Phase transition and optical behavior of PVP–MBBA microfibers

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This study discusses the fabrication and characterization of optically responsive microfibers with uniaxially ordered nematic liquid crystal molecules at their core. The liquid crystal microfibers were electrospun from a solution of polyvinylpyrrolidone (PVP) and N-(4-methoxybenzylidene)-4-butylanaline (MBBA). A study of phase transition and optical behavior was performed using optical observation by polarized optical microscope, and intermolecular interaction was investigated using Fourier transform infrared (FTIR). The diameter, orientational order of the fibers, and light intensity that passed through the fibers depended on the MBBA concentration during the electrospinning process. The nematic–isotropic temperature ($T_N$) of PVP–MBBA microfibers shifted lower from the $T_N$ of MBBA. Meanwhile a reverse correlation between MBBA concentrations and phase transition was found in the isotropic phase; a significant increase in temperature rate and response time was occurred with small weightage of MBBA. FTIR measurement confirmed that the liquid crystal molecules were self-phase separated from the PVP chains in the fibers.

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1. Introduction

Liquid crystals have shown promising potential for use as responsive materials in a wide range of technologies. The orientation of liquid crystal molecules is sensitive to temperature, electric fields, and other stimuli, which change its optical appearance. The study of liquid crystal combined with a polymer matrix has resulted in many applications—such as sensing biomaterials, displays, and biomedical applications—that use dispersed liquid crystal, emulsion liquid crystal droplets, and microfluidic of liquid crystal droplets.1–3 Liquid crystal concentration plays an important role regarding the selective wavelength and optical response of polymer dispersed liquid crystal for lasing and smart electronic glasses.4,5 The formation of liquid crystal inside microfibers has been recognized as suitable for responsive fiber for wearable technology applications. Krause et al. successfully fabricated liquid crystal fibers using a main-chain liquid crystal elastomer (MCLCE), electrospinning and crosslinking. Thin films were produced; they were oriented and then crosslinked using ultraviolet light to create single MCLCEs. The $T_N$ of MCLCE was rather high, i.e. from 40 °C (with smallest loads) to 57 °C (with high loads). The mechanical properties of the MCLCEs resembled the properties of spider silk.5,9 Liquid crystal-polymer fibers using pentyly-cyano-biphenyl (5CB) liquid crystal underwent coaxial electrospinning and non-coaxial electrospinning methods. The $T_N$ of 5CB was around 35.7 °C.7 The fiber was phase separated and self-assembled as a nematic core within a polymer shell.8,9 The reflective optical features of fibers can be controlled by changing the concentration of azo-chiral dopant in the core material, the ultraviolet irradiation intensity, and the core diameter of the fibers.10 However, the generated fibers are not suitable for specifically human body temperature sensor application because the $T_N$ of the used liquid crystal types was rather high or low, i.e. not in the range of body temperature.

Our recent study fabricated liquid crystal microfibers using N-(4-methoxybenzylidene)-4-butylanaline (MBBA) and polymer polyvinylpyrrolidone (PVP).11 The PVP has high biocompatibility, low chemical toxicity, high tensile strength, good solubility in most organic solvents, and good spinability.12,13 Its properties make it suitable for wearable microfibers applications. It is also a transparent polymer or does not have birefringence, and thus the optical behavior of liquid crystal molecules can be observed through PVP fibers.11 MBBA is a nematic liquid crystal that has no smectic phase,14 and as a result, the phase transitions of liquid crystal inside fibers can be more easily observed from changes in optical appearance. The $T_N$ of MBBA that is in the range of body temperature leads the microfiber to function as a human body temperature sensor. However, the $T_N$ of produced microfiber was remain low. Therefore, in this study, we removed the sample’s sandwich cell to improve the $T_N$ of the fiber. Further analysis was also performed to observe the effect of MBBA concentration in the morphology of liquid crystal microfibers, intermolecular interaction of liquid crystal microfibers, and the behavior of the fibers, in particular in the isotropic phase which had never been done before. The sample was required to form oriented fibers to develop the bright and dark patterns of the fibers. To achieve this, the electrospinning apparatus was modified; two parallel Cu gap collectors were added.

