

Wide-Band Reflective Polarizers from Cholesteric Liquid Crystals with Stable Optical Properties

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ABSTRACT: A wide-band reflective polarizer from glassy siloxane cyclic side-chain liquid crystals with stable optical properties was developed. The pitch gradient that formed was first stored by rapid cooling, which, by preventing the crystallization of glassy materials, was a very easy way of keeping the molecular arrangement. Then, the polymer network that formed through UV-initiated chain crosslinking of

the photopolymerizable monomers in the reflective polarizer further stabilized the cholesteric structure stored by the former rapid cooling. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2973–2977, 2007

Key words: glass transition; irradiation; photopolymerization; stabilization

INTRODUCTION

The selective reflection bandwidth of a single-pitch cholesteric liquid crystal is given by $\Delta\lambda = (n_e - n_o)P = \Delta nP$, where n_o , n_e , Δn , and P are the ordinary refractive index, extraordinary refractive index, birefringence, and pitch of the helix corresponding to a 2π molecular rotation, respectively. Within this reflection region, right circularly polarized light is reflected by a right-handed helix, whereas left circularly polarized light is transmitted. Outside the reflection band, both polarization states are transmitted.^{1,2} Much attention has been recently focused on wide-band reflective polarizers (WBRPs) from cholesteric liquid crystals because they are of great importance for practical applications.^{3–5}

Introducing a pitch gradient is an ideal method for increasing the reflective bandwidth of a cholesteric liquid crystal. The pitch difference is often formed by the molecular diffusion of optically active monomers with different optical reactivities and fixed by

photopolymerization. The correlative methods can be found in patents and research publications.^{6–11}

Glassy cholesteric liquid crystals possess the properties of conventional cholesteric liquid crystals and glassy thermoplastics. By preventing the crystallization of glassy cholesteric liquid crystals, rapid cooling is a very easy way of keeping the molecular helices. However, the helical structure of a conventional glassy cholesteric liquid crystal is strongly influenced by fluctuations of the temperature and is stable only at temperatures much lower than the glass-transition temperature.^{12–15}

In this study, a pitch gradient was formed by molecular diffusion between adjacent liquid-crystal layers with different pitch lengths during orientation. The pitch gradient was first restored by rapid cooling and further stabilized by UV-initiated chain crosslinking of the photopolymerizable monomers below the glass-transition temperatures of the siloxane cyclic side-chain liquid crystals (GSCSLCs). Then, a WBRP with stable optical properties was fabricated.

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EXPERIMENTAL

Synthesis of the GSCSLC

The GSCSLC was obtained by the hydrosilylation of SiH cycle with *p*-allyloxy-cholesterol benzoate (M_1) and *p*-allyloxy-biphenyl benzoate (M_2). The chemical structures of M_1 and M_2 are shown in Figure 1. The hydrosilylation reaction was carried out in toluene at 60–111 °C with dicyclopentadienyl platinum dichloride

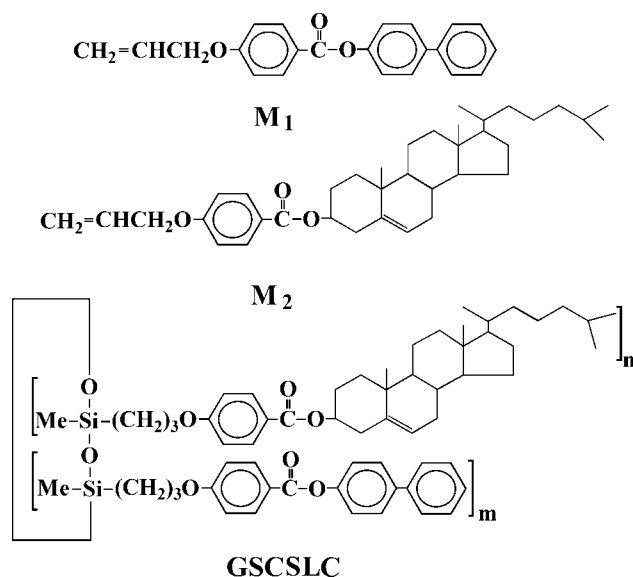


Figure 1 Chemical structures of M₁, M₂, and GSCSLC.

as a catalyst. For example, 5.15 g of M₁, 3.12 g of M₂, and 1.03 g of SiH cycle were added to toluene with dicyclopentadienyl platinum dichloride under stirring in an inert atmosphere. The reaction was completed via refluxing for 20 h. Then, the solution was poured into methanol. The filtration of the precipitate and evaporation of the solvent from the filtrate yielded the GSCSLC.

