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Broadband Reflection in Polymer Stabilized Cholesteric Liquid Crystals via Thiol–Acrylate Chemistry

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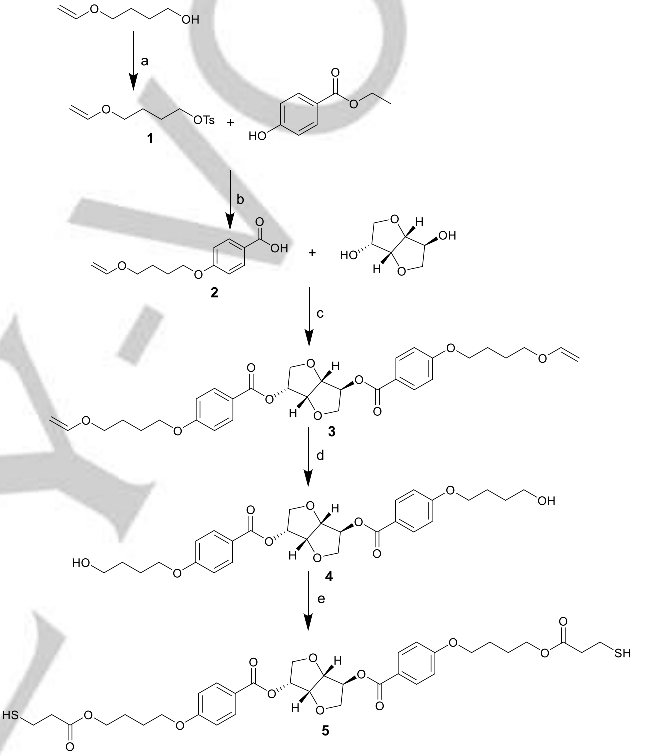
Abstract: Thiols are prone to react to high yields with a multitude of various functional groups, which have been widely used for surface and particle patterning, bioorganic synthesis, polymer modification, imprint nanolithography, fabrication of optical components, hydrogel synthesis, curing of hard protective coatings. In this work, a chiral thiol with a high helical twisting power was synthesized through an ingenious synthetic route with high selectivity, yield and cost-effectiveness, which was used to fabricate a liquid crystal composite film with ultra-wide broadband reflection via thiol-click chemistry. Cholesteric liquid crystal materials with broadband reflection have many potential applications for broadband polarizers, polarizer-free displays, organic optical data storage media, smart switchable reflective windows and continuous waveband laser protection.

Cholesteric liquid crystal (CLC) presents a unique kind of liquid crystalline phase where the rodlike molecules self-assemble into a periodic helical structure, exhibiting special selective Bragg reflection to light.[1] The reflection wavelength is related to the helical pitch *p* of the CLCs, whose magnitude can be adjusted efficiently from tens of nanometers to micrometers by employing appropriate dosage and helical twisting power (HTP, *β*) of the chiral dopant.[2] It is known that $p=1/(\beta.C)$ and $\lambda=n.p$, where $n=(n_o+n_e)/2$. Hence, the reflection bandwidth is $\Delta\lambda=\Delta n.p$, here $\Delta n=n_e-n_o$ is the birefringence of the LC.[3]

In prior studies, many effective methods had been presented to control the reflection band of cholesteric LC.[2c, 4] For example, Broer *et al.* pioneered a way to obtain a CLC film with broad bandwidth covering the entire visible spectrum by obtaining a pitch gradient.[5] Then, Mitov *et al.* fabricated a pitch gradient in a cholesteric structure using glass-forming cholesteric oligomers[6]. Moreover, Yang *et al.* proposed several effective experimental methods to achieve broadband reflection[7]

Therefore, fabricating CLC materials with pitch gradient is an effective approach to obtain the broadband reflection property.[2c] Usually, the chiral acrylate monomer was used to obtain the CLCs with broadband reflection.[5] However, the in-situ radical polymerization rate of acrylate is too high to guide further. [3b] As is well known, thiol-click reactions have been extensively used to fabricate functional polymer composites.[8] The thiol monomers are not able to homopolymerize, therefore, the employment of a thiyl chiral provider can facilitate the fabrication of pitch gradient distribution.