2. Experimental methods

2.1. Materials
The polymer used in the study was PVP which had a molecular weight of 1 300 000 g mole⁻¹ and was purchased from Sigma-Aldrich Corporation in Singapore. The study used absolute ethanol as a polymer solvent which was obtained from Merck, Indonesia. MBBA nematic liquid crystal was used which had a molecular weight of 67.37 g mole⁻¹, and was provided by the Tokyo Chemical Industry Corporation, Limited in Japan.

2.2. Electrospinning method
The electrospinning solution was prepared using two steps, which were the same as those used in our recent preparation.11 First, the polymer solution was prepared by dissolving PVP in absolute ethanol and mixing using a room temperature–hot plate stirrer for 2 h at 900 rpm. Several concentrations of PVP were used: 12.5 wt%, 15 wt%, 17 wt% and 25 wt%. Second, the PVP solutions were mixed with MBBA for 1 d using a room temperature–hot plate
stirrer. The MBBA was added to the PVP solution in 3/1 (25 wt%), 3/2 (40 wt%) and 3/3 (50 wt%) PVP/MBBA weight ratios.

The microfibers were prepared using the electrospinning method. An electrospinning apparatus was set up with a high voltage of 5 kV and a distance between the needle and collectors of 10 cm. The aligned fibers were obtained by modifying the collectors. The collectors were two-dimen-

sional modified Cu; each measured 7.9 × 1.5 × 0.15 cm, and the gap was 2 cm. A glass substrate measuring 1 × 2.5 cm was placed between the collectors, as shown in Fig. 1. The electrospinning process was performed for 10 s.

2.3. Measurements

To characterize the alignment of each fiber, the order parameter of the fibers’ orientation (S) was determined.15) The sample was put under a crossed polarizer. A polarized

optical microscope (POM) (Nikon Optiphot-pol) was used for observation. The polarizer passed light that was parallel to the x-axis, while the analyzer passed light that was parallel to the y-axis (parallel to analyzer).16) Images of the samples were taken using the ImageJ software. S can determine the degree of orientational order in nematic liquid crystal.17)

The following expression was used:

\[ S = \frac{1}{2} \left( \frac{1}{3} \cos^2 \theta - 1 \right), \]  

(1)

where \( \theta \) is either the angle between the individual fiber forms with a preferred alignment director or the angle between each molecule of nematic liquid crystal and the direction of the nematic axis. The fiber’s angle \( \theta \) was measured using the ImageJ software. The S value varied from 0, indicating random fiber alignment and an isotropic phase for the liquid crystal, to 1, which indicated perfect alignment and perfect orientation order for the nematic phase.

The transmitted light intensity of PVP–MBBA microfibers was given by Eq. (2).18) Liquid crystal microfibers were aligned planar to the plane of P/A or in other words the transmitted intensity changes with \( \sin^2(2\phi) \). The maximum intensity at \( \varphi = 45^\circ \) and the minimum intensity at \( \varphi = 0^\circ \) or multiple angle of 90°

\[ I^s = I_0 \sin^2 2 \varphi \sin^2 \frac{\delta}{2}, \]  

(2)

where \( I_0 \) is the light intensity after passing the polarizer, \( \varphi \) is the angle between optic axis or the director of liquid crystal and analyzer/polarizer and \( \delta \) is the phase difference.

An investigation of the phase transition of the liquid crystal inside the microfiber sample was completed. A heat control unit (DB500 digital-indicating controller, CHINO Corporation, Japan) was used as a heat source. The cell was put onto an enclosed hot plate that could gain heat by an induced electric field. The sample was heated from room temperature (28 °C) for the nematic liquid crystal phase to 45 °C for the isotropic liquid crystal phase. The sample was then cooled to room temperature. Images of the samples were recorded using the TouView software. The transmitted light intensity (I) was measured by analyzing sample images using ImageJ software. The sample images only showed grayscale images. Every grayscale image in the jpeg format was loaded into the ImageJ platform. The measurement of intensity was made using the mean gray value method; this takes an average of the sum of the gray values of all the pixels within a selection.

