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Optically Responsive Textile Application Based on Uniaxially Ordered Polymer-Liquid Crystal Microfibers

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Abstract: This study discusses the fabrication and characterization of optically responsive microfibers with uniaxially ordered liquid crystal molecules at their core. The liquid crystal microfibers were electrospun from a solution of PVP (polyvinylpyrrolidone) and MBBA (N-(4-Methoxybenzylidene)-4-butylaniline) using absolute alcohol as a solvent. Two parallel copper (Cu) collectors were used to obtain ordered fibers. The microfibers with oriented LC were well fabricated at a voltage of 5 kV; the distance between the needle and the collectors was 10 cm. The light intensity that passed through the LC microfibers depended on the diameter of the needle and the PVP concentration during the electrospinning process. A thermal-optical analysis revealed that the fibers were responsive to temperature. The rise of temperature resulted in a dark pattern of the fibers under a polarized optical microscope (POM) while the fibers were re-shined as the temperature was lowered. A DSC measurement confirmed that the LC molecules were confined in the fibers.

Keywords: Composite microfibers; liquid crystal microfibers; responsive fibers

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1. Introduction

Liquid crystal is a material that can be combined with many types of polymer. Many applications of liquid crystal have been demonstrated using a fabricated polymer liquid crystal composite [1–3]. Research of polymer liquid crystal composite is interesting because of the unique characteristics of liquid crystal itself. Liquid crystal molecules have a positional order similar to the positional order of molecules in solids, but the molecules can move freely similar to molecules in liquids. Therefore, although the molecules in liquid crystal form a liquid, they result in a birefringence phenomenon similar to the molecules in anisotropic crystals. The most interesting property of liquid crystal is the crystal's ability to respond to stimuli, such as external fields, lights, and temperatures. Polymers are primarily used as matrices due to their dominant volume fractions.

To obtain more potential applications, further studies have been done in combination of two different scientific topics. They took the advantages offered by electrospinning technology and liquid crystal. Krause *et al*, successfully fabricated liquid crystal fibers from *Main Chain Liquid Crystal*

Elastomer (MCLCE) through the process of electrospinning and crosslinking. Thin films were produced which were first oriented and then crosslinked by UV light to give liquid single crystal main- chain elastomers. These elastomers show exceptional mechanical properties such as strong load-dependent thermoelastic effect and a nonlinear stress–strain relation. In their mechanical properties, they resemble spider silk [4]. In other approaches, the electrospinning of liquid crystal-polymer fibers was demonstrated with the use of coaxial electrospinning [5] and non-coaxial electrospinning method to keep the liquid crystal of 5CB phase-separated and self-assembled as a nematic core within a polymer shell [6]. Furthermore, liquid crystal microfibers responded optically to temperature changes [7].

Kim *et al*, in their review, reported that liquid crystal functionalization of electrospun polymer fibers has potential applications, especially in wearable technology, such as smart textile or fibers integration with sensors [8]. In this study, we demonstrated the fabrication of polymer-liquid crystal fibers as optically responsive fibers. The fibers were electrospun by non-coaxial electrospinning and we used the same polymer as that had been demonstrated before [6], PVP is a linear polymer and transparent so it has no birefringent. A linear polymer can make liquid crystal molecules easier to be aligned. Liquid crystal of MBBA was mixed directly with polymer solution. Because of their potentials, the investigation focused on other physical properties. We applied heat to the fiber and analyzed the effect of temperature change on the morphology or optical appearance of the fiber.

2. Materials and Methods

Materials

The polymer used in the study was PVP. It had a molecular weight of 1,300,000 g $mole^{-1}$ and, was purchased from Sigma-Aldrich Corporation in Singapore. The study also used absolute ethanol as a polymer solvent; it was obtained from Merck, Indonesia. Nematic MBBA LC was used; it had a molecular weight of 67.37 g $mole^{-1}$, and it was provided by the Tokyo Chemical Industry Corporation, Limited in Japan.

Electrospinning Method

The electrospinning process was adapted by recent study [7]. First, the polymer solution was prepared by dissolving PVP in absolute ethanol using hot plate stirrer at room temperature for 2 hours. The concentration of PVP was 17 %. Second, the PVP solution was then mixed with MBBA using hot plate stirrer at room temperature for one day. The concentration of MBBA in PVP solution was 3:2 of PVP/MBBA mass ratio.