Scheme 1. Reagents and conditions: a) p-TsCl, pyridine, DCM; 0 ºC, 1h (90%). b) KOH, EtOH; 80 ºC, 20 h (88%) c) DCC, DMAP, DCM; 0 ºC, 24 h (85%). d) p-TsOH, H_2O, toluene; reflux, 8h (quantitative). e) 3-Mercaptopropionic acid , p-TsOH, toluene; Dean-Stark distillation, 16h (80%)

Isosorbide derivatives are a kind of fine chiral dopants with high HTP and miscibility with LCs , whose acrylic derivatives usually were used to fabricate CLC polymer composite.[9] Comparing to the acrylic derivatives, the synthesis of terminal thiyl isosorbide derivatives with similar structure is used to be more complicated.[10] Here, we present an ingenious synthetic route to synthesize an isosorbide derivative with double terminal thiyl functional group, and the synthesis route is outlined in Scheme 1. Since 4-halogeno-butan-1-ol can't exist stably in an alkaline condition (yielding tetrahydrofuran)[11], it is hard to obtain 4-(4-hydroxybutoxy)benzoic acid group with a high yield by general etherification condition. Here, 4-(vinyloxy)butan-1-ol was used as the etherification agent, compound 2 successfully was obtained and hydroxyl group protection process needed in the next esterification step was eliminated. Moreover, compound 4 can be easily quantitatively obtained by acidifying compound 3, then the target material was achieved via an esterification reaction by using Dean-Stark distillation trap. Therefore, this synthesis route has a high selectivity, yield and cost-effectiveness.

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Then, the photopolymerization of this thiol (RIS) and a liquid crystalline acrylate monomer (C6M) in a host NLCs was used to fabricate a polymer stabilized cholesteric liquid crystals (PSCLCs) film with broadband reflection property.

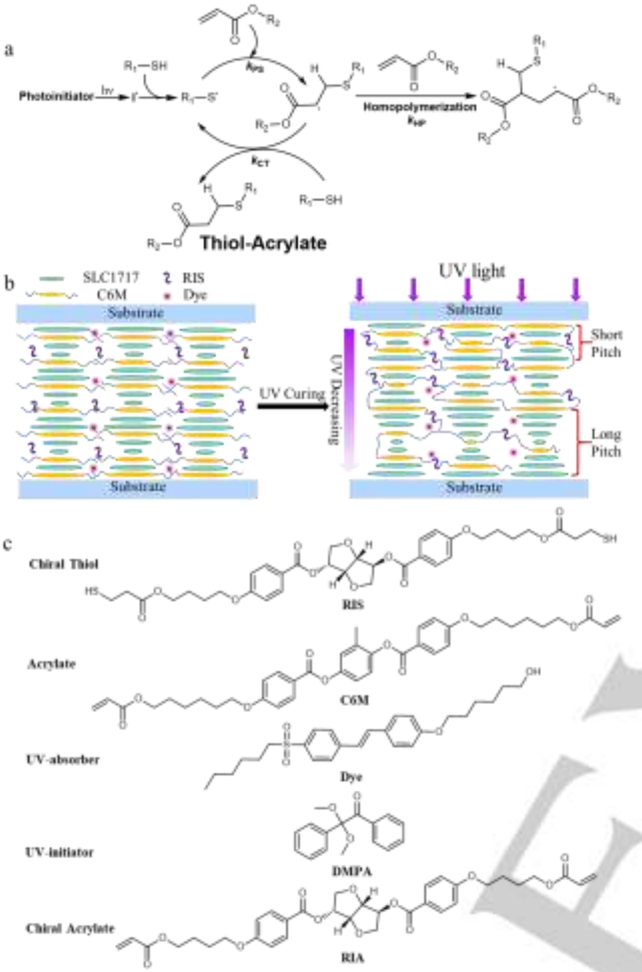

Figure 1. a) Radical initiation, propagation, chain-transfer, and homopolymerization procedure in thiol−acrylate chemistry. b) Schematic mechanism of the fabrication of PSCLCs film with broadband reflection. c) Materials used in this system.

