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# Electrospun Polymer Fibers Containing a Liquid Crystal Core: Insights into Semi-Flexible Confinement

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**ABSTRACT**: Encapsulation of the nematic liquid crystal *N*-(methoxybenzylidene)-4butylaniline (MBBA) into the core of poly(vinylpyrrolidone) (PVP) microfibers has been accomplished via coaxial electrospinning for the first time. Data from optical microscopy, 2D Raman mapping, differential scanning calorimetry, and dielectric spectroscopy have been employed to gain detailed insights into the confinement effects on MBBA in a semi-flexible polymer sheath. The electrospun fiber diameters could be tuned easily by modifying the flow rate of MBBA and both the MBBA core and PVP sheath diameters were determined via Raman line cuts. The PVP sheath induced alignment of MBBA, where its long axis is parallel to the fiber axis. Further, the alignment of MBBA led to iridescence in the fibers, which was found to be temperature sensitive and reversible. Surprisingly, at temperatures below 0 °C, the phase transition temperatures of confined MBBA are different and one of its smectic phases is inhibited by the PVP sheath; however, the phases that occur above 0 °C appear to be unrestricted. Thus, electrospun core-sheath fibers with MBBA and PVP provide a useful platform for a semiflexible material where it is especially necessary to control liquid crystal alignment and polymorphs or phases at low temperature. Overall, the results reported here provide new and important considerations for the effects of confinement on liquid crystals in semi-flexible media.

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# INTRODUCTION

Functional and self-assembling materials have found increasing attention due to their ability to respond to weak external stimuli, simplicity in device integration, and broad tunability. These characteristics have become increasingly important for wearable materials such as adaptive color textiles and flexible devices.<sup>1</sup> Such materials can be developed further by integrating enhanced optical features that control reflective, refractive, or pleochroic properties.<sup>2</sup> These optical features can be achieved by incorporating liquid crystals (LCs) into these platforms because their unique optical properties are sensitive to a variety of stimuli such as temperature, surface morphology, electrical current, and magnetism.<sup>3-6</sup> The dynamic behavior of LCs is already used widely in a variety of commercial applications namely, thermometers, bullet-proof vests, and electronic displays.<sup>3, 7-9</sup> To date, encapsulation of LCs has been limited to mostly rigid materials, and this media has restricted the potential benefits of dynamically responsive LCs from current technologies. Thus, incorporation of LCs into more flexible architectures such as polymer fibers provides an opportunity to explore the effects of elasticity on internal confinement and has the potential to bring further improvements to devices such as wearable electronics and adaptive color textiles.

Historically, the variety of flexible media used to confine LCs has been limited, although numerous potential applications as soft responsive materials have been proposed.<sup>10</sup> Some of the current applications have employed LCs in capillaries and droplets which have dynamic surface morphologies and have illustrated the importance of LC anchoring on flexible surfaces.<sup>11</sup> LCs encapsulated in micron sized droplets and polymer shells have been able to detect very low levels of toluene vapor by evaluating the LC anchoring energy in chemically patterned microwells.<sup>12</sup> Furthermore, nanoscale confinement of LCs in semi-flexible media has shown to

impart a variety of thermal changes in response to dynamic stimuli.<sup>4, 11</sup> Thus, stimuli such as surface-induced ordering, elastic strain, and topological defects dictate LC response especially in micro- and nanometer scale geometries.<sup>13</sup>

Recently, coaxial electrospinning has emerged as a facile method to create micro- and nanoscale fibers with 'core-sheath' morphology in which a liquid or polymer core is encapsulated by a surrounding polymer sheath.<sup>2, 14-17</sup> This technique was first adapted to LCs by Lagerwall and co-workers who have also recently demonstrated that electrospun core-sheath fibers can undergo reversible optical changes in response to toluene exposure.<sup>18</sup> Optical control of similar fiber materials has also been observed by modifying fiber diameter,<sup>19</sup> by the addition of dopants into the core<sup>15</sup> and under UV irradiation.<sup>20</sup> Thus, some of the current applications of electrospun core-sheath materials include: soft gas sensors, drug-delivery, and electronics.<sup>21-23</sup> Although significant progress is being made, the range of LCs and polymers that has been examined for core-sheath morphology for coaxially electrospun liquid crystal fibers is extremely limited. In fact, 4-Cyano-4'-pentylbiphenyl (5CB) and its analogues are the only LCs to be encapsulated in a polymer sheath; those polymer sheaths are limited to poly(vinylpyrrolidone) (PVP) and poly(lactic acid) (PLA). Therefore, it is critical to expand the scope of the components available for electrospun core-sheath fibers to include additional LCs and polymers. New components such as LCs with tunable electrical or optical properties<sup>24-25</sup> and polymers bearing different degrees of flexibility<sup>26-29</sup> will yield additional insights into confinement behavior, provide new morphologies and alignments, and open new avenues for LC and nanofiber research.

