control structure through the microscale resolution of the printing process and the nanoscale ordering of the liquid crystal.[32]

The complex rheological requirements of DIW inks coupled with the multifunctionality required for energy-related applications are inspiring significant research into using multicomponent inks to enhance the control of rheological properties, nanoscale structure, and device properties. Similar to the use of salts in fiber spinning coagulation baths, several researchers have explored adding salts or other ionic species to inks to increase the number of interparticle interactions between particles and to tune dispersion phase behavior and rheological properties.[4] For example, Jiang et al. found that adding 15 mM $CaCl_2$ enabled better GO ink printability by increasing the yield stress and storage modulus by one order of magnitude.[33] Two recent studies have highlighted the exquisite control of structure and properties that can be achieved through the careful design of multicomponent anisotropic nanomaterial systems. Jalili et al. simultaneously advanced both fundamental liquid crystal science and DIW manufacturing by combining nanocellulose and GO to form a biaxial nematic phase.[32] The shear forces experienced during printing caused this novel liquid crystal to undergo a transition to an even more ordered lamellar phase, thereby enabling nanoscale control over structure in the x, y, and z dimensions.[32] Similarly, Zhao et al. used V_2O_5/CNT/GO dispersions to create multifunctional inks in which the V_2O_5 drove liquid crystalline phase behavior and served as the active material, the CNT created a conductive network, and GO served as a binder that limited V_2O_5's mobility. By tuning the relative ratios of the materials, different nanoscale structures within the print could be achieved.[34] Both of these works inspire additional research on multishape, multimaterial systems by demonstrating the ability to precisely control the structure through careful consideration of the composition, relative size ratios, colloidal interactions, and shear effects.

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VI. PROGRESS AND FUTURE OPPORTUNITIES

In the past 20 years, nanomaterial liquid crystal science has been rediscovered and extended through the production of a broad array of 1D and 2D nanomaterials in quantities sufficient for rheology, phase behavior, and manufacturing studies. The field has progressed from researchers questioning whether high-aspect ratio 1D and 2D nanomaterials can form liquid crystals to 1D and 2D nanomaterial liquid crystal processing becoming the preferred method for achieving alignment in solid objects. Two decades of research on CNT liquid crystals have resulted in commercially available CNT fibers and provided a research template for understanding the phase behavior, rheological properties, and fiber spinning of more recently investigated 1D and 2D nanomaterials. Parallel advances in additive manufacturing are accelerating the development of devices, sensors, and other objects produced by DIW. As the field moves into the next decade, several issues need to be holistically addressed to move from experimentation on individual systems to the efficient manufacturing of a broad range of anisotropic nanomaterials with optimized multifunctional properties.

1. Size Polydispersity and Shape Irregularity. Size polydispersity has historically been viewed as a problem that complicates modeling and retards the formation of highly ordered systems such as smectic liquid crystals, but it can also be viewed as an opportunity. Most synthesis and extraction schemes result in a range of sizes, and size separation schemes can be time-consuming and costly. Striving for completely uniform sizes to best fit Onsager's original theory is often impractical, and on a purely theoretical basis, size distributions are no longer a strong impediment to modeling.[35−38] Moreover, a growing number of studies have shown that size polydispersity can benefit both microstructural phase formation and processing. Vroege et al. showed that for goethite nanoclay rods, polydispersity coupled with sedimentation stabilizes smectic phase formation.[39] Similarly, Honorato-Rios showed tailoring polydispersity through sedimentation-based fractionation could enhance liquid crystalline phase formation and inhibit gelation in aqueous cellulose nanocrystal (CNC) dispersions.[40] While high-aspect ratio nanomaterials are desirable for maximizing fiber and print properties, their dispersions have higher viscosities and are more prone to aggregation and jamming that can result in nozzle clogging and disruptions in the microstructure. For many dispersions, processing challenges associated with high viscosity can be mitigated by the low-shear viscosity reaching a minimum near the biphasic to liquid crystal phase transition.[22,41,42] However, for charged systems such as cellulose nanocrystals and MXenes, the viscosity continually increases with concentration.[43] In these cases, it can be beneficial to use mixtures of large and small sizes to tune rheological properties. Such mixtures also enable researchers to tune phase behavior, retard aggregation, and enhance properties by bridging microstructural voids.[44] Combined experimental and computational studies are needed to better understand the impacts of size and polydispersity on both dispersion behavior and the properties of the assembled materials.

A more complex issue is that of shape irregularity resulting from initial production or dynamic wrinkling processes in 2D materials. While exfoliated nanoclays tend to have relatively uniform shapes, this is not true for nanomaterials such as graphenes and MXenes. The current convention is to simply consider the longest lateral dimension in aspect ratio calculations used in understanding phase behavior. However, this neglects the significant differences in rigidity and packing of nearly circular disks, rectangular sheets, and various other geometric and fractal shapes. In addition, just as a ripped piece of paper will be more prone to wrinkling than a continuous one, dimension and shape affect 2D nanomaterials' wrinkling behavior under shear. Therefore, there is a need to better, and more consistently, characterize shape through parameters such as convexity, sphericity, and fractal dimension and by measuring multiple lateral diameters along different axes. Partially driven by the effects of shape on controlled drug release, size and shape characterization standards for nanomaterials have been developed by multiple organizations such as the Organization for Economic Co-operation and Development (OECD) and the International Standards Organization (ISO).[45] However, these metrics can be time-consuming and are rarely applied to laboratory dispersion and manufacturing studies. Image processing schemes based on artificial intelligence and widespread acceptance of standards for measuring shape and size are needed to understand the effects of shape irregularity on wrinkling, rheology, and phase behavior. In addition, coupled theoretical and experimental studies are needed to extend Onsager-based theories to account for flexibility and shape irregularity in the context of the full range of potential colloidal interactions. Together, these efforts will enable size polydispersity and shape irregularity to be used as tunable parameters and aid the development of quality control standards that advance the consistency of materials produced by fiber spinning and DIW.

