

Solid Polymer Films Exhibiting Handedness-Switchable, Full-Color-Tunable Selective Reflection of Circularly Polarized Light

Yuuya Nagata,[†] Keisuke Takagi,[†] and Michinori Suginome^{*,†,‡}

[†]Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

[‡]CREST, Japan Science and Technology Agency (JST), Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

S Supporting Information

ABSTRACT: Poly(quinoxaline-2,3-diyl)s bearing (*S*)-2-methylbutyl, *n*-butyl, and 8-chlorooctyl groups as side chains were synthesized to fabricate dry solid polymer thin films. These films exhibited selective reflection of right-handed circular polarized light (CPL) in the visible region after annealing in CHCl₃ vapor at room temperature. The handedness of reflected CPL was inverted to the left after annealing in 1,2-dichloroethane vapor. It was also found that the color of a particular single film along with the handedness of reflected CPL were fully tuned reversibly, upon exposure of the film to the vapor of various mixtures of chloroform and 1,2-dichloroethane in different ratios.

Physical interaction of light with a cholesteric nanostructure whose pitch falls within a range of wavelengths of visible light shows coloration by selective reflection of circularly polarized light (CPL). The wavelength (λ) of reflected CPL is determined by the product of the average refractive index (n) and the pitch (P) of the cholesteric structure.¹ Such structural coloration is widely found in nature, as exemplified by the colored skin tissue of jeweled beetles² and a certain type of plant.³ Synthetic materials exhibiting selective-reflection-based physical color are attracting increasing attention for applications in full-color electronic papers,⁴ sensing devices,⁵ low-threshold lasing,⁶ and “copy-safe” printing for security purposes.⁷ Various liquid crystalline materials have been developed, taking advantage of the ready formation of cholesteric superstructures with small chiral molecules.⁸ Liquid crystalline materials that exhibit reversible change of their color and handedness of CPL by external stimuli have been reported.⁹ They are expected to be useful as new materials for color information technology.¹⁰

Furthermore, efforts have been devoted to preparing solid, dry cholesteric materials for long-term as well as thermal stability of coloration. For this purpose, several polymer-based systems have been reported.¹¹ However, due to the solid nature, it is difficult to acquire both tunability of color and the handedness of CPL. For instance, the materials require continuous heating,¹² solvent adsorption,¹³ or cross-linking¹⁴ to retain the acquired physical colors, failing to provide dry materials with stable coloration with full-color tunability. Although dicholesteryl ester is reported to be a nonpolymer-based solid film that changes its reflection wavelength reversibly upon changing the temperature applied to melt it, it does not show the switch of CPL handedness.¹⁵ To date, reversible switching of the handedness of CPL has not been

achieved with dry solid polymer film on the basis of selective reflection.

We herein report the preparation of helical-polymer-based solid films that show selective reflection of CPL according to the helical cholesteric superstructure, which, in turn, originates from the helical structure of the macromolecules.¹⁶ The color and the handedness of reflected CPL are both tunable by altering the composition of the monomers and also by altering the nature of the solvent vapor that is applied during the solvent vapor annealing process. Of note is that a single film having a certain monomer composition exhibits full-color tunability with control of handedness of CPL by applying varying solvent vapors during the annealing process.

Poly(quinoxaline-2,3-diyl) (PQX) molecules are a unique class of helical polymers; they possess a nanoscale, rigid rod-like helical backbone.¹⁷ The unique molecular structure allows them to serve as mesogenic segments for liquid crystals.¹⁸ PQXs bearing chiral side chains show a unique solvent-dependent inversion of their helical sense.¹⁹ We have reported that the helical scaffold of PQX serves as a highly efficient chiral reaction environment. The chirality is switchable by a solvent effect,²⁰ leading to the production of a pair of enantiomeric products from a single chiral catalyst in various reactions.²¹