Herein, the nematic LC, *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA) was incorporated into the core of PVP fibers (**Figure 1**) via coaxial electrospinning for the first time. To the best of our knowledge, this is the first nematic LC other than 5CB that has been

encapsulated in a polymer sheath by electrospinning. We report the effects of relative flow rates between MBBA and PVP on fiber diameter, morphology, and LC behavior. Also, we present the first report using 2D Raman mapping spectroscopy to elucidate clearly core-sheath morphology of LC/polymer fibers, as well as, distinguish the LC orientation within the fibers and find the first evidence of the nearly complete inhibition of low temperature LC phases in electrospun polymer fibers. The spectroscopic evaluations are complemented with comprehensive thermal analyses and dielectric spectroscopy to provide new insights into the effects of encapsulation of LC behavior in semi-flexible media.



**Figure 1.** Chemical structures of PVP polymer sheath and the MBBA liquid crystal core, including the transitions for the crystalline (C), nematic (N), and isotropic (I) phases of MBBA above 0 °C.

#### EXPERIMENTAL

**Materials.** 4-anisaldehyde (98%), 4-butylaniline (97%), sodium chloride (99%), sodium bicarbonate (99%), and poly(vinylpyrrolidone) (PVP, 1,300,000  $M_w$ ) were purchased from Sigma Aldrich. Toluene (99.9%) and hydrochloric acid (conc.) were purchased from Fisher

Scientific. Ethanol (99%) was purchased from Warner-Graham. All reagents were reagent grade or better and used without further purification.

Synthesis and Characterization. Detailed syntheses of MBBA is reported in the Supporting Information (SI). The MBBA was further purified by fractional distillation and confirmed with <sup>1</sup>H NMR, DSC, and FT-IR analyses (**Figures S1** and **S2**). <sup>1</sup>H NMR spectra were obtained with a Bruker 300 MHz nuclear magnetic resonance spectrometer on samples prepared in CDCl<sub>3</sub>. Attenuated total reflectance infrared (ATR-IR) was performed on a Nicolet iS50-FT-IR with iS50 ATR attachment equipped with a Ge crystal from Thermo Scientific (Waltham, MA) with 128 scans compiled for each spectrum.

**Solution Preparation Procedures.** The PVP sheath solution was prepared by dissolving PVP into a solution of ethanol:water (90:10) containing 0.05% NaCl to achieve a final PVP concentration of 12.5 wt%. The LC, MBBA, was used as neat MBBA.

**Electrospinning Apparatus.** Coaxial electrospinning was performed on a custom built apparatus consisting of two syringe pumps from New Era Pump Systems (NE-300), one of which was equipped with a12 mL syringe filled with the PVP polymer solution and the other a 1 mL syringe containing neat MBBA. The syringes were attached with Tygon® tubing (Ramé-Hart; 100-10-TYGON125) to a custom coaxial spinneret with an inner and outer needle (Ramé-Hart; inner needle i.d./o.d. = 0.411/0.711 mm, outer needle i.d./o.d. = 2.16/2.77 mm). The spinneret was oriented vertically, pointed downward to a grounded aluminum collection plate. The fibers were collected onto the grounded plate or a glass slide at a vertical distance of 7.5 cm from the spinneret tip which was attached to a high-voltage power supply from Bertan Associates (205B) set at 15 kV. The syringe pump flow rate varied between 0.0 - 1.0 ml h<sup>-1</sup> for MBBA and was held constant for the sheath solution (3.25 ml h<sup>-1</sup>).

**Polarized Optical Microscopy (POM).** Polarized optical microscopy was performed using a Zeiss Axio Imager 2 equipped with cross-polarizers. Images were taken using EC Epiplan-Neofluar 5-50x objectives and processed using Zen Core software (Zeiss, Oberkochen, Germany). Samples were prepared on aluminum substrates or glass slides and were analyzed in reflection and transmission modes, respectively, under both polarized and 90° cross-polarized light. The microscope was also equipped with a custom built thermal stage with which the temperature was controlled room temperature to 60 °C to observe thermal transitions.

**Differential Scanning Calorimeter (DSC)**. A TA Instruments Discovery DSC was employed to investigate thermal transitions of the LC-polymer fibers. The DSC was first equilibrated to -50 °C under a nitrogen flow of 50 mL min<sup>-1</sup>. Two successive temperature ramps were then performed from -60 °C to 170 °C at a rate of 10 °C min<sup>-1</sup>, between which the sample was equilibrated to -50 °C. DSC results were analyzed with TA Instruments Trios software. Lower temperature differential scanning calorimetry (DSC) was performed using a TA Q100 calorimeter. Samples were quickly cooled (cooling rate 100 °C min<sup>-1</sup>) from the isotropic phase (23 °C) to below the glass transition and then heated at a rate of 10 °C min<sup>-1</sup>.

