Photonic shape memory polymer with stable multiple colors

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Photonic Shape Memory Polymer with Stable Multiple Colors
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ABSTRACT: A photonic shape memory polymer film that shows large color response (∼155 nm) in a wide temperature range has been fabricated from a semi-interpenetrating network of a cholesteric polymer and poly(benzyl acrylate). The large color response is achieved by mechanical embossing of the photonic film above its broad glass transition temperature. The embossed film, as it recovers to its original shape on heating through the broad thermal transition, exhibits multiple structural colors ranging from blue to orange. The relaxation behavior of the embossed film can be fully described using a Kelvin–Voigt model, which reveals that the influence of temperature on the generation of colors is much stronger than that of time, thereby producing stable multiple colors.

KEYWORDS: shape memory polymers, cholesteric liquid crystals, semi-interpenetrating polymer network, mechanical embossing, stable colors

1. INTRODUCTION
Shape memory polymers (SMPs) are a fascinating class of smart materials, as they can be deformed and locked into a temporary shape and then recover their original shape under the influence of a specific stimulus such as heat, solvent, pressure, light, and so on.1−5 Photonic SMPs with the ability to reflect light due to their photonic structure6,7 are a special class of polymers that can change the shape as well as color. Such polymers are of great interest for the development of, for example, battery-free optical sensors,8 reconfigurable and rewritable optical devices,9−14 and lasers.15−18 So far, shape memory photonic materials are limited to only two colors.9−11,19 Designing a photonic SMP that displays multiple colors that are stable over long periods of time still remains a challenge.

SMPs with stable multiple shapes have been previously reported and were obtained by incorporating two or more discrete thermal transitions, which could be glass transition (Tg) or melting (Tm) temperatures, into the polymer.20−23 The number of temporary shapes achieved is usually equal to the number of transitions. However, designing multishape polymers with this approach poses huge synthetic challenges.24 A more versatile approach is to introduce a broad thermal transition that can be considered as an infinite number of discrete transitions Tm,nun† which are so closely spaced that they form a continuum.25 A polymer with a broad thermal transition can, therefore, be tailor-programmed in several ways as per the demand by choosing the desired temperatures (one or more) out of the infinite transition temperatures for a stepwise deformation; thus, a greater degree of freedom in designing multiple temporary shapes can be achieved.25 A well-known strategy to produce a broad glass transition is to use an interpenetrating polymer network (IPN).26 Additionally, an IPN also provides the unique opportunity to combine the properties of two different polymers.27

Here, we report on a photonic semi-interpenetrating network (semi-IPN) comprising a photonic cholesteric liquid crystal (CLC) polymer28−34 and poly(benzyl acrylate) (poly(BA)). In CLC, due to helical twisting of the average orientation (director) of the molecules, selective reflection of light takes place, with the pitch of the helix determining the wavelength of reflection.28,29 The semi-IPN photonic film exhibits a broad glass transition (Tg) from 10 to 54 °C and can be deformed mechanically to a temporary shape, accompanied by a large change in color from orange to blue (Δλ ≈ 155 nm). In response to a rise in the temperature through the Tg, the shape recovery takes place in multiple stages, displaying varying structural colors covering almost the entire visible spectrum. The process of shape recovery can be fully described using a Kelvin–Voigt model, and it is shown that the multiple colors generated are stable over long periods of time.

2. EXPERIMENTAL DETAILS
2.1. Materials. RM257, RM105, and 5CB were obtained from Merck. LC756 was bought from BASF. Benzyl acrylate was purchased

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Scheme 1. Molecular Structure of the Components Used for the Fabrication of the Semi-Interpenetrating Network of CLC Polymer and Poly(benzyl acrylate)

from Sigma-Aldrich. Irgacure 651 was from CIBA. Tetrahydrofuran (THF) was obtained from Biosolve.

2.2. Preparation of Photonic Polymer Film. Mesogen mixture (1 g) consisting of 29 wt % RM257, 35 wt % RM105, 30 wt % 5CB, 5 wt % LC756, and 1 wt % Irgacure 651 was dissolved in tetrahydrofuran (4 mL) to form a homogeneous solution. The solvent was later evaporated by heating at 75 °C to obtain the cholesteric liquid crystalline (CLC) mixture. The CLC mixture was then filled in a rubbed polyimide cells with a 70 μm spacer at 40 °C followed by photopolymerization by irradiating the UV light (48 mW cm−2 intensity in the range 320−390 nm) for 5 min. The cell was opened to obtain a free-standing CLC polymer film. It was then treated with THF and dried, first at room temperature and then at 75 °C, after which the polymer film was exposed to benzyl acrylate (BA) mixed with 1 wt % of Irgacure 651 for 12 h. After wiping out excess benzyl acrylate, it was photopolymerized in N2 atmosphere by shining the UV light (48 mW cm−2 intensity in the range 320−390 nm) for 15 min. The process was repeated to incorporate a higher amount of benzyl acrylate into the system.