Thiol-acrylate photopolymerization is a binary reaction process, in which the acrylic radical participates in the photopolymerization process of a mixture of acrylate and thiol monomers: addition to another acrylate functional group or hydrogen abstraction/chain transfer to thiol.[12] This interlaced reaction modes of photopolymerization lead to complex polymer network structures, which comprise intertwined thiol-ene and homopolymerized acrylate segments.[13] The factors governing the kinetics of thiol−acrylate polymerization are the propagation rate (k_{PS}), the chain-transfer rate (k_{CT}) and the homopolymerization rate (k_{HP}), the schematic of this reaction is shown in Figure 1a. The rate of termination reactive that thiyl radicals (RS·) participated can be neglected comparing with the one of propagation, and the rate of a thiyl radical reaction with an acrylic double bond (k_{CT}) is approximate to the one of hydrogen abstraction by an acrylic radical (k_{PS}).[12b, 13a]

The schematic for fabrication of PSCLCs film with broadband reflection is proposed in Figure 1b. A mixture comprising RIS/C6M/Dye/SLC1717/DMPA were homogenized and filled into a LC cell, forming a planar oriented CLC film. Then the cell was exposed to a UV light, a UV-light-intensity gradient occurred in the transverse direction resulting from the effect of UV absorbing dye. The thiol–acrylate reaction was initiated by the UV light, and the rate of the polymerization at the upper side of the film was larger than the lower one due to a higher intensity of the UV light.[5] C6M migrated constantly upwards due to its depletion near the upper side, meanwhile RIS also migrated together with C6M in the process of thiol-acrylate reaction.[14] Therefore, a concentration gradient of RIS generates, and a pitch gradient of the CLC film was obtained. The chemical compositions of the materials used are shown in the Figure 1c.

Since thiols are unable to homopolymerize, while acrylate monomers have two possible depletion way in the photopolymerization, thus the molar ratio of functional groups is a crucial factor to the conversion of thiols.[12b, 13a] Samples A1-A4 comprising different molar ratios of -SH and C=C were listed in Table 1, and they were filled into a 50 μm-thick cell with planar-alignment layers. All samples were irradiated by a 365 nm UV light for 8 h at an intensity of 0.2 mW/cm^2, then their conversions of monomers were investigated by Fourier transform infrared spectroscopy (FTIR) and gel fraction measurement. As shown in Figure 2a, the characteristic infrared absorbance bands used to monitor the disappearance of the functional groups during the polymerization were as follows: acrylate (C=C) at 1407cm^{-1}, and thiol (S-H) at 2570 cm^{-1}.[12b, 13a] Unfortunately, there is an overlapped absorbance bands near 2570 cm^{-1} in the spectrum of C6M, therefore, the conversion of RIS cannot be clearly determined only by FTIR. The acrylate (C=C) absorption peaks of C6M all disappear in Samples A1-A4 (Figure 2b), which indicates that the conversion of C6M reaches about 100.0% in all the samples. That is, the weight loss in the gel fraction measurement was mainly attributed to the unreacted thiols. The gel fractions of Samples A1-A4 are 80.8 wt%, 90.1 wt%, 97.3 wt%, 97.6 wt%, respectively, so the calculated conversion values of the thiol are 57.8 %, 74.3 %, 91.9 %, 91.8 %. The conversions of thiol raise with the increase of C6M from Samples A1 to A3 and then keep a constant value about 92.0% in Sample A4, indicating that the conversion of thiol reach the maximum value when the molar ratio of -SH and C=C was about 1.0:2.0. Furthermore, it means that the depletion of acrylate in thiol-ene and homopolymerized reaction is approximately equal.