The microfiber was prepared using the electrospinning method. An electrospinning apparatus was set up where high voltages were 5 kV and 10 kV and the distance between the needle and collectors was 10 cm. The aligned fibers were obtained by modifying the collectors. The collectors were two-dimensional (2D) modified Cu; each measured 7.9 × 1.5 × 0.15 cm, and the gap was 2 cm. A glass substrate measuring 1 cm × 2.5 cm was put between the collectors, as shown in Fig. 1. The needle's internal diameter (ID) was 0.5 mm and 0.8 mm. Glass slides measuring 10 mm × 25 mm were

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placed between the two collectors. The electrospinning process was performed for 10 s.

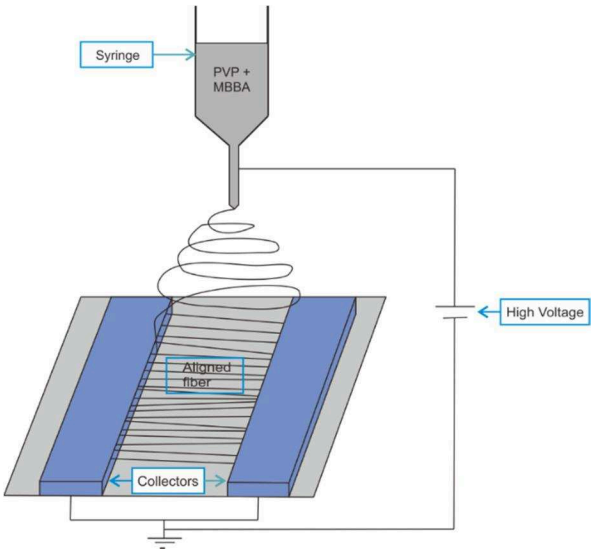

Figure 1. Electrospinning set-up using parallel copper collectors with gap 4.8 cm

Characterization and Measurements

Optic characterization of liquid crystal microfibers were carried out as follows. The sample was put under a crossed polarizer to observe the optical behavior of liquid crystal microfibers. The observation was conducted using a polarized optical microscope (Nikon, Optiphot-pol) by varying the rotation angles from 0º to 360º. Images of the sample were taken using Pixel View program. The transmitted intensity of light, I, was measured using a photo detector.

To characterize the alignment of fibers, the fiber orientation order parameter was determined to *S* [9]. The order parameter *S* could also determine the degree of order in nematic liquid crystal [10]. The *S* value varies from 0 indicating random alignment for fiber and isotropic phase for liquid crystal to 1 as a perfect alignment and perfect orientation order of nematic phase. The order parameter *S* is formulated as;

$$S = \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle \quad (1)$$

where θ is either the angle between the individual fiber forms with preferred alignment director or the angle between each molecule of nematic liquid crystal and the direction of nematic axis **n**. The angle θ of fiber was measured using *imageJ* software.

The optical behavior of liquid crystal microfibers as well as optical behavior of planar nematic liquid crystal was described by [10]. The transmitted light intensity was given by Equation (2, 3). Liquid crystal microfibers were aligned planar to the plane of P/A or in other words $\varphi = 90°$, thus $n_e = n_o$. The maximum intensity at $\varphi = 45°$ and the minimum intensity at $\varphi = 0°$ or multiple angle of 90°.

$$I = I \quad sin^2 2\varphi \quad (2)$$

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$$I \quad = I_0 sin^2 \frac{\delta}{2} \tag{3}$$

where I_0 is the light intensity after the polarizer, φ is the angle between optic axis and analyzer/polarizer and δ is the phase difference.