2.3. Characterization. Photopolymerization was carried out with OmniCure series 2000 EXPO lamp. The UV−visible (vis) spectra of the photonic films were measured by Shimadzu UV-3102 PC spectrophotometer. Differential scanning calorimetry (DSC) was performed in TA DSC Q1000. Thermogravimetric curve was measured in TA thermogravimetric analyzer (TGA) Q500. Fourier transform infrared (FT-IR) spectra were recorded using Varian 670 FT-IR spectrometer with a slide-on attenuated total reflection (Ge). Mechanical embossing was carried out in a DACA Tribotrik with a spherical glass stamp of diameter 25.8 mm. Ocean optics UV−visible spectrophotometer HR2000+ mounted on a DM6000 M microscope from Leica Microsystems was used for monitoring the shape recovery from embossed films. T95-PE from Linkam Scientific was used to study the temperature-dependent transmission spectra. Images of the embossed film were captured using Leica M80 stereomicroscope. Height profile was measured using Veeco Dektak 150 Surface Profiler. Shape memory cycle measurement was carried out in DMA Q800. Transmission electron microscopy (TEM) was carried out by microtoming slices of the polymer films embedded in an epoxy using a DiATOME Diamond Knife (cryo 35°). The samples were trimmed orthogonal to the plane of the film at room temperature and collected from the surface of a water reservoir using 200 mesh carbon-coated copper grids. The epoxy used consists of an epoxy resin (EpoFix resin) and a hardener (EpoFix hardener), manufactured by Struers, mixed in a 25:3 mass ratio. The TEM imaging was performed using an FEI Tecnai 20 (type Sphera) TEM operating at 200 kV and mapped using a bottom-mounted 1024×1024 Gatan MSC charge-coupled device camera (model 794).

3. RESULTS AND DISCUSSION

3.1. Fabrication and Characterization of Photonic Polymer Film. To obtain a photonic polymer film with a broad Tg, a semi-interpenetrating network (semi-IPN) was fabricated from a CLC polymer film with a Tg of 60 °C (Figure S1a) and poly(benzyl acrylate) (abbreviated as poly(BA)) whose pure homopolymer has a Tg of ~6 °C (Figure S1b). The benzyl acrylate (BA) monomer can readily penetrate into the CLC polymer due to the π−π interactions between the benzene ring of the monomers and the polymer. The semi-IPN photonic film was fabricated from a monomer mixture consisting of a diacrylate (RM257, 29 wt %) and a monoaCRYlate (RM105, 35 wt %) mesogens (Scheme 1). It also contained a nonpolymerizable mesogen (5CB, 30 wt %) to act as a porogen to facilitate the incorporation of BA monomers. A chiral molecule (LC756, 5 wt %) with polymerizable end groups was used to induce cholesteric (or chiral nematic) liquid crystalline phase. Irgacure 651 was added to initiate the photopolymerization reaction. The monomer mixture was filled in a polyimide-coated cells with a 70 μm spacer and was photopolymerized at room temperature to obtain a freestanding green reflecting polymer film (70 μm thick) with selective reflection band centered at λ = 515 nm (Figures S2 and S3). The porogen, 5CB, was removed by extracting with an organic solvent (tetrahydrofuran). This resulted in a large blue shift of the reflection band to λ = 380 nm, implying shortening of the helical pitch length by 26.2% (Figure S2), which is in good agreement with the 30% decrease observed in the thickness of the film (Figure S3). The TEM image of the cross section of the film revealed a periodic alternating bright and
dark bands due to the helical orientation of the molecules (Figure S4). In the FT-IR spectrum, the peak at 2225 cm\(^{-1}\) originating from the stretching vibration of (−C≡N) of SCB had disappeared (Figure S5). Moreover, no weight loss was observed below 200 °C in the thermogravimetric curve (Figure S6), suggesting a complete removal of SCB. The DSC experiments showed that the polymer film undergoes a glass transition at 60 °C (Figure S1). The blue CLC polymer film without SCB (CLC−SCB) was then treated with BA monomer mixed with 1 wt % of the photoinitiator (Irgacure 651), and this resulted in a change in the color from blue to orange due to the penetration of the monomers into the cholesteric polymer network, causing an increase in the pitch length. Photo-polymerization of the swollen orange film led to the formation of the photonic semi-IPN of the CLC polymer and poly(BA).