**Scanning Electron Microscopy (SEM).** SEM was performed on a JEOL JSM-7600F Field Emission SEM (Peabody, MA, USA) operated at an accelerating voltage of 3 kV equipped with an Oxford X-Max silicon drift detector. Samples were sputter coated with least 3 nm gold prior to SEM analysis using a Cressington 108 auto sputter coater equipped with a MTM20 thickness controller. Image J software was utilized to measure fiber sizes from the SEM images.

**Raman Spectroscopy.** Raman spectra and images were collected with a Witec alpha300 SRA optical microscope. The polarized incident laser light (532 nm) was focused through a 100x objective lens (N.A. = 0.9) onto the sample. The scattered light was collected through the same

objective lens and directed to an imaging spectrometer. Raman images were acquired by raster scanning the sample and plotting a spatial map of the Raman intensities summed over a spectral window of either  $1550 - 1650 \text{ cm}^{-1}$  or  $2800 - 3200 \text{ cm}^{-1}$  with a lateral resolution of 250 nm. The line cuts were made by scanning the laser excitation spot along a line across the fiber diameter and summing the Raman intensities from either  $1550 - 1650 \text{ cm}^{-1}$  or  $2800 - 3200 \text{ cm}^{-1}$  or  $2800 - 3200 \text{ cm}^{-1}$ , for the MBBA core or PVP sheath, respectively. Raman line cuts were performed on 6 fibers of the same sample, and the Raman intensities were then fitted to a Gaussian function, which was used to calculate the fiber full width at half maximum diameter.

**Dielectric Relaxation Spectroscopy.** Dielectric permittivity spectra were collected while monitoring frequencies of either  $10^{-2}$ - $10^{6}$  Hz or  $10^{6}$ - $10^{9}$  Hz using a Novocontrol Alpha or HP4291A Impedance Analyzer, respectively. In each setup, the samples were placed between two parallel plates with diameters of 16 mm or 10 mm, respectively. The fiber mat sample was 15 µm in thickness and neat MBBA was fixed by a Teflon spacer (50 µm thickness). The samples were in a temperature controlled, environmental chamber under nitrogen (± 0.2 °C).

#### **RESULTS AND DISCUSSION**

**Coaxial Electrospinning.** Coaxial electrospinning allows for two different liquids to be spun simultaneously where one liquid is inside the other and is easily accomplished by employing a coaxial needle. An illustration of our electrospinning apparatus is shown in **Scheme 1A**. A high voltage electric field is applied to an electrically conductive polymer solution emerging from the spinneret needle tip. The build of up charge in the solution causes repulsion and the subsequent formation of a Taylor cone.<sup>30-31</sup> The Taylor cone, from which a polymer jet emerges and is directed toward a grounded target, is the point of attraction between the jet and

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the grounded target. As the jet proceeds to the target, electrostatic whipping and spiraling causes the solvent to evaporate and the charge density of the jet to progressively increase; a combination of these events stretches the polymer jet to micro- to nano-scale diameters from Rayleigh instability.<sup>30-31</sup> In general, the core-sheath morphology in **Scheme 1B** is accomplished by mixing components in a solution that are able to undergo in situ phase separation. The phase separation occurs during the solvent evaporation step and is typically governed by the miscibility of the components and their differences in viscosity.<sup>32</sup>

PVP was selected as the sheath component because it solidifies into an amorphous state with low birefringence leading to a nearly transparent sheath.<sup>14</sup> The LC, MBBA, remained in its nematic phase at the spinning temperature (23 °C), which was evident by its cloudy yellow-orange appearance. A variety of core-sheath fibers were spun using different flow rates of MBBA at intervals of 0.25, 0.50, 0.75, and 1.0 mL h<sup>-1</sup>. All other parameters were kept constant such as the sheath flow rate (3.25 mL h<sup>-1</sup>), electric voltage (15 kV), distance between needle tip and target (7.5 cm) and temperature (23 °C). The electrospun fibers were characterized by scanning electron microscopy (SEM), polarized optical microscopy (POM), 2D Raman spectroscopy, and DSC. Note that the ratio between flow rates (vide infra) for inner and outer fluids is very important for fiber formation, morphology, and diameter.<sup>14</sup> A sub-optimal setting may lead to variations in the degree of LC filling such as portions of the fibers that are unfilled or beaded.<sup>32</sup> Specifically, a non-beaded fiber morphology is required for a reliable liquid crystal orientation because it has been found that LCs do not align well in the beaded portions of the fibers.<sup>17</sup>



**Scheme 1.** A) Illustration of the coaxial electrospinning setup used in our lab. B) Cross-sectional slice showing the composition of composite MBBA-PVP fibers via coaxial electrospinning.

