ACS APPLIED MATERIALS & INTERFACES
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New Approach toward Reflective Films and Fibers Using Cholesteric Liquid-Crystal Coatings

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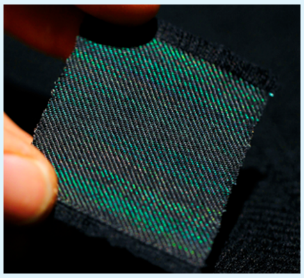
S *Supporting Information*

ABSTRACT: A new approach for the production of oriented films and fibers with angular-dependent reflective colors is presented. The process consists of spray coating a solution of cholesteric liquid-crystalline monomers onto a melt-processed and oriented polyamide-6 substrate followed by UV curing. Reflectivity measurements and optical microscopy show that a well-defined liquid-crystalline and planar alignment is obtained. It is further demonstrated that a reflection up to 80% is obtained by coating oriented films on both sides of the oriented substrate with a single-handedness cholesteric liquid-crystal coating. The high reflectivity is attributed to the close to half-wave retardation induced by the anisotropic polymer substrate. Also, polyamide-6 filaments are successfully coated and fibers are obtained with an angular-dependent color in a single dimension along the fiber direction, which originates from the planar cholesteric alignment on a curved surface.



KEYWORDS: *cholesteric liquid crystal, cross-linked network, fibers, functional coating, self-organizing, coloration*

INTRODUCTION

Colors have been present in fibers since the early use of textiles and fabrics. Conventionally, organic and/or inorganic dyes or pigments are used to generate the color based on the absorption or scattering of visible light. Colors can also be produced based on the selective reflection of light for instance, as can be seen in beetles.[1−3] The produced colors are very bright and intense and change drastically with the viewing angle or illuminating conditions (for instance, the polarization direction).[3] Driven by consumers' demand for textiles with unique appearance, we explore a new route to introduce reflection-based optical effects into oriented fibers or films using a cholesteric liquid-crystal (CLC) material.[4,5] In a CLC, molecules are arranged into a helical structure, giving unique optical properties to the material. They selectively reflect one specific circular polarization direction of light and transmit the other.[6] In other words, at normal incidence, the reflected light is circularly polarized with the same handedness as the cholesteric helix and a maximum reflection of 50% is obtained.[6,7] The reflected light also changes with the viewing angle. A blue shift of the reflected light is observed in planar CLC films at oblique incidence, i.e., when the angle between the incident light and the cholesteric helix increases.[8,9] The reflected wavelength is determined by the average refractive index of the liquid-crystalline polymer and the pitch P of the helix. In a CLC film, controlling the planar alignment of the molecules at the surface of the substrate is the key to obtaining a well-defined reflection band. The most common and inexpensive way to align liquid crystals is by mechanically rubbing the surface of the substrate.[10] More interestingly, polymer substrates stretched over 100%, such as poly(vinyl alcohol) or cellulose, have been shown to align nematic liquid-crystal molecules along the stretching direction.[11] However, the present work aims at applications in the textile area where polyamide-6 (PA6) is one of the main polymers used to produce synthetic fibers.[12] Here, we demonstrate a process for the production of oriented PA6 films and fibers with angular-dependent colors through spray coating of CLCs. The alignment is characterized and the resulting optical properties are evaluated for the coated films and fibers.

EXPERIMENTAL SECTION

1. Materials. Oriented PA6 films were purchased from Goodfellow. PA6 monofilaments were produced by melt-spinning fiber-grade PA6 pellets (Durethan B35F, Lanxess). Monomers C3M and C6M (Merck) were mixed in a 1:4 ratio.[14] The chiral mesogen LC756−BASF (5.2 wt %) was added to the monomer mixture to obtain a green reflection band. A small amount (1 wt %) of 1-hydroxycyclohexyl phenyl ketone (Sigma Aldrich) was added as a photoinitiator. The monomers and photoinitiator were dissolved in xylene (1:2.5 ratio).