¹H-NMR (CDCl₃, δ, ppm from tetramethylsilane): 6.89, 7.99 (16H, Ar), 5.37 (4H, ethene in cholesterol), 3.97 (8H, H₂COAr), 1.86 (8H, CCH₂C), 1.33 (8H, SiCH₂C), 0.13–0.17 (12H, SiCH₃). IR (KBr): 1737 (C=O), 1000–1100 (Si–O–Si), 1270 (–C–Si–), 1550–1450 cm⁻¹ (Ar, C=C). ANAL.: C, 72.65%; H, 8.63%.

WBRP preparation

The chemical structure of the GSCSLC attaching to M₁ and M₂ via spacers is shown in Figure 1. Different pitch lengths of the cholesteric structure were obtained through the grafting of different concentrations of the chiral component to the cyclic siloxane. Different pitch lengths led to different central reflective wavelengths after the cholesteric liquid crystals were oriented for the planar texture. In this study, the central reflective wavelengths of the three original cholesteric liquid-crystal layers with a planar texture were 560, 660, and 739 nm, respectively.

A pitch gradient was formed and stored by the following method. A mixture of a GSCSLC and other components [including the photoinitiator (M₃), inhibitor (M₄), and photopolymerizable monomers (M₅); Fig. 2] was molded on a glass or plastic substrate to obtain the first layer. The second layer, which included another GSCSLC and other components

(including M₃, M₄, and M₅), was molded on the first layer after the solvent (dichloromethane) in the first layer evaporated off. The third layer, which included another GSCSLC (different from those in the first and the second layer) and other components (including M₃, M₄, and M₅), was molded on the second layer after the solvent (dichloromethane) in the second layer evaporated off. Then, a composite film comprising multiple layers, each layer exhibiting a different central reflective wavelength after orienting by the same procedure, could be obtained. Another substrate was put on the composite film. The composite film with the upper substrate was rolled at a constant temperature between the highest glass-transition temperature and the lowest isotropic transition temperature of the original GSCSLCs. During the rolling, the planar texture of the cholesteric liquid crystals and a pitch gradient over the thickness of the composite film were formed. The molecular arrangement that was obtained was fixed by rapid cooling to room temperature first and then further stabilized by the UV-initiated chain crosslinking of the photopolymerizable monomers in the GSCSLCs. A WBRP with stable optical properties was obtained.

RESULTS

Fixation of the pitch gradient

Most axes of a cholesteric helix in a cholesteric liquid crystal with a planar texture are perpendicular to the substrates. Then, selective Bragg reflection occurs because of the periodic helical molecular structure. The pitch of the helix corresponds to a 2π molecular rotation. Figure 3 shows the network of oily steaks in the cholesteric planar texture after the GSCSLC is oriented.

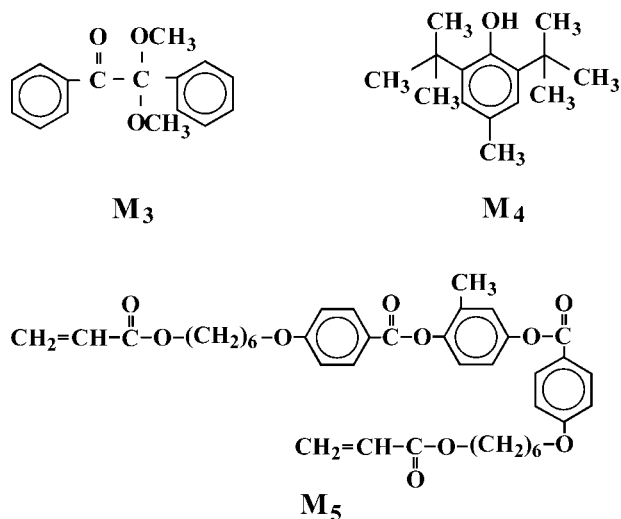


Figure 2 Chemical structures of M₃, M₄, and M₅.