**Fiber Morphology.** SEM images in **Figure 2** demonstrate that the electrospinning of core-sheath fibers produced non-woven fiber mats. The observed surface morphology of the PVP sheath surrounding MBBA is common for electrospun fibers with a PVP sheath.<sup>33-35</sup> Thus, the surface morphology of the sheath material does not appear to be influenced by the MBBA core because its appearance is similar to the unfilled PVP fibers. Notably, individual fibers had an appearance which was consistent along the length of the fiber at a rather wide range of MBBA flow rates. The surface morphology of individual fibers be detected. We attribute the fiber consistency to their diameters nor could 'beading' in the fibers be detected. We attribute the fiber consistency to the relatively small ratio between the needle diameters in the spinneret. Here, our ratio of inner diameters for the inner/outer needles of the spinneret is 0.19. In other reports, <sup>14-15, 17, 19</sup> larger needle diameter ratios (0.35 – 0.64) have been employed or no coaxial setup<sup>32</sup> at all. We suspect

that a smaller spinneret needle ratio, as the one used here, allows for more consistent filling since smaller diameters require higher velocity to achieve consistent volume discharge, resulting in improved filling compared to a larger ratio. Thus, our results illustrate the implementation of spinneret needles with small ratios between inner/outer diameters rather than larger ones as a means to optimize core/sheath filling in coaxial electrospinning experiments.



**Figure 2.** SEM images of the MBBA-PVP core-sheath fibers at different flow rates of MBBA: A) 0.0 ml h<sup>-1</sup>, B) 0.25 ml h<sup>-1</sup>, C) 0.50 ml h<sup>-1</sup>, D) 0.75 ml h<sup>-1</sup>, and E) 1.00 ml h<sup>-1</sup>. The scale bars are 50  $\mu$ m.

Relatively thick fibers that ranged from hundreds of nanometers to over a micrometer in diameter were obtained with these electrospinning parameters. The fibers diameters clearly increased as the core flow rate was increased represented by the plot in **Figure 3**. At low core flow rates the fibers appeared thin and cylindrical. Increasing the core flow rate led to fibers that increased in diameter but also appeared to be flatter. This flattening effect suggests that the cross-sections were more oval-like or rectangular and is especially noticeable when the flow rate of MBBA was 1.0 mL h<sup>-1</sup>. The deviation from cylindricity at high core flow rates is known to occur with PVP when using hydrophilic substrates such as those used here.<sup>36</sup> It has been suggested<sup>36</sup> that electrospun PVP is closer to a gel-like state just after initial impact with a surface and is soft enough to adhere to and spread out along a hydrophilic surface via capillary

forces. This spreading causes the electrospun fibers to have a more oval-like appearance. Another explanation may be that ribbon shaped fibers can result when the solid sheath-skin initially forms on the fiber exterior during electrospinning and the electrical charge accumulates, causing two opposite points on the fiber cylinder to laterally stretch the fiber.<sup>37-38</sup> Interestingly, in **Figure 3**, we find that the standard deviations in the fiber diameter increases with MBBA flow rate. Compared to the unfilled fibers, the diameter standard deviation is twice as large for the 0.25 mL h<sup>-1</sup> MBBA flow rate. The standard deviation increases by twofold at rates of 0.50 and 0.75 mL h<sup>-1</sup>. We attribute the increase in standard deviation to small differences in the cylindricity of the fiber cross-sections. However, the standard deviation decreases at the highest flow rate; this decrease is perhaps due to the cross-sections becoming, on average, more rectangular or oval and is substantiated by the SEM images in **Figure 2**. Thus, the observations made in **Figure 3** indicate that filling the PVP sheath with liquid MBBA causes the fiber-cross sections to occupy a distribution of different cylindricities at medium flow rates of MBBA but at high flow rates the fiber cross-sections tend to be more oval or rectangular.



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**Figure 3.** The average outer fiber diameters as a function of the flow rate of MBBA measured by optical microscopy ( $\bullet$ ) (standard deviations ( $\cdot$ ); n = 55 per sample) and 2D Raman linecut measurements ( $\triangle$ ) (n = 6 per sample).

**Polarizing Optical Microscopy**/ Encapsulation of MBBA by the PVP sheath as compared to unfilled PVP fibers are shown in the polarizing optical microscope (POM) images in **Figure 4**. Coaxial electrospinning produced non-woven fibrous mats of a random orientation for both filled and unfilled fibers. The unfilled PVP fibers are clearly observed under polarized light in **Figure 4A**, but under cross-polarized light (**Figure 4B**), are dark because PVP does not exhibit birefringence. As such, the intense birefringence that spans various interference colors in the center of the fibers (**Figure 4D**) is indicative of MBBA. Comparison of the POM images at 0.0 ml hr<sup>-1</sup> with 0.75 ml hr<sup>-1</sup> of MBBA also show clearly a significant increase in fiber diameter with increasing LC core flow rate. The core-sheath morphology of the coaxial MBBA filled PVP fibers is highlighted in the magnified inset of **Figure 4D** indicating encapsulation of a MBBA core by a surrounding PVP sheath.