2. Reflective Film Preparation. PA6 films were washed with isopropyl alcohol and dried with compressed air. The films were then taped to a substrate, and the liquid-crystal mixture was applied using an Iwata painting airbrush (flow rate = 2 mL·min^{-1}, and the distance between the nozzle and film was 10 cm). The films were annealed to 80 °C in an oven for 60 s to remove residual traces of solvent and successively cooled to room temperature and photopolymerized in the nematic phase. The photopolymerization was performed using a mercury lamp (EXFO Omnicure S2000, λ = 350−450 nm) in a nitrogen atmosphere for 200 s. Tapes with a coating on both sides were produced by repeating the procedure above.

3. Reflective Fiber Preparation. PA6 pellets were dried overnight at 110 °C and melt-spun using a single screw extruder

Received: April 19, 2013
Accepted: June 26, 2013
Published: June 26, 2013

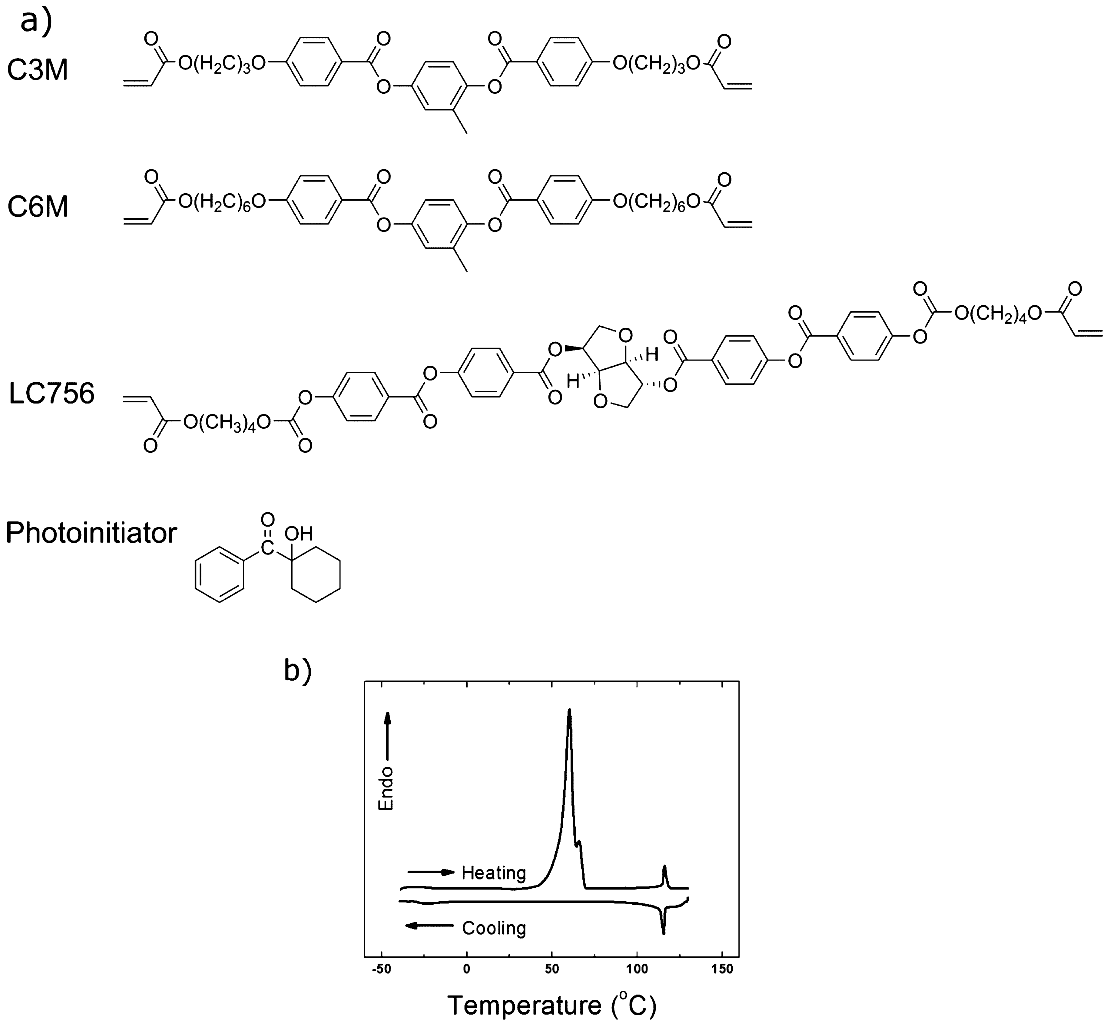


Figure 1. (a) Molecular structures of the monomers and photoinitiator composing the CLC mixture. (b) DSC thermogram of the liquid-crystal monomer mixture during the first heating and first cooling.

with monofilament die (spinning temperature = 260 °C). Oriented filaments were obtained after drawing the fibers to a draw ratio of 3 at 80 °C. The fibers were then prepared and coated following the same process as the double-side coated tape.

4. Characterization. Transmission measurements were performed using a Perkin-Elmer Lambda 950 UV−vis spectrophotometer. Left and right circular polarizers were used for the measurement on the single-side-coated PA6 film. All measurements were done by placing the samples in the path of the incident beam at the entrance of an integrating sphere. The phase transition temperatures of the nonpolymerized liquid-crystal mixture were determined using differential scanning calorimetry (DSC) characterization with a heating and cooling rate of 5 °C·min^{-1} (Mettler Toledo). Optical microscopy was done with a Leica optical microscope. Scanning electron microscopy (SEM) samples were prepared by embedding fibers in an epoxy resin. Once the epoxy was fully cured, the samples were grinded and polished with a 4000 grit finish. Finally the samples were gold coated to avoid charging. SEM images were taken using a FEI Inspect scanning electron microscope. Photographs of the fibers were taken with a digital camera.