The intermolecular interaction of PVP-MBBA microfibers was investigated using Fourier transform infrared (FTIR). An FTIR study was performed on a FTIR Thermo Nicolet is10 spectrometer with a resolution of 4 cm\(^{-1}\) over a spectral range of 500–4000 cm\(^{-1}\). No treatment was applied to the samples prior to this spectrum reading.

3. Results and discussion

Optically responsive microfibers, with diameter under 6 \( \mu m \) and based on uniaxially ordered polymer–liquid crystal microfibers were obtained using gap-collector electrospinning. In this work, the polymer (i.e. PVP) works as a matrix for the liquid crystal because the molecular weight of liquid crystal is too low to be produced as fibers using the electrospinning method. Fibers can be formed with PVP concentrations of 15 wt%, 17 wt% and 20 wt%. At 12.5 wt%, the solution was too dilute when mixed with MBBA and did not form a fiber when electrospun. Fiber also did not form at 25 wt% because the solution’s viscosity was too high. Many studies on the effect of PVP concentration demonstrate that this has an important role in the determining the fiber’s diameter, bead-on-string morphology and spinability.19–22) Therefore, this study only focused on exploring the effect of liquid crystal concentration. The 17 wt% PVP solution was chosen for mixing with three weight ratios of MBBA.

The best applied voltage for microfiber formation is 5 kV. Although it is known that low voltage may create thicker PVP fibers,23) but this voltage creates better alignment of PVP–MBBA microfibers than 10 kV. The sample was rotated 45° with respect to the polarizer (P) and analyzer (A) under a POM as shown in Fig. 2. The color figures were observed using a color charge-coupled device camera to calculate the order parameter (S) while the greyscale figures were used to measure the transmitted intensity of the sample. Figures 2(a)–2(c) shows yellow interference, which occurred when the fibers were oriented southeast to northwest and is an optical sign of positive birefringence, as previously described.11)

Differences between the bright patterns in the greyscale images in Figs. 2(d)–2(f) can be seen clearly. The 25 wt% PVP–MBBA microfibers only show dots of brightness because only limited numbers MBBA molecules could be drawn inside the fibers. The limited numbers liquid crystal molecules tend to close to each other and contract to the smallest area because of the cohesive force between the

![Fig. 1. (Color online) A schematic diagram of the electrospinning apparatus.](image-url)
molecules. Likewise, the polymer molecules also bind together separately, and thus, the few liquid crystal molecules formed small dots inside the fibers. Meanwhile 50 wt% PVP–MBBA microfibers show almost perfect bright lines, indicating that each fiber is full of liquid crystal. Diameter histograms in Fig. 2(g)–2(i) show that PVP–MBBA microfibers with 25 wt% of PVP solution have the most uniform diameter compared to the other samples.

Electrospraying often occurred during the electrospinning process with 50 wt% PVP–MBBA solution, and spraying was sometimes very heavy. More volume of the solution was dragged out and formed an unstable jet. This unstable condition influences the uniformity of diameter and orientational order of fibers. Figure 3 shows that 50 wt% PVP–MBBA microfibers have the lowest orientational order parameter ($S$), which indicates that the sample has more randomly oriented fibers among the uniaxially oriented fibers compared to the other samples. Fortunately, the randomly oriented fibers only deviate several degrees from the other fibers, and, accordingly, they still produce low brightness as shown in Fig. 2(f). These results were also confirmed by Fig. 4. It shows that the fibers has the maximum intensity at 45° with respect to polarizer and has the minimum intensity (black pattern) at 0° which correspond to the theoretical values [Eq. (2)]; the maximum intensity of liquid crystal
molecules for planar alignment occurred when the molecules were rotated at 45°. Therefore, it can be concluded that the alignment of the fibers represents the orientation of liquid crystal molecules at planar system. The graph on Fig. 4(c) shows sinusoidal pattern with different peak values indicating that the S value of liquid crystal molecules inside the fibers is not equal to 1; i.e. majority of liquid crystal molecules are uniaxially ordered along the fiber. The addition of MBBA to PVP solution decreases the solution’s viscosity; thus, the higher the MBBA concentration used, the lower the solution’s viscosity. The addition of MBBA also decreases the electrical conductivity of the solution. These two properties have a significant impact on maintaining the flow of PVP–MBBA solution from the tip of the needle to the collector. With high MBBA weightage, droplets and even spray were sometimes formed rather than continuous fibers during electrospinning of the PVP–MBBA solution. Ultimately, the jet of the solution with low viscosity and conductivity generated lots of droplets to fall from the tip of the needle and land on the ground.

