Cholesteric Materials

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Three-Way-Switchable (Right/Left/OFF) Selective Reflection of Circularly Polarized Light on Solid Thin Films of Helical Polymer Blends

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Abstract: *Two poly(quinoxaline-2,3-diyl) copolymers bearing miscibility-enhancing 8-chlorooctyloxy and (S)-2-methylbutoxy or n-butoxy side chains were synthesized. After annealing in $CHCl_3$ vapor, a polymer-blend film of these copolymers exhibited selective reflection of right-handed circularly polarized light (CPL) in the visible region. The handedness of the CPL reflected was completely inverted upon annealing of the film in THF vapor. Annealing in n-hexane vapor resulted in the phase separation of the polymer blend, which turned the selective reflection off. This three-way-switchable reflection, that is, reflection of right-handed or left-handed CPL, together with an OFF state, could be observed visually through right- and left-handed CPL filters.*

Cholesteric superstructures consist of helically aligned rodlike molecules and can exhibit structural coloration by the selective reflection of circularly polarized light (CPL).[1] Such structural coloration is expected to find application in optical sensing devices,[2] low-threshold lasing,[3] and “copy-safe” printing for security purposes.[4] Some effort has been directed towards the preparation of cholesteric materials, whose chirality can be switched by external stimuli, such as temperature, light, and solvents.[5] In particular, dry and solid cholesteric materials are in high demand, as the stability of the cholesteric superstructure is increased therein. Although several polymer-based systems have been developed for this purpose,[6] solid cholesteric materials that exhibit the ability to reversibly invert their handedness or switch between ON/OFF states of selective CPL reflection have not been reported so far.

Poly(quinoxaline-2,3-diyl)s (PQXs) are a unique class of helical polymers[7] with a rigid, rodlike helical backbone.[8] PQXs bearing chiral side chains are particularly interesting, as they show a solvent-dependent inversion of their helical sense.[9] We have previously reported that the helical scaffold of PQXs provides a highly efficient chiral reaction environment, and that solvent effects can invert the chirality of PQXs. This feature allows PQXs to serve in a variety of reactions as highly enantioselective catalysts,[10] which are able to generate both enantiomers from a single compound.

Recently, we also reported that solid PQX terpolymer films bearing (*S*)-2-methylbutoxy, *n*-butoxy, and 8-chlorooctyloxy side chains selectively reflected CPL in the visible region. Interestingly, the handedness of the CPL that was reflected could be tuned reversibly by exposure of the film to the vapor of different solvents.[11] The color of the films could be fully tuned by changing the composition of the terpolymer, as well as by the solvent vapor. For example, an increase in the mole fraction of the chiral monomer unit resulted in a hypsochromic shift of the reflected wavelength on account of a stronger twist of the cholesteric superstructure. However, changing the terpolymer composition to tune the reflection wavelength is laborious and hence undesirable from a practical perspective. It seems more attractive to use a two-component system, in which two polymers are blended in an arbitrary fashion upon fabrication to tune the mean reflection wavelength of the film. Potential problems that may arise in this context are general difficulties with respect to polymer blending to avoid phase separation.

Herein, we report the preparation of dry, solid polymer films, which consist of two PQX copolymers and exhibit selective reflection of CPL according to their helical cholesteric superstructure. The color of the reflected CPL could be tuned by changing the ratio of the two polymers in the PQX polymer blend. Moreover, we observed that a single film with a certain blend ratio exhibited three-way-switchable reflection behavior upon exposure to different solvent vapors, that is, the reflection of right- or left-handed CPL (ON state), or no reflection (OFF state).