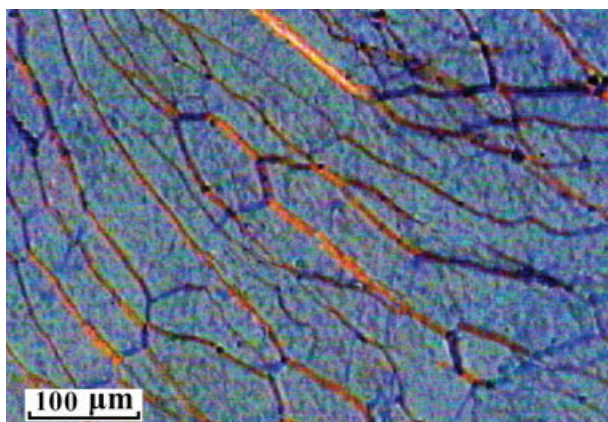


Figure 3 Polarized optical microphotograph of the planar texture of the cholesteric liquid crystal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Forming a pitch gradient is effective for widening the reflective bandwidth of the cholesteric liquid crystal. Once the pitch gradient of the cholesteric liquid crystal has been formed, storing it effectively and permanently is another key point. Figure 4 presents a schematic representation of the method used to prepare a WBRP in this study. When a composite film comprising multiple layers, each layer exhibiting a different central reflective wavelength after orienting by the same procedure, was rolled for orientation at a constant temperature between the highest glass-transition temperature and the lowest isotropic transition temperature of the original GSCSLCs, a planar texture of the cholesteric liquid crystals was formed. At the same time, a pitch gradient was formed by the molecular diffusion between the adjacent cholesteric liquid-crystal layers with different pitch lengths. The pitch

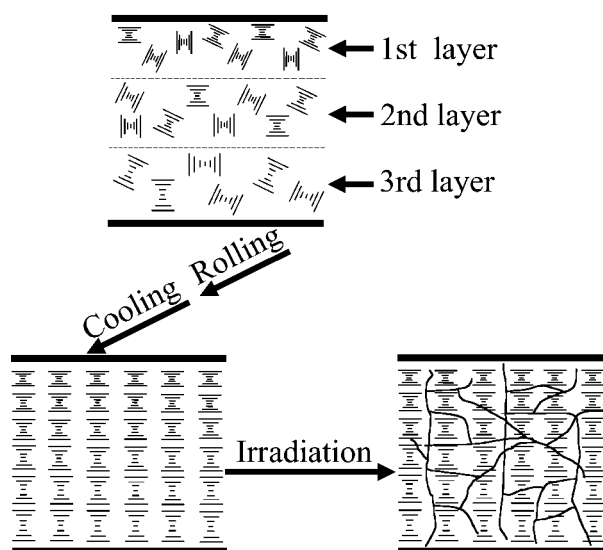


Figure 4 Schematic representation of the method used to prepare the sample.

gradient was kept by rapid cooling at first. To stabilize it further, the polymer network that was formed by the UV-initiated chain crosslinking of the photopolymerizable monomers in the GSCSLCs was used to impose a further restriction on the molecular motion. A WBRP with stable optical properties was developed.

Figure 5 presents a scanning electron micrograph of a specimen fabricated by the former process. There is a pitch gradient along the transverse direction. The polymer network that was formed by the UV-initiated chain crosslinking of the photopolymerizable monomers is shown in Figure 6. Figure 7(d) presents the transmittance spectrum of the WBRP obtained by the former fabrication method from multiple layers laminated by the three original layers of GSCSLCs. Figure 7(a–c) presents the transmittance spectra of the three original layers oriented by the same process used for the WBRP. Figure 7 shows that the WBRP can reflect light over the reflection wavelengths of the original liquid crystals. We think that during rolling between the highest glass-transition temperature and the lowest isotropic transition temperature of the original GSCSLCs, different liquid-crystal layers with different pitches were formed. When the temperature was not high enough or the orientation time was not long enough, the molecules could not diffuse as quickly between the adjacent liquid-crystal layers, so different pitches were still kept in different liquid-crystal layers, and a pitch gradient was formed along the transverse direction. When the planar texture (most axes of the cholesteric helix were perpendicular to the substrates) was formed after orientation, different liquid-crystal layers reflected light with different reflection wavelengths. Of course, a solid WBRP reflecting light over the reflection wavelengths of the original liquid crystals would be obtained after the aforementioned molecular arrangement was frozen by quenching.

