Thermal-optical analysis of polymer–liquid crystal microfibers
Rusliana Fatayati1, Ahmad Kusumaatmaja1,2, and Yusril Yusuf1,2*

1Department of Physics, Faculty of Mathematics and Natural Science, Gadjah Mada University, Sekip Utara Yogyakarta 55281, Indonesia
2Nanomaterial Research Groups, Gadjah Mada University, Sekip Utara Yogyakarta 55281, Indonesia
*E-mail: yusril@ugm.ac.id
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In this paper, the analysis of optically responsive microfibers with uniaxially ordered liquid crystal (LC) molecules at their cores is discussed. LC microfibers were electrospun from a solution of poly(vinyl pyrrolidone) (PVP) and N-(4-methoxybenzylidene)-4’-butylaniline (MBBA) using absolute alcohol as a solvent. Two parallel copper (Cu) collectors were used to obtain ordered fibers. The microfibers with oriented LC molecules were well fabricated at a voltage of 5 kV. A thermal-optical analysis revealed that the fibers were responsive to temperature. The rise of temperature from nematic to isotropic phase of LC decreased the LC intensity under a polarized optical microscope (POM).

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A microfiber is a one-dimensional (1D) ultrafine microstructure. Microfibers have gained significant interest in recent years owing to their potential applications to adsorption, filtration, drug delivery, and electrochemical fields, among others.1–3 A conductive polymer is used as the main material in electrospinning, and it is dissolved in a solvent solution to be produced as fibers using an electrospinning apparatus. Recently, many researchers have studied electrospinning by combining a polymer with other materials, such as nanoparticles and liquid crystals (LCs). Many applications of LCs have been demonstrated using a fabricated polymer LC composite.4,5 Research on polymer LC composites is interesting because of the unique characteristics of LCs. LC molecules have a positional order similarly to that of molecules in solids, but they can move freely similarly to molecules in liquids.7 The most interesting property of LCs is their ability to respond to stimuli, such as external field, light,10,11) and mechanical stress.12) Recent studies have examined electrospinning and LCs to discover potential LC applications.13–16) Kim et al. reported that the LC functionalization of electrospun polymer fibers has several potential applications, especially in wearable technologies, such as fibers integrated with sensors.17) In this study, functional optical fibers were fabricated using polymer LC fibers. The fibers underwent noncoaxial electrospinning. The sample needed to form oriented fibers to develop bright and dark microfiber patterns. Therefore, the electrospinning apparatus was modified; two parallel Cu gap collectors were added. A polymer used in previous studies was used.18) Poly(vinyl pyrrolidone) (PVP) is a transparent linear polymer, so it does not have birefringence. This study focused on other physical properties. Heat was applied to the fibers and the effect of temperature change on the optical appearance of the fibers was analyzed.

The polymer used in this study was PVP (1,300,000 g mole−1) purchased from Sigma-Aldrich. The polymer solvent used was absolute ethanol obtained from Merck. A nematic N-(4-methoxybenzylidene)-4’-butylaniline (MBBA) LC (67.37 g mole−1), provided by Tokyo Chemical Industry was also used.

The electrospinning solution was prepared using two steps. First, the polymer solution was prepared by dissolving PVP in absolute ethanol for 2 h using room-temperature hot plate stirrers. Second, the PVP solutions were mixed with MBBA for 1 d using a room-temperature hot plate stirrer. An electrospinning apparatus was set up with high voltages of 5 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 cm2, and the gap between them was 2 cm.

Thermal-optical transmittance measurements of the samples were completed. Two glasses coated with indium tin oxide (ITO) were used as substrates to obtain a sample cell. The substrates were separated by two parallel Mylar spacer strips. The cell construction was aimed to maintain a stable thermal condition around the fibers. A heat control unit (CHINO DB500) was used as a heat source. The cell was put on an enclosed hot plate that could gain heat by inducing an electric field. The transmitted light intensity (I) was measured using a photodetector equipped with a photodiode and an amplifier.