**Figure 4**. Transmission polarized optical microscopy images of PVP fibers without MBBA cores  $(0.0 \text{ ml h}^{-1})$  in polarized (A) and cross-polarized (B) light; and PVP fibers with MBBA cores  $(0.75 \text{ ml h}^{-1})$  in polarized (C) and cross-polarized (D) light; and. Polarizer orientations are denoted by parallel or crossed arrows. The scale bars are 100 µm.

Core-Sheath Morphology: 2D Raman Mapping. Polarized 2D Raman mapping and Raman line cut analysis were performed on the fibers in order to examine the core-sheath morphology. A combination of these techniques allowed us to verify that the liquid crystal was encapsulated by the PVP sheath and to investigate its alignment. Reference Raman spectra of neat MBBA and an unfilled PVP fiber sample, as well as the excitation polarization dependence are shown in Figures S3 - S5. The Raman spectrum of neat MBBA has a group of three strong peaks between 1550 – 1650 cm<sup>-1</sup> from overlapping aromatic -C-C- and imine (-N=C-) modes and another prominent set of peaks between 1150 - 1225 cm<sup>-1</sup> from its methoxy group (Figure S3). The unfilled PVP fiber has an intense and distinct signal from 2800 - 3200 cm<sup>-1</sup> corresponding to alkyl –C-H modes (Figure S4). Note that the unfilled PVP fiber has a weak signal in the region of 1550 - 1650 cm<sup>-1</sup> (amide group) that overlaps with the signal of MBBA; however, the intensity of the PVP signal is much weaker than MBBA and the Raman characterization of MBBA in the PVP sheath is straightforward (Figure S5). Moreover, the intensity of the MBBA signal at 1500 - 1650 cm<sup>-1</sup> shows a clear dependence on the orientation of the polarization from the laser, whereas the intensity of the PVP signal is polarization independent. Thus, the Raman spectra of an LC/polymer fiber show clearly that MBBA is present within the fiber when compared with the reference spectra (Figure S5).

For the first time, a liquid crystal (MBBA) core and PVP sheath of a single coaxial fiber are individually visualized using 2D Raman mapping using their respective signals at  $\sim 1600$  cm<sup>-1</sup>

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and ~3000 cm<sup>-1</sup> in **Figure 5** and in **Table S1**. The images in **Figure 5** were collected using an excitation laser polarized either parallel or perpendicular with respect to the orientation of the long-axis of the fiber. A clear polarization dependence for MBBA is demonstrated by the images **Figure 5** since Raman intensities at 1600 cm<sup>-1</sup> increase, but do not for the PVP sheath at 3000 cm<sup>-1</sup>. The Raman intensity from each of the modes around 1600 cm<sup>-1</sup> depends on the angle between the excitation polarization and the particular vibrational axis orientation. Maximal intensity occurs when the excitation polarization and vibrational axis orientation align. The angle between the MBBA long axis and the vibrational axes of the three Raman modes located around 1600 cm<sup>-1</sup> was previously found to be  $< 6^{\circ}$ .<sup>39</sup> Thus, the Raman intensities of the Raman signals from the polarization dependence of MBBA are most intense when the excitation polarization is parallel with direction of the fiber long axis. Thus, the long axis of MBBA must align along the fiber direction as illustrated by the diagram shown in **Figure 5**.



**Figure 5.** 2D Raman mapping images taken with excitation polarization (1600 cm<sup>-1</sup> or 3000 cm<sup>-1</sup>) either parallel or perpendicular (white double-sided arrows) to the fiber long axis; scale bars are 1  $\mu$ m. (top). MBBA is shown with a blue arrow to indicate the approximate direction of the vibration at ~1600 cm<sup>-1</sup> and its arrangement in an electrospun fiber (bottom).

**Figure 6** presents the 2D Raman map of a location on a fiber mat where fibers intersected in a perpendicular orientation. Importantly, in **Figure 6A**, the Raman signals are most intense when the excitation polarization is parallel with fiber 1 (vertical) than for fibers 2 and 3 (perpendicular). However, in **Figure 6B**, when the excitation polarization orientation is set to perpendicular with fiber 1, its Raman intensities become dark and the intensities for fibers 2 and 3 increase since they are now in a parallel orientation with the excitation polarization. These

results demonstrate clearly the polarization dependence of the MBBA encapsulated in PVP, as well as the parallel orientation of the molecular axis of MBBA relative to the fiber direction.