The experiment considered the average diameter of the PVP–MBBA microfibers. It is known that increasing polymer content in the solution increases its viscosity, which can induce the formation of fibers with larger diameters. Conversely, in this experiments, the addition of MBBA content into the electrospinning solution decreased the solution’s viscosity, but, unusually, it produced fibers with larger diameters than the PVP–MBBA solution with less MBBA (higher viscosity), as presented by the average fiber diameter graph in Fig. 5(a). Most 50 wt% PVP–MBBA fibers have larger diameters than fibers from the other samples. This result reveals that the diameter of fibers is affected by the formation of MBBA molecules inside the fibers—greater numbers of liquid crystal molecules inside the fibers yield greater diameters and sometimes flattened fiber structures due to the low solution viscosity, as seen in Figs. 2(b) and 2(c).

The intensity of light transmitted by the PVP–MBBA microfibers was also considered by measuring the intensity of light that passed through the crossed polarizer, as shown in Fig. 5(b). As described in the above discussion, an increase in the number of liquid crystal molecules inside the fibers also increases the transmission of light waves by MBBA molecules. Fibers only appeared to be fully bright along their length if the MBBA molecules were attached throughout the fibers.

The nematic (N)-isotropic (I) phase transition of MBBA inside the fibers can be analyzed by optical observation. The transmitted intensity was measured during the heating and cooling of the sample and formed deficient hysteresis curves, as shown in Fig. 6. The bright PVP–MBBA microfibers slowly turned dark as their temperature rose above the nematic–isotropic temperature ($T_{NI}$) of pure MBBA; this indicates that the liquid crystal molecules in the fibers undergo a transition from the nematic to the isotropic phase. Subsequently, as the sample was cooled, the fibers became bright again. The $T_{NI}$ of all samples was observed during the heating and cooling process, and the results are shown in Fig. 6. The inset graph shows that all $T_{NI}$ values of the three MBBA weightages are below the $T_{NI}$ of MBBA (37.3 °C in the ambient condition). These results indicate that the presence of thin fiber that confines MBBA highly disturbs the long-range orientational order of liquid crystal molecules.

Figure 6 also shows an increase in the transition temperature with MBBA concentration; in other words, the transition temperature of PVP–MBBA microfibers decreases as the relative amount of PVP solution to MBBA increases. This relation indicates that the introduction of PVP causes a decrease in the intermolecular potential of MBBA by separating MBBA molecules in the fibers; therefore, 25 wt% PVP–MBBA microfibers undergo the liquid crystal transition from the nematic to the isotropic phase more easily than the other samples. The maximum $T_{NI}$ value of PVP–
MBBA microfibers is achieved when the MBBA to PVP solution weight ratio is 3/3. Above 50 wt% of MBBA, the mixed solution could not be drawn to obtain parallel-aligned fibers during the electrospinning process due to its viscosity.