Thermal-optical transmittance measurements of the samples were carried out as follows. Two indium tin oxide (ITO) coated glasses as substrates were used to make a sample cell separated by two parallel strips of Mylar spacer with 50 μm thickness, one layer of ITO glass consisting of polymer-liquid crystal fiber that had been collected before. This cell construction aims to keep the thermal condition around the fibers stable. A heater control unit (Digital Controlled CHINO DB500) was used as a heat source. The cell was put into an enclosed hot plate that could gain heat by inducing electric field. The sample was heated from a room temperature around 25°C to 35°C as an isotropic phase for liquid crystal, then was cooled back to room temperature again. A photodetector was used to measure the intensity of fibers, and the fibers were observed by polarized optical microscope (Nikon, Optiphot-pol). The thermal properties of the sample were analyzed using DSC. A DSC-60 Plus from the Shimadzu Corporation in Japan was used. Temperatures ranged from -10ºC–60ºC; the heating rate was 10ºC every minute, and it was maintained using a nitrogen flow of 30 ml every minute.

3. Results and Discussion

3.1 Optic Behavior of Liquid Crystal Microfibers

Uniaxially oriented polymer-liquid crystal microfibers with diameter under 6 μm were successfully fabricated using the modified electrospinning as shown in Fig. 2. Two copper (Cu) gap collectors were applied to draw uniaxially aligned fibers. The liquid crystal microfibers were uniaxially aligned across the gap with their longitudinal axes oriented perpendicular to the edges of the gap. Figure 2 shows the difference between microfibers with liquid crystal and only pure PVP observed under cross polarizer. In Fig. 2(a), the x-axis light passing from polarizer (P) is converted to elliptically polarized light by liquid crystal molecules inside microfibers, therefore the polarized light direction can pass the analyzer (A). While pure PVP (Fig. 2(b)) cannot convert the polarized light, causing the light unable to pass the analyzer. Also, the liquid crystal microfibers in Fig. 2(a) shows a positive birefringence presented by liquid crystal molecules in the fiber as had been described in a recent study [7]. The modified collector of electrospinning system successfully delivered a good value of orientation order parameter $S + \Delta S = 0.990 \pm 0.014$.

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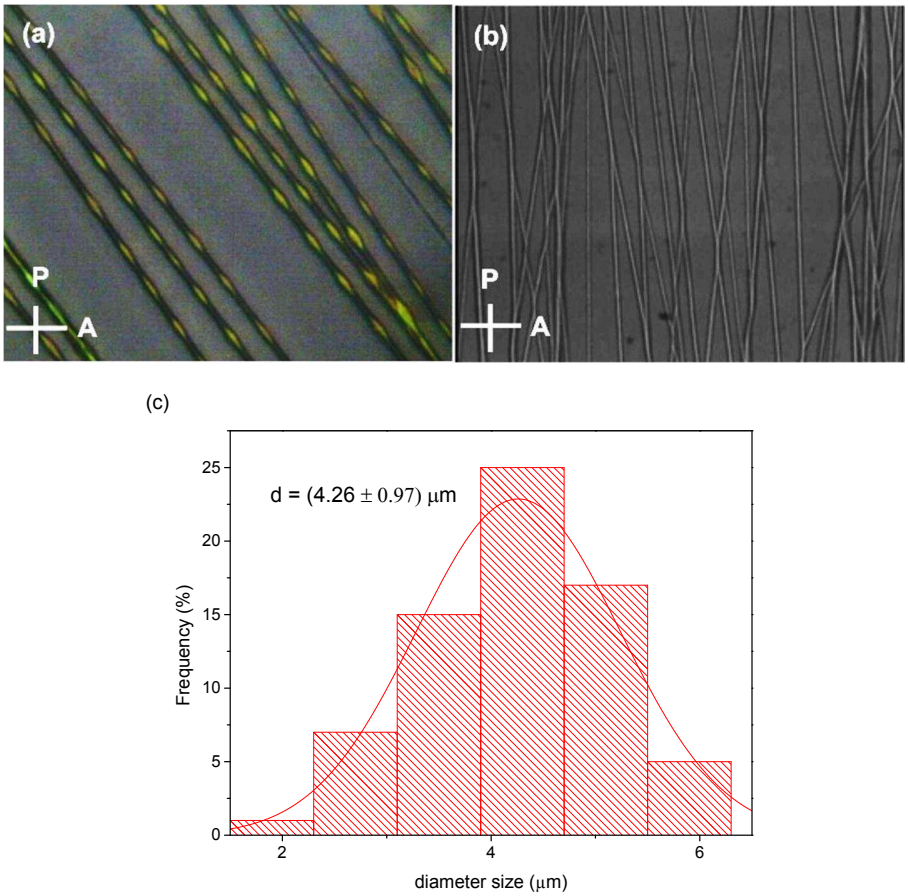