**Figure 6.** A) and B) 2D Raman mapping images of the intensities at 1600 cm<sup>-1</sup> showing the line cuts (2); scale bars are 3  $\mu$ m. C) and D) Normalized Raman intensities along the line cut for 1600 cm<sup>-1</sup> (2) and 3000 cm<sup>-1</sup> (2).

The effect of relative core and sheath flow rates on fiber dimensions were measured using Raman line cuts on fiber samples where the flow rate of MBBA was either 0.5 or 1.0 mL  $h^{-1}$ . The corresponding locations of the line cuts are shown in **Figure 6** by the red lines. The core and

sheath diameters determined from each line cut measurement are listed in **Table S2**. The average diameter of the fibers determined by the line cuts are also shown in **Figure 3** and compared well to those measured from the SEM images. As expected, the core diameter increased as the core flow rate was increased. Specifically, a doubling of the core flow rate increased the core diameter by two fold. The sheath diameter was also increased by twofold, although the magnitude of error in measuring the sheath thickness obscure its potential significance.

Temperature Sensitive Iridescence and Thermal Analysis/ The presence of MBBA within the fibers induced a temperature sensitive iridescence from birefringence in its nematic phase under cross-polarized light as shown in **Figure 7**. The nematic phase birefringence of MBBA is observed between 21 - 41 °C. Above 41 °C, MBBA proceeds through the nematic to isotropic transition, turning into an isotropic liquid and loses its unique optical properties. Thus, when the fibers with MBBA were heated above this temperature they appeared dark under crosspolarizers because MBBA reached its isotropic phase. Although the fibers do not go completely dark, it is known that encapsulation of MBBA may considerably affect the temperature ranges of its phase changes as found in other systems.<sup>40</sup> Importantly, since the temperature range at which birefringence in the fibers is lost corresponds well with the known isotropic transition for neat MBBA, it suggests that the MBBA encapsulated in PVP behaves similarly to its bulk state. Thus, confinement or surface interactions are small at these temperatures. Furthermore, the iridescence was reversible and repeatable over several heating and cooling cycles. The repeatability also confirms that MBBA is encapsulated in a distinct sheath where it is able to freely transition from one phase to another in response to temperature.



**Figure 7.** Cross-polarized optical microscopy photographs of PVP fibers containing MBBA (flow rate =  $0.50 \text{ ml h}^{-1}$ ) at different temperatures.

Past studies on the confinement effects of MBBA show that its phase transitions can be affected by cavity size on the nanometer scale although most of these studies employed rigid cavities. It has been shown that the phase transition temperatures of MBBA decrease with decreasing pore size and have a tendency to broaden.<sup>40-41</sup> In some cases very small pores, on the angstrom scale, have led to phase transitions which cannot be resolved by DSC measurements.<sup>40</sup> Thus, the rigidity of these cavities provided strong confinement by steric interactions limiting the ability of MBBA to align. Here, we anticipate that the effects of confinement occurred to a lesser degree since the PVP sheath has a greater degree of flexibility than a rigid pore. Thus, confinement of MBBA was explored by DSC analyses. Thermograms of neat MBBA and of the fibers are shown in Figure 8. As expected, the intensity of the endotherm corresponding to the C (crystalline)  $\rightarrow$  N (nematic) transition increased as the core flow rate of MBBA was increased because the amount of MBBA in the fiber cores increased. Although the peak corresponding to the  $C \rightarrow N$  did not appear to broaden, the temperature of the transition to the nematic phase of MBBA in the fiber was approximately 3 °C lower than neat MBBA. A lowering of this transition indicates that the alignment of MBBA may be kinetically hindered due to encapsulation from anchoring without position order,<sup>17</sup> perhaps for MBBA located at the core-sheath interface. Still, these results suggest that MBBA can align in PVP nearly as well as it can in its bulk state at the

temperatures shown in **Figure 8**. One could expect this from the 2D Raman line cuts for the core-sheath measurements because the core is relatively thick compared to the sheath material.



**Figure 8.** DSC thermograms on heating of neat MBBA (black line) and as encapsulated in PVP sheath fibers produced with different flow rates of MBBA. The crystalline (C) to nematic transition (N) (light blue) and nematic (N) to isotropic (I) transition (grey) are highlighted. The thermogram of neat MBBA has been scaled to 1% of the original value.