RESULTS

Oriented Films. Experiments were first carried out on a uniaxially oriented PA6 film in order to investigate the alignment of the polymerized mesogens and reflective properties of the coating. The CLC mixture used to coat the substrates was produced by adding a chiral mesogen to a nematic liquid-crystal host (Figure 1a).[13,14]

The transition temperatures of the liquid-crystal host (C3M/C6M) were determined by DSC. The blend showed a first nematic transition upon heating to 60 °C followed by the isotropic transition at 115 °C. During cooling, the mixture showed a broad temperature range in which the mixture is nematic (Figure 1b). The liquid-crystalline diacrylates used here enable the formation of a cross-linked network upon polymerization while preserving the CLC order.[15,16]

Optical microscope observations of the coating showed the characteristic oily streak morphology, typical of a CLC planar texture (Figure 2).[17]

The reflection band was characterized by measuring the transmittance of the film in the visible spectrum (400−800 nm) for two different polarization states, e.g., left- and right-handed circularly polarized light (LHCPL and RHCPL; Figure 3a). Measurements done with RHCPL showed a strong reflection band centered at λ_0 = 535 nm and a width $\Delta\lambda$ = 65 nm (measured at half of the maximum reflection). The reflection, almost completely absent in LHCPL, confirmed the right-hand helical arrangement of the liquid-crystal molecules.[18] When the incident light was at an oblique incidence, the reflection band

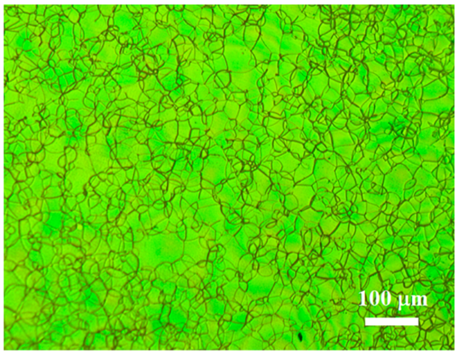


Figure 2. Microscopic image in the reflection mode without polarizer of a green reflecting film showing the characteristic oily streak morphology of a CLC film with a planar alignment.