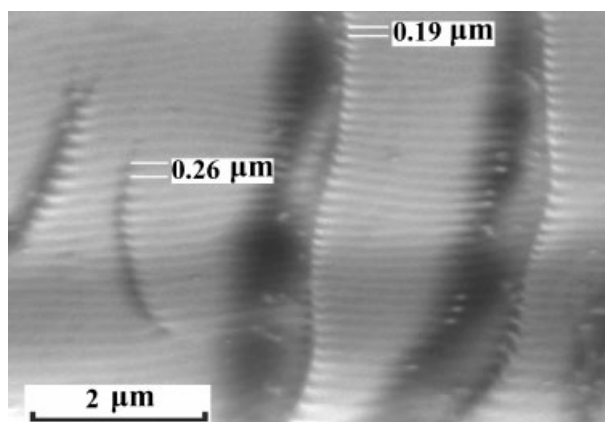


Figure 5 Scanning electron micrograph of freeze-fractured surface of the reflective film with a pitch gradient.

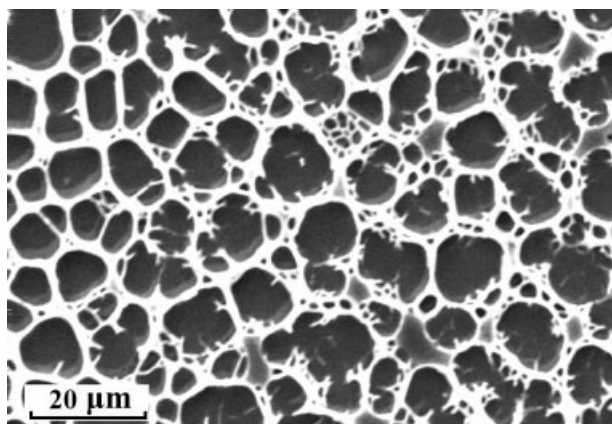


Figure 6 Scanning electron micrograph of the polymer network in the sample.

On the other hand, the central reflective wavelength of the wide-band reflective film did not shift before and after UV radiation at room temperature. The reason was that the motion of the chain segment of the GSCSLC was frozen at room temperature (below the glass-transition temperatures of the GSCSLCs), so the UV-initiated chain crosslinking of the photopolymerizable monomers almost could not destroy the orientation arrangement of the mesogenic subunits restored by the former rapid cooling. The polymer network that was formed by the UV-initiated chain crosslinking of the photopolymerizable monomers could restrict the motion of the chain segment of the GSCSLC, so the molecular arrangement could be stabilized further. Therefore, the pitch gradient of the WRBP was formed and kept effectively and permanently.

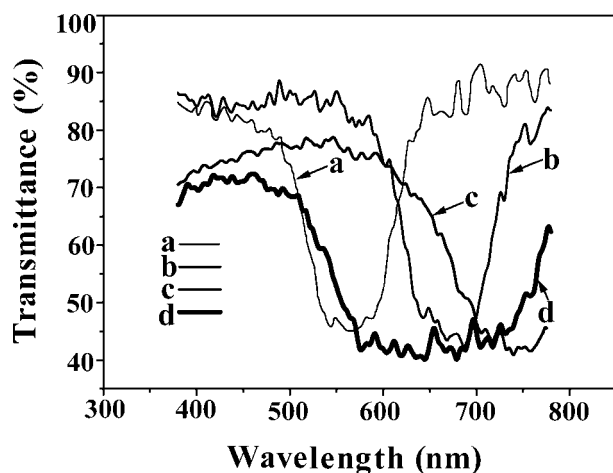


Figure 7 Transmittance versus the wavelength of the reflective films. (a) The first original layer is oriented at 100°C, (b) the second original layer is oriented at 100°C, (c) the third original layer is oriented at 100°C, and (d) the WRBP fabricated from the three layers is oriented at 100°C.