Newly synthesized random copolymers P($x^*/0/z$) bearing (*S*)-2-methylbutyl and 8-chlorooctyl groups as side chains (Figure 1a) formed an *M*-helical polymer backbone in chloroform (CHCl₃) solutions at room temperature. The screw-sense excess of the *M*-helical structure varied with the ratio (x/z) of the two monomers. Higher screw-sense excess was observed for the PQX bearing more chiral units. Thin films of those PQXs were then fabricated (Figure 1b). A concentrated solution thereof in xylene (0.6 g/mL) was applied on a glass substrate. After drying, the films were transparent, with no color, as a result of lack of absorption by PQX in the visible light region. The film formed on a glass substrate was exposed to CHCl₃ vapor for 4 min at 20 °C and then dried under vacuum. Although copolymers P(50*/0/50) and P(25*/0/75) as well as homopolymers P(100*/0/0) and P(0*/0/100) still had no color, one copolymer, P(75*/0/25), did show blue color (Table 1, entries 1–5). This was eventually known to arise from selective reflection of visible light. It should be noted here that the film reflected right-handed CPL selectively over left-handed CPL, suggesting the formation of a right-handed helical supra-

Received: May 14, 2014

Published: June 18, 2014



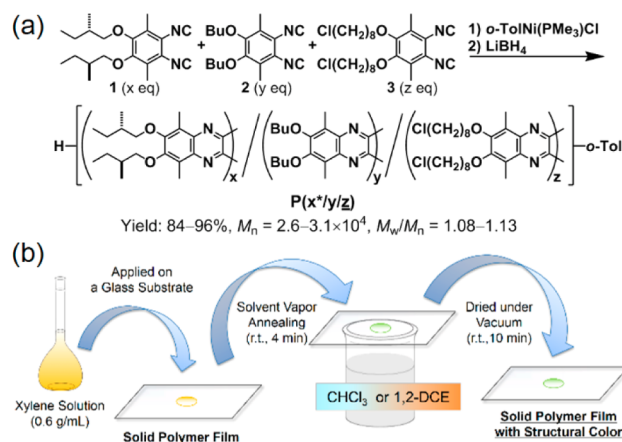


Figure 1. Synthesis (a) and fabrication of solid polymer films (b) of terpolymers $P(x^*/y/z)$.

Table 1. The g_{abs} Values (CHCl_3 and 1,2-DCE Solutions) Determined by CD Measurements and d -Spacing Values Obtained From XRD and Reflection Maximum Wavelength R_{max} (Solid Polymer Films Annealed in CHCl_3 or 1,2-DCE) of Terpolymers $P(x^*/y/z)$

entry	$P(x^*/y/z)$			CHCl_3		1,2-DCE	
	x	y	z	XRD d (nm) ^a	R_{max} (nm) ^b	XRD d (nm) ^a	R_{max} (nm) ^b
1	100	0	0	— ^e	ND ^f	— ^e	— ^e
2	75	0	25	1.59	<400	1.81 ^c	<400 ^c
3	50	0	50	— ^e	ND ^f	— ^e	— ^e
4	25	0	75	— ^e	ND ^f	— ^e	— ^e
5	0	0	100	— ^e	— ^c	— ^e	— ^e
6	50	25	25	1.60	<400	1.65 ^d	<400 ^d
7	40	35	25	1.59	411	1.61	406
8	30	45	25	1.58	440	1.57	451
9	28	47	25	1.58	490	1.57	466
10	25	50	25	1.58	521	1.57	549
11	22	53	25	1.58	540	1.55	567
12	20	55	25	1.58	573	1.57	630
13	18	57	25	1.58	612	1.54	ND ^f
14	16	59	25	1.58	633	1.51	— ^e
15	15	60	25	1.57	643	1.58	— ^e
16	0	75	25	— ^e	ND ^f	— ^e	ND ^f
17	25	65	10	1.53	405	1.52	ND ^f
18	25	60	15	1.53	424	1.54	512
19	25	55	20	1.57	443	1.56	530
20	25	45	30	1.63	601	1.61	585
21	25	40	35	1.67	>700	1.63	596

^aAverage intermolecular distance calculated from the XRD peak positions 2θ . ^bWavelength of maximum selective reflection. ^cAnnealing time was set to 20 min. ^dAnnealing time was set to 10 min. ^eNot measured. ^fNot detected.

molecular structure which corresponds to the cholesteric phase of liquid crystals.¹ The relationship between the screw-sense of the copolymer (left-handed) and the twist-sense of the supramolecular structure (right-handed) was in agreement with Straley's theory.²²

To obtain insight into the observation of the selective reflection, a "spectator monomer" that has an achiral *n*-butyl side chain with no ω -chlorine atom was introduced as the third monomer into the polymer backbone, in addition to the monomers used for the synthesis of the binary copolymers.