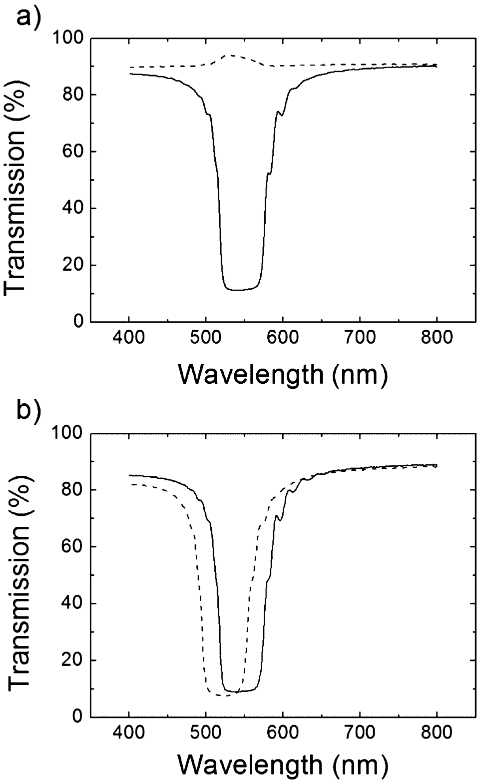


Figure 3. (a) Transmission spectra recorded for the same film for RHCPL (—) and LHCPL (---) at normal incidence. (b) Influence of the incident angle for RHCPL. Films perpendicular to the beam (—) and tilted by 30° (---).

shifted toward lower wavelengths (Figure 3b), which is expected in CLC films with a planar texture.[8]

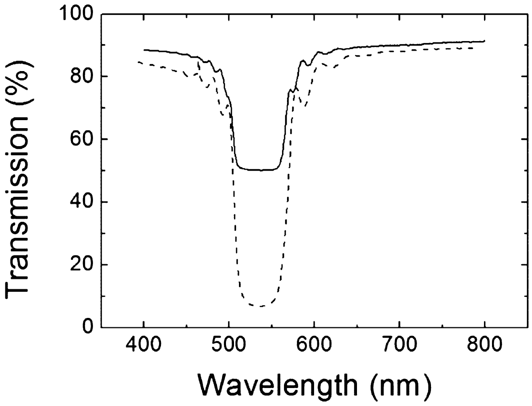


Figure 4. Transmission spectra of single-side-coated (—) and double-side-coated (---) PA6 films obtained for nonpolarized light.

The reflection of a CLC film under nonpolarized light is less than 50%, although it can be increased by introducing a half-wave optical retardation between two CLC films of identical handedness.[19] Here, it is attempted to use the oriented PA6 substrate as an optical retarder and increase the reflection of the film by coating both sides of the substrates with the same CLC. The reflective properties of the double-side-coated film were measured with nonpolarized light and compared to a single-side-coated film. The spectra are given in Figure 4. The double-side-coated film showed a reflectivity of 80%, which is 40% higher compared to the single-side-coated film. To verify the optical retardation of the substrate, the birefringence of the pure oriented PA6 film was calculated following the method described by Escuti and co-workers.[20] It was found that the 25-μm-thick PA6 film had a birefringence $\Delta n = 0.01$. On the basis of this result, the retardation could be estimated as 250 nm, which is indeed close to half-wave retardation of the reflected wavelength ($\lambda_0 = 535$ nm).

Oriented Fibers. Reflective fibers were produced by coating stretched PA6 monofilaments following the same process as that above and using the same CLC mixture. SEM observations of the fibers' cross section showed a conformal coating around the fiber with a thickness of 6−10 μm (Figure 5a). In the close-up view of the coating (inset), the layered morphology of the