In our previous study,[11] we developed a fabrication method for dry solid polymer films that selectively reflect CPL in the visible region. A solution in *o*-xylene ($0.6\,\mathrm{g\,mL^{-1}}$) of a random terpolymer **P1** bearing (*S*)-2-methylbutoxy, *n*-butoxy, and 8-chlorooctyloxy side chains in a ratio of 30:45:25 was deposited on a glass substrate and dried (Scheme 1a). We used *o*-xylene for the deposition because of its high boiling point and moderate viscosity. The freshly deposited film from the solution in *o*-xylene did not exhibit any selective reflection in the visible-light region. The film was then exposed to $CHCl_3$ vapor at room temperature (solvent-vapor annealing) and dried under reduced pressure. The obtained solid polymer film of **P1** exhibited the efficient selective reflection of CPL in the blue region of the visible spectrum. To develop a comparable polymer-blend system, we prepared three homopolymers **P2**, **P3**, and **P4**, with (*S*)-2-methylbutoxy, *n*-butoxy, and 8-chlorooctyloxy side chains, respectively (Scheme 1b). These homopolymers were mixed in a molar ratio of 30:45:25 to give the corresponding polymer blend **P2/P3/P4(30*/45/25)**.[12] However, the film did not exhibit

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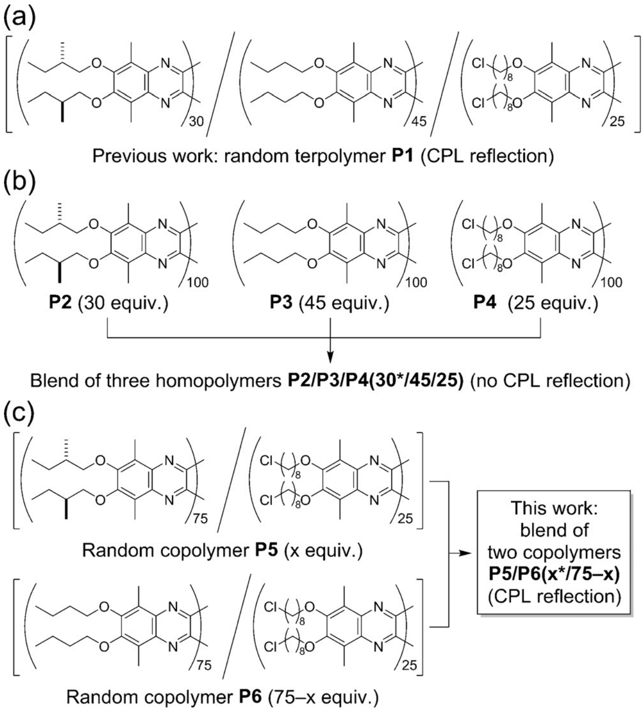

Scheme 1. a) Structure of terpolymer **P1**, which exhibits chirality-switchable selective reflection of CPL (our previous study).[11] b) Preparation of **P2/P3/P4(30*/45/25)** from homopolymers **P2**, **P3**, and **P4**. c) Preparation of **P5/P6(*x**/*y*)** from copolymers **P5** and **P6**.

selective reflection of CPL after annealing in $CHCl_3$ vapor. X-ray diffraction (XRD) measurements of the **P2/P3/P4(30*/45/25)** mixture of the three homopolymers revealed multiple diffraction peaks, indicative of a phase separation, which most likely arises from the low miscibility of the homopolymers (Figure 1).

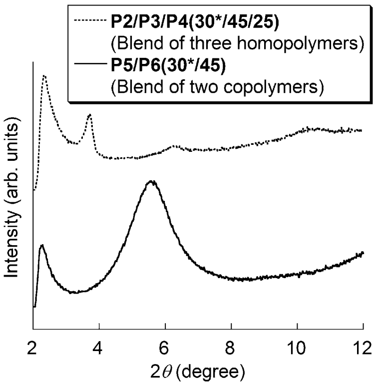

Figure 1. XRD ($Cu_{K\alpha}$) patterns of thin polymer films of **P2/P3/P4(30*/45/25)** and **P5/P6(30*/45)** after solvent annealing in $CHCl_3$ vapor.

Therefore, we subsequently synthesized two random copolymers **P5** and **P6**, bearing 8-chlorooctyloxy side chains together with either (*S*)-2-methylbutoxy (**P5**) or *n*-butoxy (**P6**) side chains (Scheme 1c). **P5** and **P6** were mixed in a 30:45 ratio to afford the polymer blend **P5/P6(30*/45)**, which maintains the same 30:45:25 ratio of the three different types of side chains as for **P1**. After annealing in $CHCl_3$ vapor, an XRD measurement showed a unimodal peak, thus indicating that the two copolymers formed a homogeneous cholesteric superstructure (Figure 1). The **P5/P6(30*/45)** film exhibited the selective reflection of light in the red region of the visible spectrum.