Further optical observation was conducted to investigate the effect of MBBA concentration on the continuous nematic–isotropic phase transition temperature. The change in temperature and the time to reach a specific light intensity was recorded after the sample passed the \( T_{NI} \). For the sake of simplicity, the variation in transmitted intensity for the almost-dark pattern of the sample (approaching the isotropic phase) was chosen as a parameter for observing the change in temperature and response time for the fibers’ transition. Figure 7 indicates that as the concentration of MBBA increases, the isotropic phase temperature shifts towards a higher temperature, as does the response time. However, when the sample eventually reaches the isotropic phase, the 25 wt% PVP–MBBA microfibers require more temperature width and time than the other higher concentrations to achieve the completely dark pattern. This is denoted by the graph in Fig. 7 showing 25 wt% PVP–MBBA fibers, which has the greatest curve among the samples, while the 50 wt% PVP–MBBA fibers show an almost flat graph. To reach the total dark pattern from a similar certain transmitted intensity, the 25 wt% PVP–MBBA fibers require 140 s, the 40 wt% PVP–MBBA fibers require 80 s, and 50 wt% PVP–MBBA fibers require 30 s, and the temperature rates of 3.77 °C, 1.27 °C and 0.21 °C, respectively.

Infrared spectroscopy was performed to study the molecular interaction between MBBA molecules and PVP chains. The molecular motion of MBBA is shown by the stretch vibration of C–N and C= N bonds (imine group) and –OCH3 (methoxy group) and the out-of-plane distortion vibration of the benzene rings attached to the imine bond. Figure 8 shows peaks at 834 and 885 cm\(^{-1}\), which represent the distortion vibrations of the two benzene rings of MBBA, and a peak at 1625 cm\(^{-1}\) corresponds to the stretch vibration of the imine group\(^{29}\) with various MBBA concentrations. The intensity of the peaks at 834 and 885 cm\(^{-1}\) decrease in both imine stretch and benzene ring distortion vibration, as the MBBA content in the fibers increases. This result indicates that the dispersion of MBBA and PVP chains causes a loss of interaction between imine stretch and the benzene rings of MBBA molecules.\(^{28}\) The molecular interaction between PVP chains and MBBA molecules is also confirmed by the transmitted light observations of the PVP–MBBA microfibers in the previous discussion.

The peak at 1652 cm\(^{-1}\) is correlated to PVP which indicates the existence of asymmetric stretching of CH2 and

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**Fig. 5.** Effect of MBBA concentration on (a) average diameter of fibers and (b) transmitted light intensity.

**Fig. 6.** Transmitted light intensity of PVP–MBBA microfibers presenting the nematic–isotropic phase transitions of MBBA during cooling (black symbol) and heating (white symbol). Right inset: nematic–isotropic temperature (\( T_{NI} \)) of PVP–MBBA microfibers versus concentration plot for various MBBA contents.

**Fig. 7.** Optical measurements of PVP–MBBA microfibers in the isotropic phase (dark pattern) of MBBA. The solid line denotes the temperature graph and the dashed line denotes the time graph against transmitted intensity.
stretching of C–O. MBBA molecules increase the intensity of these two stretching as shown in Fig. 8(b). The introduction of benzene ring vibration in MBBA molecules generates higher inter-chain interaction. The MBBA molecules are also considered to be dispersed between PVP chain bundles in the fiber rather than along PVP chains. This formation is determined by the spectrum of PVP at 2800 and 3000 cm$^{-1}$. MBBA forms as a spacer between PVP chain bundles. Therefore, in the case of 50 wt% PVP–MBBA microfibers, MBBA molecules are distributed uniformly within the PVP bundles, resulting in full brightness along the fibers.

4. Conclusions
Optically responsive microfibers were fabricated from a liquid crystal-polymer solution using gap-collector electrospinning. The MBBA concentration is one of the key factors that determines the morphology of PVP-MBBA fibers—for example, increased MBBA weightage decreases the orientational order parameter, while the diameter and light intensity of the fibers increase. MBBA concentration also has a strong influence on the phase transition of PVP–MBBA fibers. The nematic–isotropic temperature decreases due to fiber confinement disturbing the long-range orientational order of MBBA and the existence of a polymer weakening intermolecular interaction between MBBA molecules is confirmed by infrared spectra. In addition, the result of FTIR indicates that the MBBA molecules are self-phase separated from the PVP chains in the fibers.

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Fig. 8. (Color online) Fourier transform infrared (FTIR) spectra of pure MBBA (black), PVP fibers (red), and 25 wt% (blue), 40 wt% (yellow), and 50 wt% (purple) PVP-MBBA microfibers.
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