Low Temperature DSC and MBBA Confinement. MBBA is known to have rich polymorphism depending upon if it is fast or slow cooled to temperatures below 0 °C.<sup>42-43</sup> Note that the data presented in Figure 8 is of MBBA subjected to slow-cooling and the features that will be discussed below (at low temperatures) were not present in that scenario. Numerous solidstate studies of fast-cooled MBBA have reported several solid phases at low temperatures using a variety of experimental techniques.<sup>42-45</sup> In general, these phases are thought to be metastable glassy or smectic phases and are dependent on the rate of cooling (or heating). Low temperature <sup>1</sup>H NMR analyses<sup>43</sup> of MBBA have suggested that the MBBA molecule can undergo rotational

motion at either its methoxy group, aryl rings, or butyl chain, although the exact nature of these structures are unknown.

The various solid forms of MBBA are summarized in **Scheme S1**.<sup>43</sup> Samples of MBBA which have been fast-cooled from the nematic phase initially form an amorphous (glassy) phase (C<sub>0</sub>). Heating the C<sub>0</sub> phase allows the various functional groups of MBBA to undergo relaxation which results in multiple metastable phases, C<sub>1</sub>-C<sub>4</sub>, that are different in structure. The metastable phases C<sub>1</sub> and C<sub>2</sub> arise primarily from rotation and re-orientation of the methoxy group, respectively, and have been suggested to be smectic A and C phases, respectively.<sup>46.47</sup> The crystalline phases, C<sub>3</sub> and C<sub>4</sub>, occur primarily from motions of the butyl chain, which were frozen at the lower temperatures. It is expected that the aryl rings of MBBA will occupy a small distribution of different torsion angles throughout all of the C<sub>0</sub>-C<sub>4</sub> phases.

The DSC thermogram of fast-cooled MBBA in **Figure 9** shows nicely each of the aforementioned transitions in both neat MBBA and the MBBA filled fibers; the literature transition temperatures from proton NMR are shown in the insets. First, heating a fast-cooled sample of neat MBBA from its initial  $C_0$  state, we found the glass transition for  $C_1$  to be -72 °C. Heating above the glass transition is a sharp exothermic peak for  $C_2$  at -57 °C, followed by a second more broad crystallization peak ( $C_3$  and  $C_4$ ) from -40 to -10 °C, with a maximum at -28 °C. The transitions to the nematic phase occur at 16 °C and 22 °C resulting from at least two distinct types of solid phase populations upon heating. Thus, the phase transitions found in the DSC here compare well to values reported in the literature from proton NMR.<sup>43, 48</sup>

Interestingly, when fast-cooled MBBA is heated inside the fibers the DSC thermogram is markedly different. Although its glass transition for  $C_1$  occurs at approximately the same temperature (-72 °C), the sharp crystallization peak for  $C_2$  is absent and the transition peak to  $C_3$ 

and C<sub>4</sub> broadens and occurs 8 °C lower than in the neat MBBA. Perhaps, the C<sub>2</sub> phase of encapsulated MBBA becomes suppressed from confinement in the polymer sheath, shifting to higher temperatures and coalescing with the broader crystallization peak for C<sub>3</sub>-C<sub>4</sub>. However, its irregular shape indicates that there may be two or more broad overlapping peaks with maxima at -42 °C and -27 °C and the dielectric spectra (vide infra) are consistent with the phase being C<sub>1</sub>. Thus, solid phases of MBBA are restricted and it appears the C<sub>2</sub> phase is completely lost due to confinement in the PVP sheath at low temperatures.



**Figure 9.** DSC thermograms of fast-cooled neat MBBA (top panel) and MBBA (0.50 ml hr<sup>-1</sup> flow rate) encapsulated in the PVP sheath fibers (bottom panel). The various solid phases from MBBA are indicated in the insets. The rate of heating and cooling was 10 °C min<sup>-1</sup> and 100 °C min<sup>-1</sup>, respectively.

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Confirmation of Alignment and MBBA Phases: Dielectric Spectroscopy. Dielectric spectroscopy was performed on neat MBBA and MBBA filled PVP fibers with a core flow rate of 0.5 mL h<sup>-1</sup>. First, the results of neat MBBA compared to its encapsulation in the PVP fibers at 30 °C is discussed and then the low-temperature results (Figure 10). The dielectric loss spectrum at 30 °C for neat MBBA shows a simple absorption peak with a frequency of 360 kHz, indicative of its nematic phase and corresponding to motions from its methoxy group.<sup>49-51</sup> However, two peaks for the nematic phase should be expected; a low frequency peak for the component of the dielectric constant parallel to the LC director ( $\varepsilon_{l/l}$ ) and one a higher frequency related to that perpendicular to the LC director ( $\varepsilon_1$ ). Thus, a more reasonable interpretation of the peak in Figure 10A is that it is the superposition of the two expected contributions, which is consistent with the slight broadening at low frequency; note that the crystallization point of MBBA is not low enough to obtain decoupling measurements of the two peaks on cooling. Further, the similarity in the dielectric spectra for neat MBBA and its encapsulation in PVP suggests that significant confinement effects are absent at 30 °C; the ability of MBBA to align and adopt its preferred orientation is mostly unaffected. Perhaps, the thick MBBA core in the fibers allows for interactions between molecules of MBBA to dominate rather than interactions with PVP at the core-sheath interface and allows for MBBA to align. This result agrees with the findings in the DSC thermograms in **Figure 8** as discussed previously, which had shown that the orientation of MBBA was not restricted in the PVP sheath fibers because the C  $\rightarrow$  N transition of MBBA did not shift nor broaden compared to the bulk.