To gain further insight into the nature of the selective reflection, we prepared a series of polymer blends **P5/P6(*x**/*y*)** with varying mixing ratios (Figure 2). We found that the mean wavelength of the light that was selectively reflected from the polymer-blend films after annealing in $CHCl_3$ vapor depended on the mixing ratio of the two copolymers, and varied from blue (**P5/P6(50*/25)**), to green (**P5/P6(40*/35)**), and red (**P5/P6(25*/50)**; Figure 2a). Moreover, all **P5/P6(*x**/*y*)** films annealed in $CHCl_3$ vapor selectively reflected right-handed CPL. The circular dichroism (CD) spectrum of **P5** in $CHCl_3$ revealed that the backbone of **P5** adopted the *M*-helical conformation in $CHCl_3$ (see the Supporting Information), which in turn induced a right-handed cholesteric superstructure.

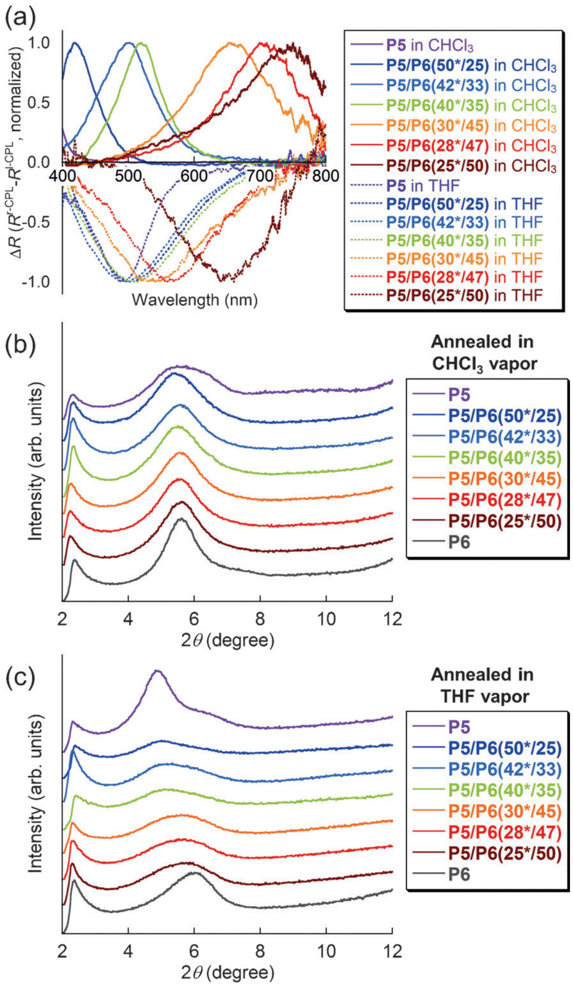

Figure 2. a) Difference reflection spectra of **P5** and **P5/P6(*x**/*y*)** annealed in $CHCl_3$ (solid lines) or THF vapor (dotted lines). **P6** did not exhibit selective reflection. b, c) XRD ($Cu_{K\alpha}$) patterns of polymer films annealed in $CHCl_3$ (b) or THF vapor (c).

When THF vapor was used for the solvent annealing, these polymer-blend films selectively reflected left-handed CPL, thus suggesting a left-handed cholesteric structure. The CD spectrum of **P5** in THF indicated that the backbone adopted the *P*-helical conformation in THF (see the Supporting Information). At this point, we assume that the helix inversion of the **P5** backbone leads to an inversion of the twist sense of the cholesteric superstructure. The mean wavelength of the selectively reflected light after annealing in THF vapor was bathochromically shifted (500–650 nm) as the **P5** ratio decreased. Although **P5**/**P6**(**50***/**25**), **P5**/**P6**(**42***/**33**), and **P5**/**P6**(**40***/**35**) showed a clear mixing-ratio-dependent peak shift after exposure to $CHCl_3$ vapor, these blends exhibited a virtually identical selective reflection after annealing in THF vapor. XRD measurements revealed distorted peaks for these films, thus suggesting a partial phase separation between **P5** and **P6** (Figure 2c). Accordingly, it seems feasible to attribute the almost identical selective reflection observed for **P5**/**P6**(**50***/**25**), **P5**/**P6**(**42***/**33**), and **P5**/**P6**(**40***/**35**) to an upper limit for the mixing ratio of **P5** and **P6** during the formation of the cholesteric superstructure in the THF annealing process.