Initially, PQX ternary co-100mers $P(x^*/y/25)$ containing various ratios of chiral (x) and achiral units (y), along with a fixed number of chlorooctyl units ($z = 25$), were prepared to investigate the role of chiral units (Table 1, entries 6–16). As observed for the binary polymers, the polymers in CHCl_3 solution showed *M*-helical structures whose screw-sense purity increases as the ratio of chiral units increases (Figure 2, solid

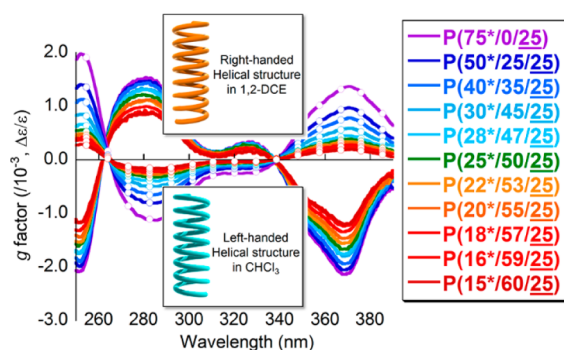


Figure 2. CD spectra of polymers $P(x^*/y/25)$ ($x + y = 75$, $x = 75, 50, 40, 30, 28, 25, 22, 20, 18, 16$, and 15) in CHCl_3 (solid line) or 1,2-DCE (line with circles).

lines) in accordance with the Green's theory.²³ The color of the thin films after CHCl_3 vapor annealing varied from blue to red through green according to the ratio of chiral monomer units (Figure 3a). The change in color was clearly correlated to the screw-sense excess of the helical macromolecules and, in turn, to the degree of the screw-sense of the cholesteric-like superstructures. The mean reflection wavelength was red-shifted as the number of chiral units decreased, resulting in coverage of the

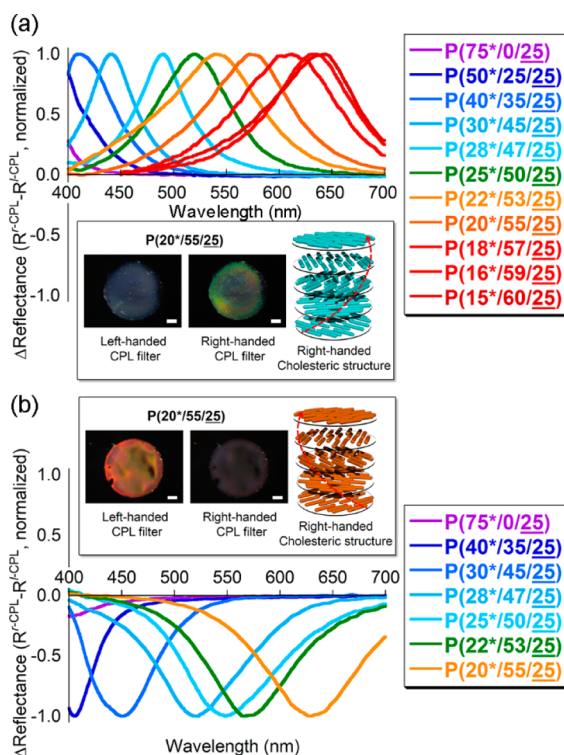


Figure 3. Difference reflection spectra of $P(x^*/y/25)$ annealed in (a) CHCl_3 or (b) 1,2-DCE vapor. Photographs are taken through left- or right-handed CPL filters. Scale bar = 1.0 mm.

entire visible region, 400–650 nm, by changing the number of chiral units from 50 to 15.