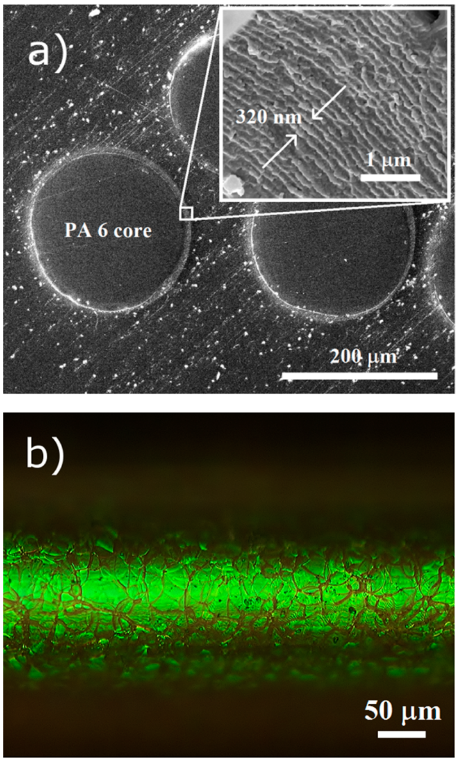


Figure 5. (a) SEM cross-sectional images of coated PA6 fibers. The inset shows the layered structure of the liquid-crystal coating. The succession of bright and dark lines corresponds to half the pitch. Here a complete pitch is measured. (b) Microscopic image in the reflection mode of the green reflecting fiber. The image is focused on the top part of the fiber. Magnification: 50×.

CLC, consisting of a succession of bright and dark lines, can be seen. Optical microscopy images of the CLC layer showed the characteristic oily streaks, indicating a planar alignment (Figure 5b).

The filaments with a diameter of 200 μm had a reflection band in the green region of the spectrum, as measured by UV–vis spectroscopy (Figure 6). A broad reflection band $\Delta\lambda$ = 96 nm with a maximum reflection of 26% for nonpolarized light was measured originating from the curved geometry of the fiber. Outside of the reflection band the transmission is found to be lower when compared to the PA6 flat substrate. This might be due to lens effects or to the collimated beam being deviated by the geometry of the fiber. Reflectivity measurements were also performed on the array of fibers (see Supporting Information). Results confirmed the reflection measured in transmission.

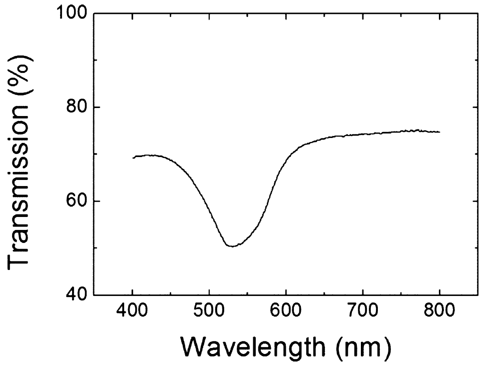


Figure 6. Transmission spectrum of the coated fibers obtained for nonpolarized light at normal incidence.

In fact, optical microscopy observations showed that the reflection was green in the middle of the fiber only and blue closer to the edges (Figure 7a). The CLC has a planar alignment, with the helix axis perpendicular to the fiber surface. Therefore, the angle between the incoming light and the helix (denoted as θ) is expected to increase from the middle of the fiber toward the edges (Figure 7b), which causes the blue shift at the edges. Similar observations were reported for CLC microcapsules.[21]

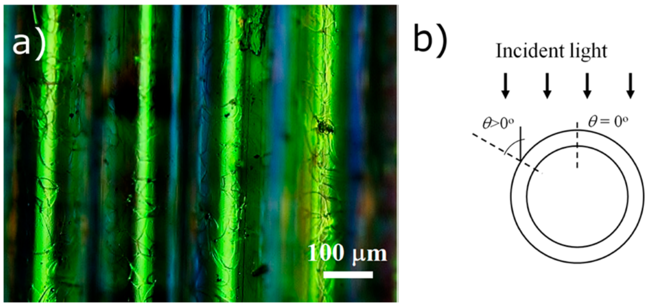


Figure 7. (a) Microscopic image in the reflection mode of an array of coated fibers with nonpolarized light. Magnification: 10×. (b) Representation of the coated fiber with the CLC helixes normal to the incident light θ = 0° and at an angle of θ > 0°.