On the basis of this two-component system, we fabricated a polymer-blend film that exhibited a structural color upon deposition on a glass substrate (Figure 3). For that purpose, solutions of **P5** and **P6** in *o*-xylene were applied simultaneously on a glass substrate. The polymer-blend films thus deposited were exposed to $CHCl_3$ vapor at room temperature and then dried under reduced pressure. The obtained films exhibited the efficient selective reflection of light in the visible region. The mean reflection color could be fully tuned from blue (Figure 3b), to green (Figure 3c), and red (Figure 3d) by changing the mixing ratio of **P5** and **P6**.

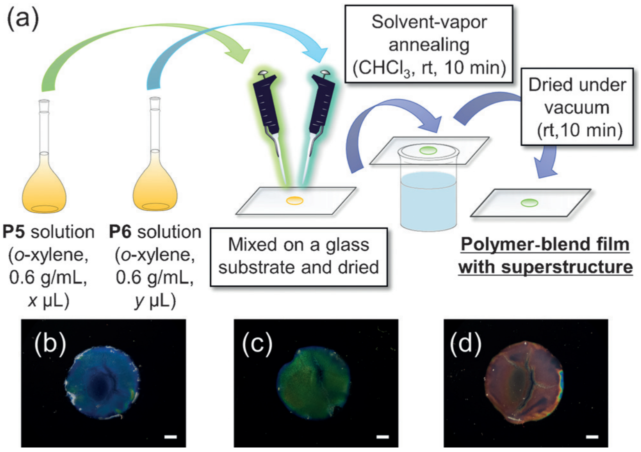

Figure 3. a) Fabrication of **P5**/**P6** polymer-blend films with a cholesteric superstructure. b–d) Photographs of polymer-blend films with mixing ratios (*x*/*y*) of 2.1/1.1 (b), 1.7/1.5 (c), and 1.3/2.0 (d). Scale bars: 1.0 mm.