In 1,2-dichloroethane (1,2-DCE) solutions, we observed an inverted, right-handed helical structure for the same series of PQX ternary co-100mers $P(x^*/y/25)$ in circular dichroism (CD) spectra (Figure 2, dotted lines). As-casted films obtained from their xylene solutions were treated with 1,2-DCE vapor at room temperature for 4–20 min. The films again exhibited varying colors, from blue to red, as shown by the difference reflection spectra (Figure 3b). It should be noted that left-handed CPL was reflected by these polymer films treated with 1,2-DCE vapor, suggesting that their cholesteric structure was inverted to the right. It seems likely that the handedness of the cholesteric superstructures depends on the sense of the helix of the helical polymer backbone. We found that the formation of *P*- and *M*-helical superstructures was essentially reversible. A CHCl_3 vapor-treated thin film of $P(30^*/45/25)$, which reflected right-handed blue CPL, was exposed to 1,2-DCE vapor at room temperature for 4 min. Although the dried thin film still reflected blue light (~ 450 nm), the handedness of reflected CPL was inverted to the left (See SI). This reversible switch of handedness of the CPL can be repeated by exposing the film to either CHCl_3 or 1,2-DCE vapor, alternately, without any change in the mean reflection wavelength for each CPL.

Having found the dependence of the reflection wavelength on the ratio of the chiral monomer units, we then examined the role of the chlorooctyl monomer units. Maintaining the number of chiral units x at 25, the ratio (y/z) of the spectator units and chlorooctyl units in ternary co-100mer $P(25^*/y/z)$ was changed (Table 1, entries 17–21). All the co-100mers $P(25^*/y/z)$ showed almost constant CD spectra, either in CHCl_3 (*M*-helix, $g_{\text{abs}} \approx -1.6 \times 10^{-3}$) or 1,2-DCE (*P*-helix, $g_{\text{abs}} \approx -0.5 \times 10^{-3}$) (See SI). These results clearly demonstrated that the screw-senses of the PQXs depend solely on the ratio of the chiral monomer units. It was, however, interesting to observe a bathochromic shift of the reflected wavelength by the thin film upon increasing the content of the chlorooctyl monomer units by both CHCl_3 vapor treatment (Figure 4, solid lines). For instance, CHCl_3 -vapor-annealed films of $P(25^*/60/15)$ and $P(25^*/45/30)$ exhibited blue (424 nm) and red (601 nm) color with reflection of right-handed CPL.

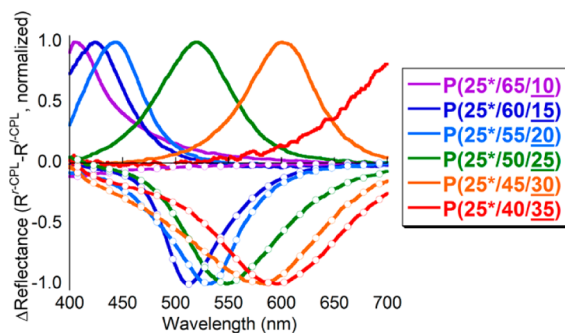


Figure 4. Difference reflection spectra of $P(25^*/y/z)$ annealed in CHCl_3 (solid line) or 1,2-DCE vapor (line with circles).

To determine the origin of the difference in reflected wavelength, X-ray diffraction (XRD) measurements were conducted for a series of co-100mers $P(25^*/y/z)$ (Table 1, entries 17–21, see also SI). Each co-100mer showed a diffraction peak, whose angle 2θ decreased with an increase in the ratio of the chlorooctyl monomer. The values of 2θ suggested the

formation of the organized structure, with mean distances ranging from 1.5 to 1.7 nm. It is presumed that the XRD signals correspond to the distances of the two neighboring polymer main chains, because the diameter of PQXs is estimated to be around 2 nm (by molecular model calculation, see SI). The results of XRD measurements therefore suggest that the mean distance between the polymer main chains increases with an increase in the proportion of chlorooctyl monomer units, due to the steric and/or electronic effect of the chlorooctyl side chains. Consequently, the pitch length of the cholesteric structure is elongated, leading to the observed bathochromic shift of the reflected wavelength. We observed parallel results with the 1,2-DCE-vapor-treated thin films, although they all reflected left-handed CPL (Figure 4, lines with circles). By contrast, XRD measurements of a series of co-100mers $P(x^*/y/25)$, in which the number of 8-chlorooctyl side chains are fixed, showed almost the same diffraction peaks (Table 1, entries 6–15). This clearly suggests that the ratio of the chlorooctyl monomer is the determinant of the mean distance between the polymer main chains.