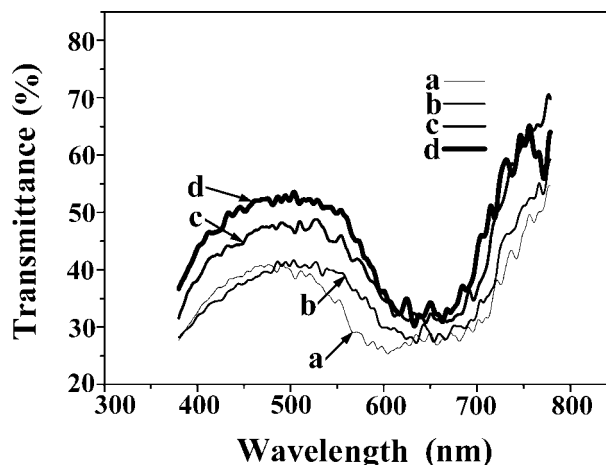


Figure 8 Reflective bandwidth as a function of the heat treatment: (a) room temperature, (b) 73°C/30 min, (c) 73°C/60 min, and (d) 73°C/90 min.

Temperature dependence of the optical properties

The helical structure of a conventional glassy cholesteric liquid crystal whose cholesteric structure is stored only by rapid cooling is strongly influenced by fluctuations of the temperature. Especially for a glassy siloxane liquid crystal, the orientation arrangement of the mesogens is much easier to change when it is heated near or above the glass-transition temperature because the highly flexible siloxane backbone, coupled with flexible spacers spacing the mesogens from the backbone, can supply enough free room for the motion of the chain segments.

The polymer network can restrict the motion of the chain segment, and the cholesteric structure restored by the former rapid cooling can be stabilized further when the polymer network is formed by the UV-

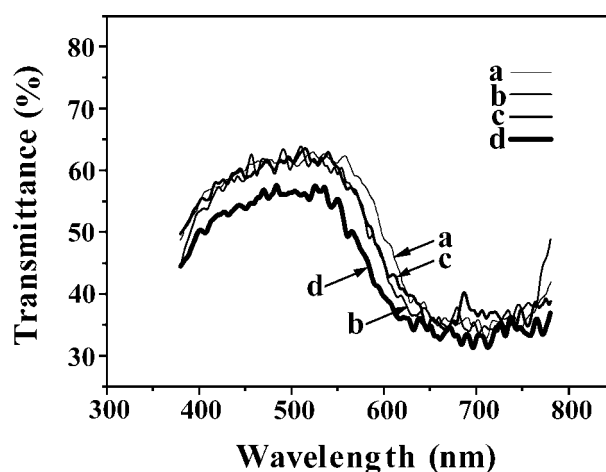


Figure 9 Transmittance versus the wavelength of the reflective films treated by different thermal cycles: (a) 43°C/90 min, (b) 58°C/80 min, (c) 65°C/160 min, and (d) 75°C/60 min.

initiated chain crosslinking of the photopolymerizable monomers below the glassy temperatures of the GSCSLCs. Therefore, for the WBRP whose cholesteric structure is fixed by rapid cooling and the polymer network, the heat stability can be improved greatly.

For example, the reflective bandwidth of a WBRP whose cholesteric structure was restored only by rapid cooling became narrower as the time of the heat treatment became longer (Fig. 8). However, for the WBRP, when the pitch gradient was fixed by rapid cooling and the polymer network was formed by the UV-initiated chain crosslinking of the photopolymerizable monomers below the glassy temperatures of the GSCSLCs, the reflective bandwidth did not change even after several thermal cycles from lower temperatures to temperatures higher than the glass-transition temperatures of the liquid crystals (Fig. 9).

CONCLUSIONS

In this study, a pitch gradient of cholesteric liquid crystals was fixed into a WBRP by rapid cooling at first, and then a polymer network that was formed by the UV-initiated chain crosslinking of the photopolymerizable monomers in the glassy film was employed to stabilize it further. The heat stability of the WBRP

whose pitch gradient was restored by the former technology was elevated.

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