Because RIS is the only chiral agent in this PSCLCs film, theoretically, the pitch gradient distribution of the film is determined by the conversion of RIS.[15] Therefore, there are broader reflection bandwidth in Samples A3 and A4 comparing to A1 and A2 (Figure 2c). Although more C6M is beneficial to the conversion of RIS, but the planar textures will be disturbed when excess monomers participate in the photopolymerization and the migration. Therefore, the reflectivity of Sample A4 is decreased distinctly comparing to Samples A1-A3, but the reflection bandwidth is approximate to Sample A3. To sum up, 1.0:2.0 is the optimal molar ratio of -SH and C=C for preparing the PSCLCs film with broadband reflection. Then, Sample A3 was filled into two cells, one of which has alignment layers and the other without. Moreover, another planar oriented cell was filled by Sample A3 abandoning the dye. Three samples were irradiated for 2 h at 0.2 mW/cm^2, and their transmittance spectra were compared to verify the effect of the alignment layers and the dye, respectively. Figure

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2d indicates that the alignment layer is indifferent in the fabrication process of this film, because there is a flow alignment effect in the sheared cholesteric liquid crystals during the process of flow into the cell.[16] The fine planar textures of Sample A3 in a unalignment cell before and after UV irradiation are obtained by POM as shown in Figure S3. Moreover, a narrow reflection bandwidth was obtained without the dye (Figure 2d), it reveals that the dye plays a crucial role in obtaining a pitch gradient.[5]

Table 1. Different Compositions of Samples

Sample NO.	RIS/C6M/Dye/SLC-1717/DMPA wt %	-SH: C=C Molar Ratio
A1	5.0/6.0/1.0/88.0/0.5	~1.0:1.2
A2	5.0/8.0/1.0/86.0/0.5	~1.0:1.6
A3	5.0/10.0/1.0/84.0/0.5	~1.0:2.0
A4	5.0/12.0/1.0/82.0/0.5	~1.0:2.4
A5	3.0/6.0/1.0/80.0/0.5	~1.0:2.0
A6	3.5/7.0/1.0/78.5/0.5	~1.0:2.0
A7	4.0/8.0/1.0/77.0/0.5	~1.0:2.0
A8	4.5/9.0/1.0/75.5/0.5	~1.0:2.0
A9	5.0/10.0/1.0/74.0/0.5	~1.0:2.0
A10	6.0/12.0/1.0/77.0/0.5	~1.0:2.0
A11	5.0[a]/10.0/1.0/74.0/0.5	-

[a] RIS is replaced by RIA.

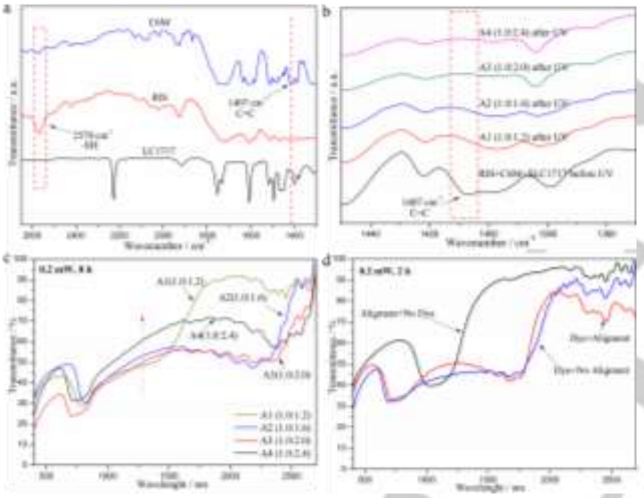

Figure 2. Characterization of the reaction kinetics and transmittance spectra of the sample comprised of different compositions. a) FTIR spectra of C6M, RIS and LC1717. b) FTIR spectra of Samples A1-A4 before and after UV irradiation for 8 h at 0.2 mW/cm^2. c) Transmission spectra of Sample A1-A4 after UV irradiation. d) The influence of dye and alignment to transmission spectra.