**Figure 10.** Permittivity spectra of the dielectric loss of neat and encapsulated MBBA (0.5 ml hr<sup>-1</sup>) at different frequencies at A) 30 °C and B) -66 °C.

Comparing the dielectric loss of neat MBBA and its encapsulation in the PVP sheath fibers at low temperatures (**Figure 10B**) provides unique insights into how the PVP sheath fibers affect the ability of MBBA to adopt its preferred orientation. A complete profile of the dielectric spectra of neat MBBA as a function of frequency at various temperatures is shown in **Figure S6**. The dielectric loss spectrum for neat MBBA in **Figure 10B** shows two peaks with peak frequencies of 6.5 Hz and 6.5 kHz during reheating to  $-66 \,^{\circ}$ C from  $-120 \,^{\circ}$ C. The presence of the two peaks is consistent with MBBA in a supercooled smectic phase, perhaps in its C<sub>2</sub> phase, where the two peaks correspond to the  $\varepsilon_{l/l}$  and  $\varepsilon_{\perp}$  contributions, which could not be observed at 30  $^{\circ}$ C (**Figure 10A**) because of the superposition of the two peaks.

The dielectric signals at different temperatures of encapsulated MBBA were found to behave similarly to neat MBBA, however, their relative intensities are different. In **Figure 10B**, the dielectric spectra are shown for both neat MBBA and encapsulated MBBA at -66 °C. At this temperature, the loss peak at lower frequency ( $\varepsilon_{l/l}$ ) is suppressed relative to that at higher frequency ( $\varepsilon_{\perp}$ ). The suppression of the dielectric signal corresponds to the inability of encapsulated MBBA to reach its smectic  $C_2$  phase by re-orientation of its methoxy group and compliments well to the results found by DSC (loss of the  $C_2$  phase) in **Figure 9**. Evidently, the PVP sheath fibers become rigid enough to suppress important functional group motions from MBBA at this temperature and the MBBA molecules are no longer able to align in their preferred orientation. Note that because of a very complicated sample geometry for the encapsulated MBBA, the absolute value of the dielectric constant cannot be determined accurately and only relative comparisons of the two peaks can be made.

#### CONCLUSIONS

The liquid crystal MBBA has been encapsulated as the core material in core-sheath fibers for the first time via coaxial electrospinning and a detailed analysis of the effects on its confinement has been made. The electrospun fibers exhibited a temperature sensitive iridescence from the encapsulated MBBA and the optical and thermal changes in response to confinement were explored using a wide variety of experimental techniques including SEM, optical microscopy, DSC, 2D Raman mapping, and dielectric spectroscopy. The optical analyses show that the electrospun fibers could be produced with a consistent morphology (no 'beading') by employing an inner spinneret needle with a smaller diameter than is commonly used. Also, as the flow rate of the MBBA core was increased, the average diameter of the fibers increased linearly with a concomitant shift in the cylindricities of the cross-sections from circular to oval or rectangular. For the first time, 2D Raman mapping was used to confirm the core-sheath morphology of electrospun fibers and was also able to assess the core and sheath diameters. Further, the orientation of the Raman laser polarization elucidated that the long axis of MBBA is parallel with the direction of the fiber.

The thermal analyses by DSC indicated that the phase transitions of encapsulated MBBA above 0 °C are relatively unaffected, perhaps, because the core volume is thick relative to the polymer sheath; the MBBA molecules interact primarily with themselves rather than the PVP. However, at temperatures below 0 °C, the PVP sheath becomes rigid enough to suppress the formation of the smectic ( $C_2$ ) phase of MBBA. The absence of the  $C_2$  phase is because the sheath restricts re-orientation of the methoxy group of MBBA as observed by the dielectric relaxation measurements.

Incorporation of MBBA, as well as other LCs with different thermal properties, into higher order and helical structures in electrospun core-sheath fibers is a subject of ongoing research in our laboratory.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX. Details of synthetic procedure for MBBA; <sup>1</sup>H NMR and FT-IR of MBBA; Raman spectra and Raman polarization dependence of MBBA, PVP, and the MBBA filled fibers; additional 2D Raman mapping images; core and sheath diameters from Raman line cuts; summary of various solid forms of MBBA; dielectric relaxation spectra of MBBA at different temperatures.

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## NOTES

The authors declare no competing financial interest.

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