FT-IR spectroscopy of the semi-IPN photonic film showed a band centered at 748 cm\(^{-1}\) due to the rocking motion of the long (−CH\(_2\)) polymer backbone in poly(BA) (Figure S5). The amount of poly(BA) incorporated was determined by the difference between the weight of the polymer film before and after polymerization.
after the treatment with BA, and was found to be 42.4 wt %.
The reflection band of the semi-IPN (~76 μm thick; Figure S3) was centered at $\lambda = 590$ nm, which translates to 40.8% increase in the pitch length (Figure 1a). This is in good agreement with the observed 43% increase in the film thickness. Moreover, the TEM cross-sectional image of the semi-IPN also showed alternating bright and dark bands with a periodicity of 170 nm (Figure 1b); the periodicity corresponds to half a pitch length and correlates well with the observed reflection wavelength. The pitch length was found to be uniformly distributed throughout the semi-IPN film, suggesting that the cholesteric polymer and poly(BA) are well mixed.

The DSC curve of the semi-IPN is markedly different from that of the pure cholesteric polymer CLC–5CB and the pure homopolymer poly(BA). A broad glass transition that onsets at 10 °C ($T_{\text{low}}$) and ends at 54 °C ($T_{\text{high}}$) was observed instead of two distinct glass transitions due to noncovalent $\pi-\pi$ interactions between the poly(BA) and the CLC polymer network (Figure 1c). In the heating curve, however, the broad transition can be noticed to consist of two overlapping broad humps that are centered at 22 °C ($T_{\text{mid1}}$) and 45 °C ($T_{\text{mid2}}$) and can be assigned as $T_g$ of the poly(BA)-dominant and the CLC polymer-dominant domains, respectively. It can be said that physically, the semi-IPN behaves nearly like a single polymer with the thermal transition smeared out over a broad range of temperature.

3.2. Mechanical Embossing of the Photonic Polymer Film. The semi-IPN photonic film was mechanically embossed in two steps by using a spherical glass stamp (radius of curvature = 25.8 mm)—first, above the glass transition at $T_1 = 75$ °C (i.e., $T_{\text{high}} + 21$ °C) and second, in between $T_{\text{mid1}}$ and $T_{\text{mid2}}$ at $T_2 = 40$ °C (i.e., $T_{\text{mid1}} + 18$ °C) (Figure 2a). At $T_1$, a load of 0.7 kg was used for embossing. Upon cooling to $T_2$, an extra load of 3.5 kg was added. With a total load of 4.2 kg, the film was then cooled down below the glass transition. At 0 °C, the load was finally removed and a spherical indentation with a diameter of 1.7 mm was obtained.

The central region of the indentation appeared blue and the UV–vis transmission spectrum showed that the reflection band has blue shifted by ~155 nm with the new position centered at $\lambda = 435$ nm (Figure 2b,c). The low transmittance value at 0 °C is due to the condensation of water vapor on the surface of the film, and this was not accounted for while making the baseline correction. On moving outward from the central blue embossed region, the degree of compression of the pitch length decreases due to the spherical shape of the stamp used and the color shift toward a higher wavelength (Figure 2b). When the photonic semi-IPN was embossed in just one step at 75 °C with a load of 5.2 kg and cooled directly to 0 °C, the color change was smaller ($\Delta \lambda = \sim 112$ nm) (Figure S7). This implies that the method to emboss in two steps results in a more efficient compression of the helical pitch. Therefore, only the investigations carried out on the two-step embossed film will be presented in the following sections. It should be noted here that the mechanical embossing of the pure cholesteric polymer CLC–5CB resulted in a blue shift of the reflection band by only 7 nm (Figure S8). This emphasizes the role of having a softer second polymer network, poly(BA) in our case, interpenetrated with the CLC polymer in obtaining an enormous blue shift of the reflection band.