Figure 2. Uniaxially aligned microfiber of (a) liquid crystal inside the PVP microfiber rotated at 45 ºC and (b) pure PVP at 0º under crossed polarizers; polarizer (P) and analyzer (A), and (c) diameter distribution of liquid crystal microfibers

Polarized optical microscope (POM) also showed another unique optical phenomenon exhibited by varying rotation angle of the fibers. In Fig. 3(c), the dark pattern appeared when the sample of PVP-MBBA fiber is in position 0° to the polarizer or analyzer and the bright pattern was seen in fibers when the sample was rotated at 45° with respect to polarizer and analyzer in Fig. 3(d). Meanwhile, the sample of PVP fiber only showed the dark pattern in Fig. 3(a) and Fig. 3(b). Optical measurement on the fibers aims to measure the intensity of light passing through fibers to every turning angle change. As shown in Fig. 3(e), we can see that the intensity remained low at every angle in PVP fiber. This happened because the PVP fiber could not convert the polarized light coming from polarizer, hence it was blocked by the analyzer, while the liquid crystal microfibers displayed a change in intensity. The intensity graph in Fig 3(f) showed a sinusoidal pattern similar to the pattern that appears when polarized light is converted to elliptically polarized light with a component that can pass through the crossed polarizer. Therefore, the maximum intensities occurred when the liquid crystal microfibers were rotated to 45º with respect to the polarizer and analyzer. This result was confirmed by Eq. (2); the $\sin^2(2\varphi)$ was equal to 1, so the maximum light intensity was able to pass through the sample. Rotating the sample so that it was parallel to either the polarizer or the analyzer resulted in minimum light intensities. Additionally, the needle's diameter was an important

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parameter. Using a needle with a 0.8 mm ID, the fibers were brighter than the fibers yielded using a needle with a 0.5 mm ID.

It can be concluded that the drawing conditions on the fibers alignments affected the transmitted light-intensity magnitude. With randomly oriented liquid crystal microfibers, fibers parallel to the polarizer were possible; thus, the light intensity decreased. Meanwhile, the uniaxially aligned LC microfibers, which were rotated to 45º with respect to the polarizer and the analyzer, clearly had a maximum transmitted light intensity.