Finally the effect of the viewing position on the perceived color was investigated. Photographs were taken at different angles varying respectively in the plane perpendicular (α) and the plane parallel (β) to the fiber axis (Figure 8a). From the pictures, it is clear that an increase in the radial angle α did not change the perceived color, which is due to the symmetric geometry of round cross-sectional fibers (Figure 8b,c). On the other hand, a blue shift was observed when β increased (Figure 8b,d). These results indicate that the observed color is only influenced by the viewing angle along the fiber axis.

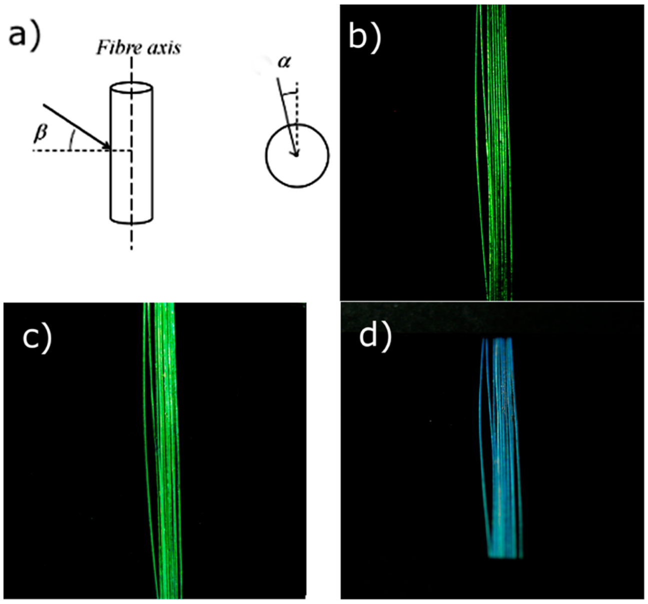


Figure 8. (a) Schematic representation of the different viewing angles. Pictures of the array of fibers are taken at different viewing angles: (b) α = 0° and β = 0°; (c) α = 30° and β = 0°; (d) α = 0° and β = 60°. Pictures are taken with a black background.

DISCUSSION

The experiments performed on oriented tapes showed that a well-aligned CLC layer and, consequently, a narrow reflection band are obtained with the spray deposition process. The high reflection obtained in double-side-coated tapes would suggest that flat fibers could be used in textiles, for instance, in clothing applications. On the other hand, round cross sections are far more common in textiles.[12] We showed here that the curved geometry of a round fiber changes the reflection band as well as the perception of the fiber, with a blue shift under oblique incidence observed in one dimension only. Although in this work we demonstrated the potential to generate colors using a green reflecting CLC coating, it should be noted that other colors are easily generated by changing the chiral dopant concentration in the nematic liquid-crystal host.[14,22] Hence, the reflection band could also be tuned to produce fibers that reflect UV or IR radiations, thereby broadening the field of application of the process. For instance, fibers reflecting IR radiation could be used as heat reflectors for heat management in buildings.[23] Experiments were also performed using poly(ethylene terephthalate) (PET) as the substrate. Uniaxially oriented films and fibers with a reflective CLC coating were produced in the same way as the PA6 films/fibers. Characterization of the films and fibers showed that a planar alignment and narrow reflection band were also obtained with PET substrates.

CONCLUSION

A CLC coating is applied to oriented PA6 films and fibers to generate colors based on the selective reflection of light. Here the reflected light is centered in the green region of the visible spectrum. A planar cholesteric alignment was obtained for both films and fibers with the mesogens aligned parallel to the substrates' surface. By adjusting the optical retardation of the substrate, high reflection was achievable. The curved geometry of the fibers affected the reflected color under oblique incidence. It was blue-shifted in the longitudinal direction and remained invariant when the observer moved around the fiber axis. Finally, the process was not restricted to oriented PA6 substrates. Experiments were done with oriented PET tapes and fibers, which showed similar results.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1 showing the reflectivity measurement of the coated fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): This research forms part of the research program of the Dutch Polymer Institute (Project 679).

■ ACKNOWLEDGMENTS

This research forms part of the research programme of the Dutch Polymer Institute (Project 679). The authors also acknowledge Nanoforce Technology Ltd. for use of their facilities and financial support.

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