2. Multishape and Multimaterial Systems. Particularly in the context of DIW, studies of multimaterial and/or multishape systems are highlighting the advantages of moving beyond single-nanomaterial systems.[13] However, much remains to be understood about the complex array of excluded volume interactions, density gradients, and electrostatic interactions in multishape and multimaterial lyotropic liquid crystals. Rod/sphere mixtures are generally well understood, but less is known about rod/sheet, sheet/sphere, and ternary mixtures, particularly given the thermodynamic interactions, polydispersity, and shape irregularity present in real systems.[13] Fully exploiting the potential for using anisotropic nanomaterials' liquid crystalline phase behavior to precisely engineer fibers' and prints' nanoscale structure and micro- to macroscale performance will require a concerted computational and theoretical effort that couples fundamental rheology and phase behavior studies with manufacturing experiments.

3. Processing Advancements. In fiber spinning, coagulation bath conditions and drawing provide opportunities to enhance interparticle interactions, alter microstructure, and control fiber density, alignment, and properties. The fundamental colloid science and fiber spinning literature provides an ample foundation for the rational design of fiber coagulation baths and drawing schemes. However, while several authors have already shown success in extending established approaches such as incorporating ions in the coagulation bath to increase the number of interparticle interactions,[6,17] coagulation studies are often considered an afterthought in process development. A systematic approach to coagulation based on fundamental colloid science and transport phenomena would rapidly increase the rate of nanomaterial fiber property improvements and guide process development for future materials.

In the case of DIW, the majority of printing is still limited to ink deposition and drying in ambient air. Similar to dry spinning, while altering the temperature and humidity can have some

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effects, printing into air drastically limits the ability to tune structure and interactions during solidification. Some researchers are exploring DIW post-processing methods such as lyophilization and immersion in a fluid bath. Another particularly promising method is an approach similar to wet spinning in which the print is immersed in a bath. This method is known as fluid bath-assisted printing and is widely used by biomaterials, particularly tissue engineering, researchers because living cells must be printed into media to survive.[9] The translation of this technology to anisotropic nanomaterial printing coupled with knowledge gained from fiber spinning could dramatically increase the range of printed material properties and compositions. However, just as the rheological requirements for DIW inks are more complex than those for fiber spinning dopes, there are more parameters to consider for printing baths than fiber coagulation baths. Fiber spinning baths can be Newtonian. A yield stress and viscoelasticity are typically required in printing baths because of the need to support the printed structure and limit bath movement during the printers' motion. However, if the storage modulus of the bath is too high compared to that of the ink, the bath can compress the print and deform its structure.[9] Another difference is that in fiber spinning the forming fiber is continuously pulled out of the bath onto a spinning drum; this is not possible in DIW. If the bath is integral to the print's function, it is sometimes cross-linked around the print. If the bath material is undesirable, the print and the bath must be carefully separated by print removal or bath drainage followed by the removal of any residual bath material. This can result in a disruption of the print structure and may require additional rinsing or drying to obtain a completely solidified material.[9] Therefore, while fluid bath-assisted printing is possible, more research is needed to utilize its potential.

VII. CONCLUSIONS

Just as the discovery of small molecules with rigid cores and rod-like polymer mesogens enabled revolutionary applications such as liquid crystal displays and high-strength fibers, respectively, anisotropic nanomaterials promise exciting new materials for energy applications, sensing, biomedicine, electromagnetic shielding, transportation, and many other industries. The study of recently produced 1D and 2D nanomaterials' liquid crystalline phase formation and rheological behavior is extending our fundamental understanding of liquid crystal and colloid science just as nanoscale tobacco mosaic virus and nanoclays did nearly 100 years ago. The translation of these exciting scientific advances to useful products requires understanding the coupling of these dispersion properties with manufacturing technologies. The ability to tune the size and shape of individual nanomaterials and combine materials to achieve multifunctionality will enable liquid crystalline science to have an even greater impact than before by enabling nanotechnology to fulfill its promise through extrusion-based manufacturing methods such as fiber spinning and DIW.

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Notes

The author declares no competing financial interest.

Biography

Virginia A. Davis received her B.S. and M..E. in Chemical Engineering from Tulane University in 1990 and 1993, respectively. She then worked for 11 years in the United States and Europe for Shell Chemical Company's polymer businesses. She began her doctoral research with Matteo Pasquali and Richard Smalley at Rice University in 2001; this was at the beginning of their single-walled carbon nanotube fiber spinning research. After finishing her doctorate, she became a faculty member in Auburn University's Department of Chemical Engineering where she continues to focus on the rheology, phase behavior, and processing of anisotropic nanomaterial systems. Her other research interests include polymer recycling, nanocomposites, and interventions that facilitate diversity, equity, and inclusion in STEM disciplines.

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