Obviously, the polymerization rate (R_p) and conversion rate of the photopolymerization are correlative to the intensity of UV light and irradiate time, and the performance of the PSCLCs film is also impacted by these factors.[13a] Moreover, the migration rate (R_m) of the monomers in the photopolymerization is another crucial factor to the property of the materials. The monomers polymerizing in-situ or upwards are determined by both the R_p and the R_m: when the polymerization rate of the upper position R_{pu} is equal to lower one R_{pl}, the monomers will not migrate upwards, indicating that R_m tends to be zero; thus, only if the $R_{pu} >> R_{pl}$, a larger R_m can be obtained. Since the R_p is controlled by the UV intensity, a UV intensity gradient will induce a R_p gradient. The transmission spectra of Sample A3 irradiated with 365 nm UV light for different intensities and time are shown in Figures 3a-d, and the intensities are 5 mW/cm^2, 1 mW/cm^2, 0.2 mW/cm^2 and 0.05 mW/cm^2, respectively. The polymerization and migration occurred at the same time with the irradiation beginning, hence the reflection bandwidth became broader with the irradiation time. Comparing the reflection bandwidth in Figures 3a-d, it indicates that a wider bandwidth will be obtained by using a lower intensity of UV light. If the intensity is too high, the UV intensity gradient induced by dye is not distinct and the R_p is so large that the monomers are immobilize by the polymer networks before migration. At 0.05 mW/cm^2, the widest bandwidth exceeds 2000 nm (Figure 3d).

The selective reflection band of CLCs can be altered by adjusting the pitch via the concentrate of the chiral agent. Samples comprising 3.0 wt%, 3.5 wt%, 4.0 wt%, 4.5 wt%, 5.0 wt% and 6.0 wt% RIS (Samples A5-A10) were used to fabricate the PSCLCs films, respectively. As shown in Figure 3e, the selective reflection band generate a blue-shift with the increase of RIS, hence the broadband reflection can efficiently adjust to any optional wavelength to satisfy the requirement of application. Meanwhile, Samples A5, A9 and A10 were filled into 20 μm-thick cells to fabricate the PSCLCs films(Figure 3f), comparing with those in 50 μm-thick cells, the bandwidths are narrower because of the restricted space for gradient distribution of pitch.