3.3. Shape Recovery and Optical Response to Temperature. The color response of the embossed polymer was investigated by heating stepwise through the $T_g$. The film was first heated to 8 °C. There was no visible color change even after keeping at 8 °C for 7 h (Figure 2b). However, the UV–vis spectrum showed a small red shift of the reflection band ($\Delta \lambda$) of the central blue region by ~10 nm after an hour (Figure 2c), and keeping at 8 °C for longer than an hour hardly shifted the reflection band further. The temperature was then increased to 20 °C and, within an hour, the central region of the embossed area became bluish-green ($\Delta \lambda \approx 50$ nm, $t = 1$ h), and the change in color was clearly visible to the naked eye (Figure 2b,c). The UV–vis transmission spectrum was also recorded for the embossed film after an hour for every 2 °C rise in the temperature from 0 to 20 °C. As can be seen from Figure 2d, the amount of red shift of the reflection band, $\Delta \lambda$, increases steadily with an increase in the temperature. However, the change in color is quite small (<20 nm) at very low temperatures (<10 °C) to be distinguishable to the naked eye. On increasing the temperature to 25 °C, the embossed area turned green ($\Delta \lambda \approx 80$ nm, $t = 1$ h). Heating the film to 35 °C resulted in the yellow reflective color ($\Delta \lambda \approx 110$ nm, $t = 1$ h), which returned to the original orange ($\Delta \lambda \approx 155$ nm, $t = 1$ h) finally at 55 °C, basically covering almost the entire visible color spectrum (Figure 2b,c). Lowering the temperature at any stage did not reverse the color of the indentation to what was observed prior to the increase in the temperature, demonstrating the characteristic behavior of the one-way shape memory. The photonic film, however, can be mechanically embossed and recovered again. The recyclability of the film was investigated for three shape memory cycles, and it was found to be completely reversible (Figure S9).

The height profile measurement of the embossed area at room temperature (25 °C) showed that the spherical indentation is 6 μm deep at the lowest point (Figure S10). It translates to a 6% decrease in the thickness at the center of the indentation. This value is much lower than the calculated 13% shortening of the pitch length of the polymer, obtained by assuming that the optical response of the indentation is independent of the angle of incidence of light. This reveals that the optical response seen is, in fact, largely dependent on the angle of incidence due to the curvature of the indentation.

To determine if the path followed to reach a temperature $T$ in the regime of glass transition has an effect on the optical response of the embossed polymer film, two different heating routes were employed—(a) it was initially heated to $T = 5$ °C and later up to the desired temperature $T$ and (b) it was directly heated from 0 °C to $T$, and the amount of red shifts observed after 1 h at $T$ was examined (Figure S11). The samples that were preheated to $T = 5$ °C were found to show slightly higher values of $\Delta \lambda$, as they have had quite some time at the temperatures just lower than the target temperature to recover to their initial (nonembossed) configuration. It can therefore be stated that when sufficient time has not been provided for the complete recovery to take place (vide infra), they will always show a slightly higher optical response than those that are directly heated to the target temperature.

To determine the temperature-dependent optical response in the entire glass transition region, different embossed films were heated directly from 0 °C to different temperatures $T = 8$–75 °C. After keeping at the desired temperatures for 7 h, the red shifts ($\Delta \lambda$) of the reflection band were recorded (Figure 2e). What is intriguing is that $\Delta \lambda$ follows a near-double sigmoidal trend—the first phase from 0 to 30 °C and the second phase from 30 to 55 °C—similar to the shape of the DSC heating curve (Figure 1c). This may be attributed to the existence of a
broad glass transition comprising two overlapping transitions ($T_{mid1}$ and $T_{mid2}$) corresponding to the poly(BA)-dominant and the CLC polymer-dominant domains. In the first phase, the chains of poly(BA) gain flexibility and begin to recover their original configuration. The CLC polymer chains, due to their strong noncovalent interaction with poly(BA), are compelled to recover simultaneously to a certain extent. This is supported by the red shift of the reflection band of the embossed area. On raising the temperature further to $T_{mid2}$ and above, the CLC polymer network acquires full flexibility; consequently, complete shape recovery takes place at 55 °C.

The kinetics of the recovery of original shape of the embossed photonic film was also studied in detail. Each embossed film was heated from 0 °C to a specific temperature ($T_{8\degree C} \leq T \leq 55 \degree C$) and was kept at isothermal condition for 7 h. Meanwhile, the reflection band of the films was monitored by the UV–vis spectroscopy. As the temperature was increased to and maintained at $T$, there was a steep increase in the amount of red shift of the reflection band ($\Delta \lambda_i$), with respect to the reflection band at 0 °C. Figure 3a plots the extent of shape recovery as a ratio of $\Delta \lambda_i$ to the maximum red shift observed ($\Delta \lambda_{max} = 155$ nm), when the complete recovery takes place at 75 °C, as a function of time. As time progressed, the rate of change of $\Delta \lambda_i/\Delta \lambda_{max}$ decreased continuously, and after an hour at $T$, it had slowed down considerably, so the difference between $\Delta \lambda_i/\Delta \lambda_{max}$ after 1 h and that after 7 h was very small.