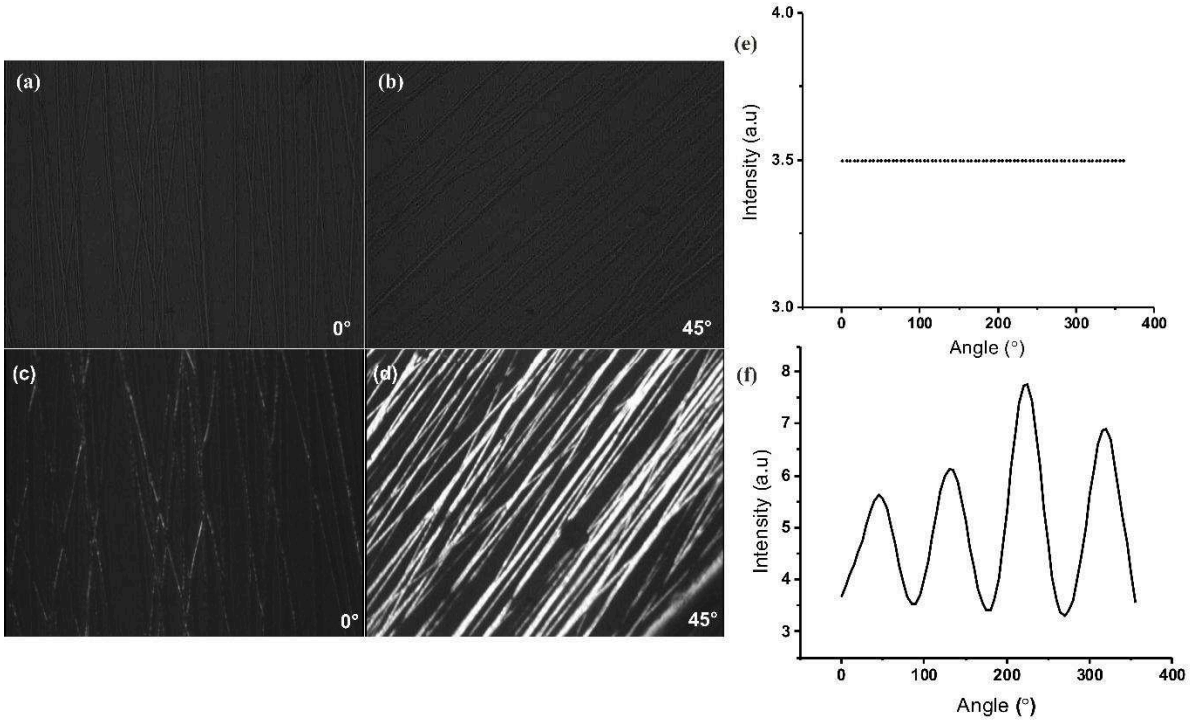

Figure 3. PVP fiber at 0° (a) and 45° (b), and PVP-MBBA fiber at 0° (c) and 45° (d) with respect to P and A (c). The black dot represents light intensity of PVP fiber (e) and the black line represents light intensity of PVP-MBBA fiber (f).

3.2. The thermal behaviors of liquid crystal microfibers

The liquid crystal microfibers nematic and isotropic phase transitions underwent an endothermic process. In Fig. 4, the first curve describes the liquid crystal transition from crystal phase to the nematic phase and the second curve describes the liquid crystal transition from the nematic phase to the isotropic phase. A DSC measurement of pure MBBA resulted in a nematic-isotropic transition temperature (T_{NI}) at about 47.7ºC, as shown in Fig. 4(a). The second curve in Fig. 4(a) shows isothermal phase transitions starting at 47.7ºC; the transitions indicate the LC molecules began transitioning from the nematic phase to the isotropic phase (the value of T_{NI}).

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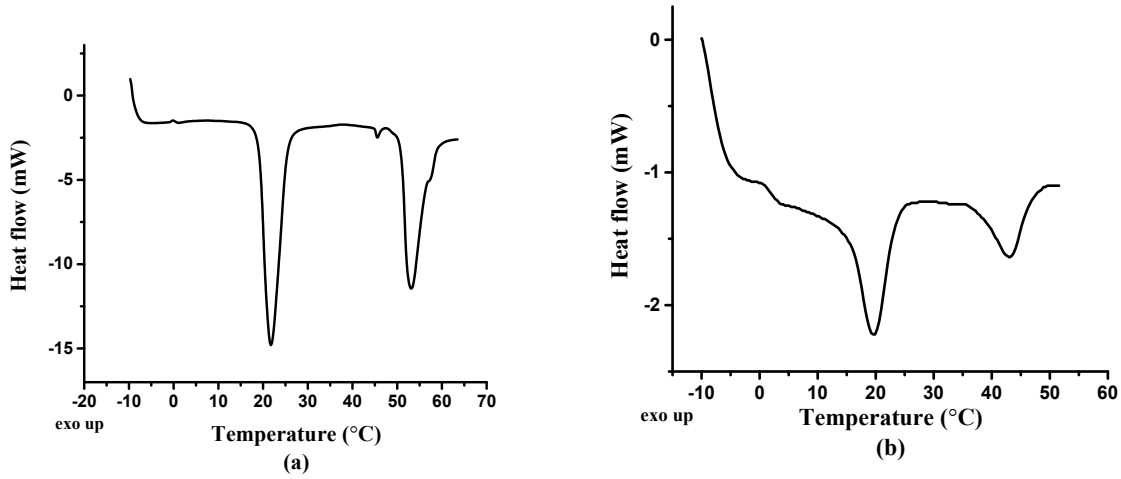

Figure 4. The DSC measurements of (a) pure MBBA (b) and LC microfibers.