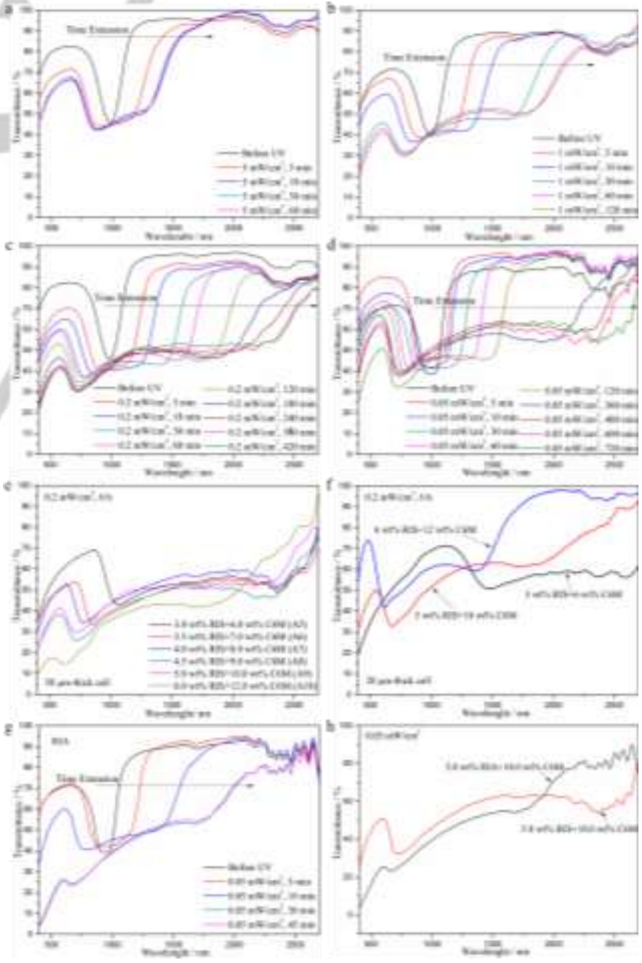

Figure 3. Transmission spectra of the samples. a) Sample A3 before irradiation and after irradiation for different time at 5 mW/cm^2; b) 1 mW/cm^2; c) 0.2 mW/cm^2 and d) 0.05 mW/cm^2. e) Samples A5-A10, 0.2 mW/cm^2 6 h. f) Samples A5, A9 and A10 in 20 μm-thick cells, 0.2 mW/cm^2 6 h. g) Sample A11 before irradiation

and after irradiation at 0.05 mW/cm^2 for different time. h) Comparison of the reflection bandwidth of Samples A3 and A11 after irradiation at 0.05 mW/cm^2 until to the constant state.

In prior studies, chiral acrylate monomers usually was used to fabricate the CLC film with broadband reflection property.[5] To make a comparison, a chiral diacrylate monomer RIA with the similar structure to the RIS was synthesized. The HTP values of RIA is 34.1 μm^{-1} at 25 °C in the host LCs SLC1717, which is approximate to RIS (33.6 μm^{-1}). Sample A11 composing 5.0 wt% RIA, 10.0 wt% C6M, 1.0 wt% Dye, 0.5 wt% DMPA and 84.0 wt% SLC1717 was filled into a 50 μm-thick cell and irradiated at 0.05 mW/cm^2. After 30 min, the reflection bandwidth stops broadening with the irradiation, which indicates that the migration of monomers has finished (Figure 3g). The widest reflection bandwidth from RIA is about 1100 nm, which is approximately half of the one from RIS at the same fabrication condition (Figure 3h). This result can attribute to the high R_p in this system, the in-situ homopolymerization of RIA result in that the chiral monomers are immobilize by the polymer networks before migration.

To verify the mechanism, the microstructures of the films from Samples A3 and A5 was observed by a field emission scanning electron microscopy (SEM).[17] From the SEM images of the fractured surface of the films, the distribution of the self-organized helical pitch gradient from top to bottom can be evidently observed (Figure 4a-i, p1<p2<p3 and 4b-i, p4<p5<p6). The energy-dispersive X-ray spectrometry (EDS) mappings of O and S elements were used to characterize the distribution of the monomers in the PSCLCs. It can be seen that both O and S exhibit obvious content gradient from top to bottom (Figures 4a-ii, iii and 4b-ii, iii). The content of O and S in RIS are 27.16% and 9.07% according to the chemical formula $C_{34}H_{42}O_{12}S_2$, and the contents of O in C6M is 23.78% according to the chemical formula $C_{39}H_{44}O_{10}$. There are high content of O in both monomers, but RIS is the only source of S. Therefore, the gradient distribution S indicates that the RIS had extensive migration in the polymerization, which explicitly confirm the mechanism proposed above.

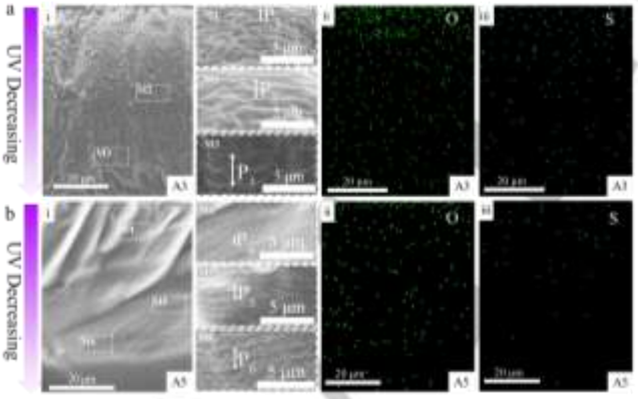

Figure 4. SEM images and EDS mappings of the fractured surface in the PSCLCs films. a) SEM image (i), EDS mapping of O element (ii and S element (iii) of Sample A3. b) SEM image (i), EDS mapping of O element (ii) and S element (iii) of Sample A5.