The data of Figure 3a have been replotted in Figure 3b on a semilogarithmic plot to model the response of the photonic polymer film at a specific temperature. It becomes clear from this plot that the relaxation mechanism does not approach an equilibrium state at a given temperature, but rather continuously relaxes back to its original orange color.

By using the horizontal shifting along the time axis, that is, using time–temperature-superposition (TTS), a master curve with respect to a reference temperature—here arbitrarily chosen as 20 °C—was obtained (Figure 3c). The relaxation behavior of the photonic polymer film as displayed by the master curve can be described using a simple Kelvin–Voigt model, in which a spring and dashpot are modeled in parallel.37

The parallel spring here enforces the reversibility of the deformation and the dashpot governs the relevant time and temperature response. The nonexponentiality of the response is accounted for by using the empirical Kohlrausch–Williams–Watts equation,38–42 which is a stretched-exponential equation often used to describe the distributions of relaxation times in a continuous rather than discrete manner, consisting of two adjustable relaxation constants, namely, $\tau_{ref}$ and $\beta$

$$\Delta \lambda_i/\Delta \lambda_{max}(t, T) = \left(1 - \exp\left(\frac{t_{ref}(t, T)}{\tau_{ref}}\right)\right)^{\beta}$$

Figure 3. (a) Red shifts ($\Delta \lambda_i$) of the reflection band of the central embossed area measured at different temperatures over time with reference to the red shift observed at 75 °C ($\Delta \lambda_{max}$) on complete recovery. (b) Shape recovery data of (a) shown on a logarithmic time axis. (c) Master curve constructed from the data of subgraph (b) using time–temperature-superposition (TTS); solid line is a fit according to eq 1. (d) Shift factors used to construct the master curve; solid line is an Arrhenius fit.
where \( \tau_{ref} \) is the average relaxation time with respect to a reference temperature and \( \beta \) is a parameter that describes the nonexponential behavior of the relaxation process, or in other words, it is a measure of the width of the distribution of relaxation times. The best fit of the master curve was obtained when \( \tau_{ref} \) has a value of \( 1.47 \times 10^4 \) s at 20 °C and \( \beta \) has a value of 0.14. As \( \beta \ll 1 \), the distribution of relaxation times is very broad and correlates well with the experimentally observed very broad thermal transition that the photonic semi-IPN displayed. This shows that the model fully describes the relaxation behavior of the embossed film.

The TTS shift function \( a_f \) used to construct the master curve (Figure 3c) follows a standard Arrhenius type of temperature dependence (Figure 3d)

\[
a_f(T) = \exp \left( \frac{\Delta U}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)
\]

(2)

where \( \Delta U \) is the activation energy, \( R \) is the universal gas constant, \( T \) is the temperature, and \( T_{ref} \) is a reference temperature. The activation energy, \( \Delta U \), was found to be 432 kJ mol\(^{-1}\), a rather large value indicating that the influence of temperature is (much) stronger than that of time. It must be noted that although the value might appear large when \( T \) is (much) stronger than that of time. It must be noted that although the value might appear large when

\[
\text{the recovery, therefore, basically takes place with the formation of nonequilibrium configurations that display quasi-stable multiple colors ranging from blue to orange in the broad thermal transition regime.}
\]

4. CONCLUSIONS

A photonic shape memory polymer film that displays stable multiple colors covering almost the entire visible spectrum from blue to orange has been fabricated from a semi-interpenetrating network of a CLC polymer and poly(benzyl acrylate). The multiple structural colors are generated as the mechanically embossed photonic film recovers on heating through the broad thermal transition. The recovery process can be fully described using a Kelvin–Voigt model, which revealed that the recovery is dominated by temperature. In the first hour of recovery, the embossed photonic film displays a time–temperature integrating behavior, and its influence on the recovery continuously decreases as time progresses, thereby generating stable colors. This makes such photonic shape memory polymers with stable multiple colors attractive for various applications ranging from optical sensors to reconfigurable optical materials and devices. As the change in color can be fully described as the function of temperature and time, these photonic materials can be easily programmed by changing the chemical composition of the semi-interpenetrating network in a modular approach.


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