Uniaxially oriented polymer LC microfibers were successfully fabricated. They had diameters smaller than 6 μm. These fibers formed at PVP concentrations of 15 to 20 wt%. The PVP–MBBA mass ratio that could produce fibers was smaller than 3 : 3 g. The best voltage was 5 kV, which was much lower than that in a previous study.15) This could be due to the fact that the modified collectors used for this study had higher conductivities; thus, they could draw a stronger electric field.10) The fibers were observed using a POM. The POM was equipped with a first-order retardation plate (λ = 530 nm) to determine the optical signs of birefringence of each sample. The planar alignment of MBBA in the fibers was determined from the interference color shift. When the slow axis of the retardation plate (RP) coincided with that of LCs, the fibers displayed a negative birefringence. Otherwise, the fibers displayed a positive birefringence. The fibers were placed at 45° with respect to the transmission orientations of the polarizer (P) and analyzer (A). As shown in Figs. 1(a) and 1(b), yellow interference was observed when the samples were oriented southeast to northwest, while green interference was observed when the samples were oriented northeast.
to southwest. Both colors indicated a positive birefringence. Because PVP has no birefringence, the positive birefringence was formed by the LC molecules in the fibers. The sample also showed that the optic axis (N) followed the fiber axis, resulting in the director of LC alignment along with the fiber axis.

LCs respond optically to temperature changes. The thermal-optical measurement procedure used in this study was simple. The PVP MBBA fibers were placed on a hot plate and heated from room temperature (25 °C) to 40 °C. The fibers were optically observed using the POM to determine the effect of temperature on the morphology or optical appearance of the fibers shown in Fig. 2. As the temperature increased, the brightness of the fibers slowly decreased until it became completely dark, as shown in Fig. 2(c). The fibers were cooled to room temperature. The fibers shone [as shown in Fig. 2(d)] as the temperature decreased, indicating that they had reached the nematic phase again. As MBBA does not have a smectic phase and only exhibits a nematic–isotropic transition, the decrease in the intensity of transmitted light passing through the molecules was stable from nematic (maximum intensity) to isotropic (minimum intensity). This result shows that PVP MBBA fibers have potential applications. For example, they could sense the temperature of a human body, as they do not need high temperatures to react.

The light intensity of the PVP MBBA fibers was measured. A photodetector was used to observe the heating and cooling of the fibers. Figure 3 shows that, during heating, the intensity of transmitted light slowly decreased until it saturated at 32.5 °C. This indicates that the LC molecules reached the isotropic phase, as shown by the dark pattern in Fig. 2(c). The temperature at which the sample reached the isotropic phase (32.5 °C) was much lower than that at which pure MBBA reached the isotropic phase in previous studies. This could be due to the polymer material.

During cooling, the intensity of transmitted light became maximum. It then saturated when it reached the nematic phase and its value was the same as it was initially. Different temperature points (ΔT_N) for the nematic phase (or bright pattern) were observed during heating and cooling. The temperature point for the nematic phase was 26 °C during heating, while that for the nematic phase was 25.2 °C during cooling. This means that the time it took for the molecules to rise from the isotropic phase and reach the perfect nematic phase (maximum intensity) was longer than that it took for the molecules to move during heating and reach the dark
condition. Note that hysteresis occurred during the transition of LC microfibers from the nematic phase to the isotropic phase, as shown in Fig. 3.\textsuperscript{21} The hysteresis was $\Delta T = 30^\circ C - 29.3^\circ C = 0.7^\circ C$. Polymer concentrations could modify the hysteresis.

PVP MBBA fibers were successfully fabricated by non-coaxial electrospinning. Uniformly oriented LC microfibers were obtained with modified Cu collectors, a high voltage of 5 kV, and a polymer with a high molecular weight. A thermal-optical analysis showed that the fibers responded to temperature stimuli.

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