In conclusion, we present an ingenious synthetic route with high selectivity, yield and cost-effectiveness for fabricating a rigid chiral thiol with terminal thiyl functional group, and then successfully demonstrated a simple and effective method via thiol-acrylate chemistry to prepare a PSCLCs film with a reflection bandwidth over 2000 nm which is prominently wider than the pure acrylate system. The influence factors in fabrication procedure were systematically investigated and the mechanism was explicitly verified by SEM and EDS. Thus, this work indicates a great potential of thiol−click chemistry in designing and preparing functional materials with tailored properties for practical applications.

Experimental Section

A room temperature commercial nematic LC, SLC-1717 (SLC Co. Ltd. n_o = 1.519, n_e = 1.720, $\triangle n = n_e - n_o = 0.201$, $T_{Cr\text{-}N} < -40$ °C, $T_{N\text{-}I} = 91.8$ °C), was used as the host LC. Isosorbide bis(4-(4-((3-mercaptopropanoyl)oxy)butoxy)benzoate) (RIS) was synthesized in our lab, whose HTP value is about 33.6 μm^{-1} at 25 °C in a host LCs SLC1717. The acrylate was a conventional photopolymerizable LC monomer, 1,4-di-[4-(6-acryloyloxy) hexyloxy benzoyloxy]-2-methyl benzene (C6M, HCCH Co. Ltd.). 2,2-dimethopxy-1,2-diphenylethanone (DMPA, TCI Co. Ltd.) and 6-[4-[2-[4-(Hexylsulfonyl) phenyl] ethenyl] phenoxy]-1-hexanol (Dye, Merck Co. Ltd.) were used as the UV-initiator and UV-absorber, respectively. Isosorbide bis(4-(4-(acryloyloxy)butoxy)benzoate) (RIA), the HTP value of RIA is about 34.1 μm^{-1} at 25 °C in the host LCs. The syntheses of RIS and RIA are described in the Supporting Information.

The optical textures of the films were observed using a polarizing optical microscope (POM, Carl Zeiss Axio Vision SE64). HTP value were measured with the Cano-Wedge technique. The kinetics study of model thiol-acrylate was investigated by Fourier transform infrared spectroscopy (FTIR, Bruker, Vector-22). The gel fractions were obtained by measuring the residual weight of the sample in the cell, which were immersed in adequate dichloromethane for about 48 h after photopolymerization and then dried to constant weight. The selective reflection spectra of the films were obtained by a UV/Vis/NIR spectrophotometer (Perkin Elmer, Lambda 950), and the transmittance of a blank cell was normalized as 100.0%. The microstructures of the PSCLCs films after samples quenched to rupture by liquid nitrogen were observed by a field emission scanning electron microscopy (SEM, Hitachi S-4800) equipped with an Inage J as a software tool and an energy-dispersive X-ray spectrometer (EDS, Bruker Quantax).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Keywords: thiol-acrylate chemistry • chiral thiol • liquid crystals • broadband reflection • photopolymerization

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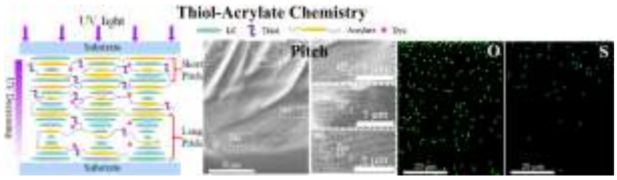

A polymer stabilized cholesteric liquid crystals film with broadband reflection property was obtained via thiol–acrylate chemistry, whose pitch gradient distribution was clearly presented by scanning electron microscope and the migration of the monomers in photopolymerization was explicitly verified by energy-dispersive X-ray spectrometry.

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