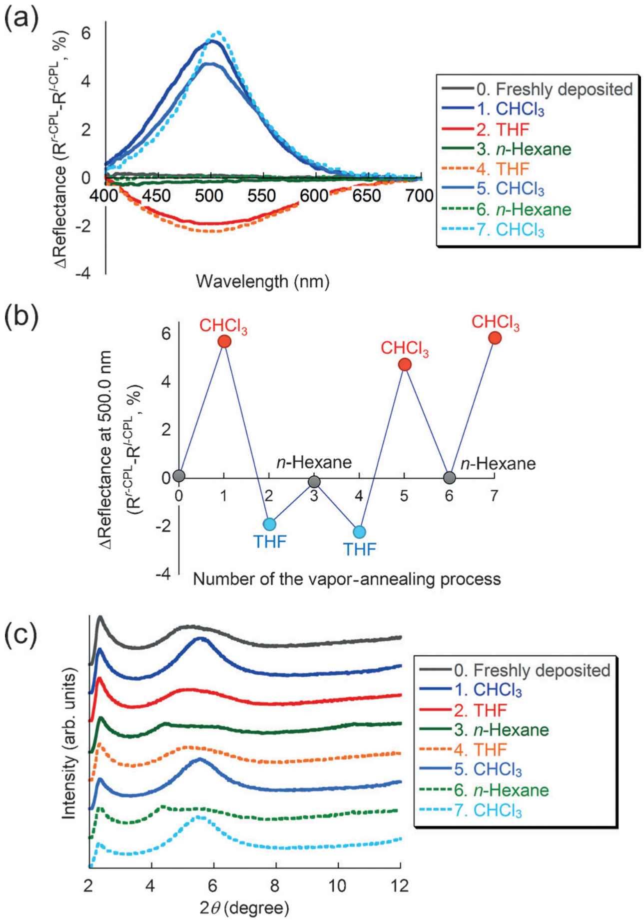

Figure 4. Consecutive solvent-vapor annealing of **P5**/**P6**(**42***/**33**) in different solvents: $CHCl_3$, THF, and *n*-hexane. a) Difference reflection spectra; b) difference reflectance at 500.0 nm; c) XRD ($Cu_{K\alpha}$) patterns.

Finally, we tried to demonstrate the three-way switching of the selective reflection from such polymer thin films (Figure 4). As previously mentioned, these polymer-blend films exhibited a selective reflection of right- or left-handed CPL (ON) in the visible region after vapor annealing in $CHCl_3$ and THF, respectively. We found that the structural color can be turned off by solvent annealing in *n*-hexane (OFF). Consecutive exposure of **P5**/**P6**(**42***/**33**) to $CHCl_3$, THF, and *n*-hexane vapor revealed that the selective reflection is reversible (Figure 4a). A solution of **P5**/**P6**(**42***/**33**) in *o*-xylene (0.6 $g\,mL^{-1}$) was applied on a glass substrate to give a thin film of the polymer blend after removal of the solvent. This film did not exhibit any selective reflection of light in the visible region. After the film was exposed to $CHCl_3$ vapor (10 min) and then dried under reduced pressure, a green film that selectively reflected right-handed CPL was obtained. Subsequently, the same film was exposed to THF vapor (10 min), which resulted in the selective reflection of left-handed CPL (for a graph indicating the course of the vapor annealing process over time, see the Supporting Information). Interestingly, after exposure to *n*-hexane vapor (10 min), the selective reflection of the film disappeared. Most remarkably, the inversion of the reflection was reversible and could be maintained during several annealing cycles (Figure 4b). For example, the handedness of the reflected CPL could be switched from right to left and then from left to right by exposing the film to THF and then $CHCl_3$ vapor. It was also possible to turn the selective reflection off by using *n*-hexane, and to turn it on again by using either $CHCl_3$ or THF vapor. We recorded the XRD pattern for each state to elucidate the superstructure of the polymer-blend film (Figure 4c). After solvent-vapor annealing with $CHCl_3$, clear unimodal peaks were observed, which indicate the formation of homogeneous cholesteric superstructures. In the case of solvent-vapor annealing with THF, broad peaks were observed, which suggest the formation of partially phase separated cholesteric superstructures. Conversely, several peaks were observed after solvent-vapor annealing with *n*-hexane; this result is consistent with a phase separation of the two copolymers.

A plausible mechanism based on the XRD patterns is outlined in Figure 5 for the three-way switching of the selective reflection. After solvent-vapor annealing in $CHCl_3$ or THF, right- or left-handed cholesteric structures are formed, which selectively reflect right- or left-handed CPL. Solvent-vapor annealing with *n*-hexane induces the phase separation of the copolymers, and thus turns the selective reflection off. At this stage, although the detailed mechanism of the suppression of the selective reflection upon exposure to *n*-hexane vapor is still not clear, we can conclude that phase separation disturbed the formation of a cholesteric superstructure and thus led to the OFF reflection state. We also confirmed that thin films of the terpolymer **P1** annealed in THF or *n*-hexane vapor exhibited the selective reflection of left-handed CPL without a phase separation (see the Supporting Information). These results indicated that the OFF state based on phase separation is a key feature of this polymer-blend system.