The DSC of the liquid crystal microfibers is shown in Fig 4(b). This DSC result focusses on observing the behavior liquid crystal inside the fibers. The T_{NI} of the liquid crystal was observed at about 36ºC, which is much lower than T_{NI} of pure MBBA. The small size of fibers greatly disrupted the long range orientational order of liquid crystal molecules and the addition of polymer (PVP) caused the intermolecular force between liquid crystal molecules to decrease, making them easier or faster to undergo of transition from nematic to isotropic phase. A previous study explained that the T_{NI} of MBBA could be influenced by the addition of other material types [11]. This analysis was confirmed by enthalpy changes in the nematic-isotropic phase. PVP is an amorphous polymer, so it caused the enthalpy to decrease, as shown in Fig. 4. The enthalpy in liquid crystal microfibers nematic-isotropic phase was lower than the enthalpy in pure MBBA's nematic-isotropic phase.

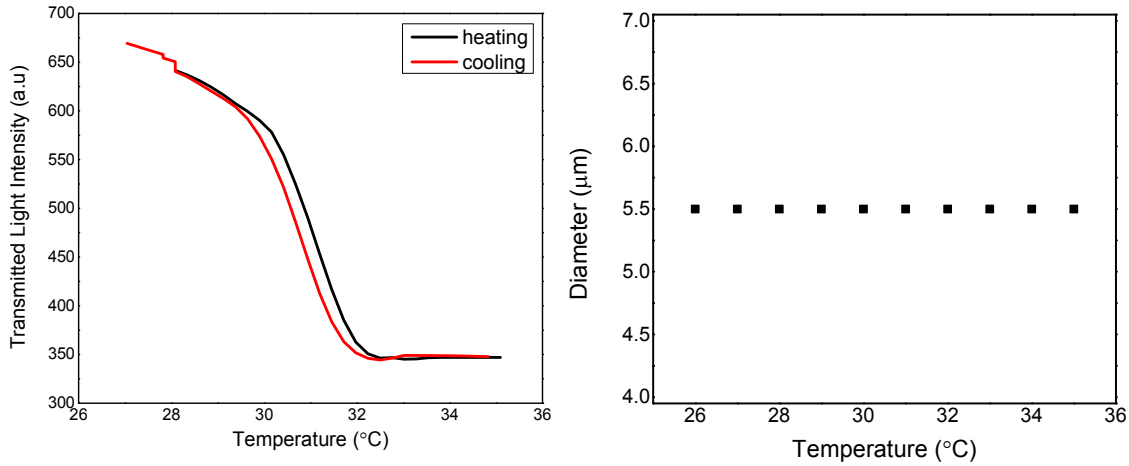

Figure 5. Temperature effect on transmitted intensity (a) and (b) on diameter of PVP-MBBA fiber.

The phase transitions of liquid crystal microfibers were also confirmed by thermal-optical measurement. A photodetector was used to observe the heating and cooling of the sample. As shown

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in Figure 5(a), heating the sample decreased the light intensity of the fibers (dark pattern) due to the phase transition from nematic phase to isotropic phase. It means, as the temperature rose, the molecules which were uniaxially aligned along the fibers got oriented randomly. Hence, they could not transmit the light through the analyzer. While cooling the sample from the temperature of isotropic phase to nematic phase increase the light intensity (bright pattern). The result of thermal-optical measurement had been reported before on a recent study [Rusliana]. The morphology showed that a temperature change did not affect the fibers' diameters, as shown in Fig 5(b), and this was most likely due to the high melting temperature of the PVP. The results indicate that liquid crystal microfibers have a strong potential to be used as smart-textile components. For example, the fibers can be used as body-temperature sensors in integrated textiles.

4. Conclusions

Optically responsive liquid crystal microfibers were successfully fabricated using non-coaxial electrospinning. Uniaxally oriented LC microfibers were obtained with modified Cu collectors, a high voltage of 5kV and a polymer with a high molecular weight. A POM analysis showed that the samples had unique optical behaviors. The fibers maximum intensities occurred when the fibers were aligned uniaxially and rotated to 45º from the polarizer and analyzer. A thermal-optical analysis showed the fibers responded to temperature stimuli. A DSC measurement confirmed that the LC molecules were confined when using the PVP as a polymer matrix. Adding the amorphous polymer changed the T_{NI} and decreased the enthalpy in the nematic-isotropic phase. The liquid crystal microfibers can be used as body-temperature sensors in integrated textiles. This is because the human body does not emit high temperature; it only emits between the fibers nematic- and isotropic-phase temperatures.

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