We have thus far shown that the reflection wavelength (color) is controllable by polymer structures with a varying ratio of chiral and/or chlorooctyl monomer units and that the handedness of the reflected CPL is switchable by changing the solvent used for vapor annealing. In particular, the reflection wavelength crucially depends on the screw-sense purity of the helical polymer backbones. Because the findings of our previous study suggested that the macromolecular screw-sense purity is tunable by changing the ratio of the two solvents,¹⁹ we became interested in the preparation of a single film where the color and handedness of reflected CPL are fully tunable by the solvent effect alone.

We chose to consider $P(30^*/45/25)$, which showed reflection of right-handed blue CPL on exposure to 100% CHCl_3 vapor (Figure 5a). Increasing the ratio of 1,2-DCE to 33% and 50%

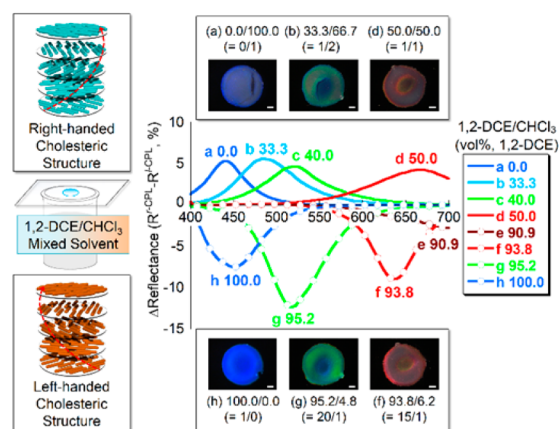


Figure 5. Difference reflectance spectra of $P(30^*/45/25)$ after solvent vapor annealing by using mixed solvent of 1,2-DCE and CHCl_3 . Photographs of the annealed polymer films were shown in the inset. Scale bar = 1.0 mm.

resulted in a bathochromic shift of the reflected wavelength, showing green (b for 33% 1,2-DCE) and red (d for 50% 1,2-DCE) color. Further increases in the ratio of 1,2-DCE caused the visible light reflection to disappear. It is presumed that the reflected wavelength became longer than that in the visible light region (>700 nm) in association with a decrease in the excess of left-handed helical structures. When the ratio of 1,2-DCE was

further increased to 90% (e), a right-handed helical structure with left-handed helical superstructure becomes predominant, resulting in reflection of left-handed red CPL. Blue shift of reflection of left-handed CPL was observed with an increase in the ratio of 1,2-DCE (*f*–*h*), resulting in the observation of green (g) and blue (h) color. Both the wavelength and the chirality of the reflected light could be fully tuned by changing the ratio of the mixed solvents for the vapor annealing process.

In summary, we have synthesized PQXs bearing (*S*)-2-methylbutyl, *n*-butyl, and 8-chlorooctyl groups as side chains. Polymer thin films, fabricated from these terpolymers by solvent casting, exhibited selective reflection of right-handed CPL in the visible region after annealing in CHCl₃ vapor at room temperature. With a decrease in the ratio of (*S*)-2-methylbutyl units, the mean wavelength of the selective reflection was red-shifted. After annealing in 1,2-DCE vapor, the handedness of reflected CPL was inverted to the left. We propose that the increase in the number of chlorooctyl units increases the distance between two polymer main chains, resulting in a red-shift of the structural color by elongation of the cholesteric pitch. It was ultimately demonstrated that a particular single film exhibited full color tunability with switch of handedness of CPL by changing the ratio of 1,2-DCE and CHCl₃ used in the solvent vapor annealing. We believe that this study will open up new possibilities for the development of new chirality-switchable materials,²⁴ not only through their unique macromolecular structures but also the highly ordered supramacromolecular structures of PQXs.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

suginome@sbchem.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Shun Tanaka and Makoto Uno for help with experiments and analyses. Financial support for this research was provided by the Japan Science and Technology Corporation (CREST, "Development of High-Performance Nanostructures for Process Integration" Area).

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