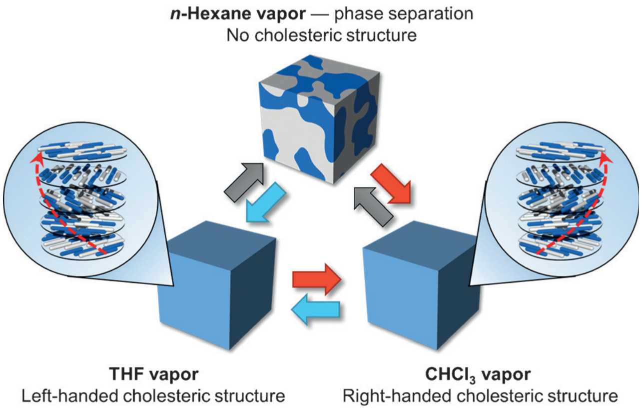

Figure 5. Schematic illustration of the three-way switching of thin films of a **P5**/**P6**(**42***/**33**) polymer blend by solvent annealing in $CHCl_3$, THF, or *n*-hexane vapor (blue arrows: exposure to THF vapor; red arrows: exposure to $CHCl_3$ vapor; gray arrows: exposure to *n*-hexane vapor).

The three-way switching of the selective reflection of CPL could be observed by the naked eye through CPL filters. Photographs of a thin film of **P5**/**P6**(**42***/**33**) were taken through left- and right-handed CPL filters after solvent annealing in $CHCl_3$, THF, or *n*-hexane vapor. Although the thin film did not exhibit a selective reflection immediately after deposition (Figure 6a, OFF), a selective reflection of green right-handed CPL was clearly observed after solvent annealing in $CHCl_3$ vapor (Figure 6b, ON: reflection of right-handed CPL). The selective reflection could be switched to green and left-handed CPL by exposure to THF vapor (Figure 6c, ON: reflection of left-handed CPL), before being turned off by exposure to *n*-hexane vapor (Figure 6d, OFF). The selective reflection was turned on again by exposing the film to THF vapor (Figure 6e), and the switching of the reflection modes could be repeated (Figure 6 f–h).

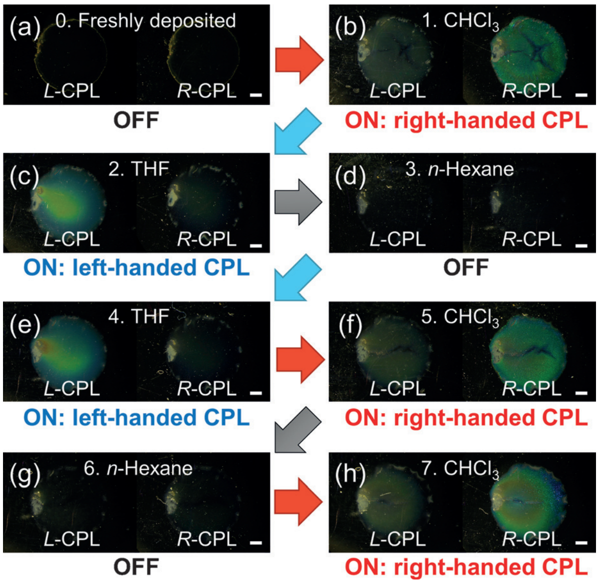

Figure 6. Photographs taken of a thin film of **P5**/**P6**(**42***/**33**) through left- and right-handed CPL filters after consecutive exposure to the vapor of different solvents: $CHCl_3$, THF, and *n*-hexane (blue arrows: exposure to THF vapor; red arrows: exposure to $CHCl_3$ vapor; gray arrows: exposure to *n*-hexane vapor). Scale bars: 1.0 mm.

In summary, we created thin films of polymer blends of chiral and achiral poly(quinoxaline-2,3-diyl) copolymers containing 8-chlorooctyloxy side chains to enhance miscibility during fabrication. These films exhibited the selective reflection of right-handed CPL in the visible region after annealing in $CHCl_3$ vapor at room temperature. The mean wavelength of the selective reflection could be tuned by changing the mixing ratio of the chiral and achiral copolymers. Annealing in THF vapor induced a solvent-dependent helix inversion of the chiral polymer, which resulted in an inversion of the handedness of the CPL that was reflected from these films. This study should thus open new research avenues for the development of unprecedented chirality-switchable chiroptical materials based not only on one-dimensional macromolecular structures of PQXs, but also on their highly ordered three-dimensional supramacromolecular structures.

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[12] The asterisk denominates the molar ratio of the chiral-side-chain fraction.

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