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Lasing and Narrowing of Spontaneous Emission from Responsive Cholesteric Films

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Lasing from dye-doped cholesteric liquid crystals and polymers used as active optical resonators has recently become a subject of intense study.[1−8] Ideal cholesteric structure is expected to be an effective optical resonator with extremely low lasing threshold.[1,2] In this communication, switchable optically pumped lasing achieved in cholesteric polymers sensitive to pH changes is reported for the first time.

Cholesteric polymers selectively reflect light with the same sense of polarization as a cholesteric helix. The selective reflection band (SRB) is centered at the wavelength *np* where *n* is an averaged refraction index and *p* is a pitch of the cholesteric helix. Coherent multiple scattering from the periodic helical structure[9,10] in cholesteric liquid crystals (CLCs) produces a photonic band gap for light with the same sense of circular polarization as the helicity of a liquid crystal. Light transmission of the opposite circular polarization is unimpeded by the chiral structure. The new modes appear at the band edge in a series of closely spaced narrow peaks. The residence time for light within the CLC, and hence the opportunity for optically pumped stimulated emission, is greatly enhanced at these band-edge modes and reduced[1] within the stop band. This may result in low-threshold lasing.[1,2,5−8] Optically pumped lasing was recently demonstrated in dye-doped cholesteric polymers[3], thermotropic[4,7] and lyotropic liquid crystals,[5,8] and polymer-dispersed chiral liquid crystals.[6]

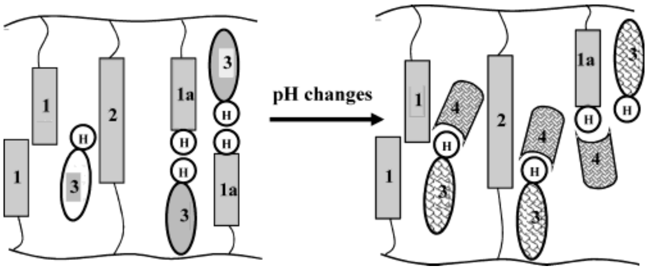

Figure 1. Schematic representation of polymer structure (1 is nematic group, 2 is nematic cross-linker, 1a is H-donor/acceptor moiety, 3 is chiral dopant, 4 is acid/base molecules, and H is hydrogen donor/acceptor group).

Recently, new polymer cholesteric materials sensitive to environmental changes have been synthesized and studied. In general, solid cholesteric materials might be created (1) by cross-linking monomers in a particular cholesteric state,[11,12] (2) by synthesis of side- or main-chain polymers,[13,14] or cyclic oligomers,[7,15,16,17] which may form a glassy state with a frozen cholesteric structure. Some of these materials are sensitive to light irradiation and temperature.[18]

Here, we study new lasing dye-doped polymer compositions based on hydrogen-bonded compounds sensitive to changes in pH of the chemical environment, namely, the concentration of base.[19] This composition displays optically pumped lasing at the various wavelengths, depending on the SRB position determined by the pH of the chemical environment.

All reactive compounds were synthesized in accordance with the procedures described in refs 12, 19, and 20; nonreactive compounds were supplied by Aldrich Chemical Co. and used as received. The synthesis and characterization of monomers have been described elsewhere.[12,19,20] The structure of the polymer matrix is shown in Figure 1. The polymer matrix is formed by the photoinduced polymerization of cholesteric liquid crystal containing hydrogen donor−acceptor groups able to form hydrogen bonds with the chiral dopants. The weakening/strengthening of hydrogen bonds between the components of the polymer matrix results in changes of the cholesteric pitch and the optical properties of the cholesteric material. The changes in strength of the hydrogen bonds are achieved via the reaction of the hydrogen-bonded components of the polymer matrix, with the base molecules diffusing from aqueous solutions in which the polymer films are immersed.

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(1) Kopp, V. I.; Fan, B.; Vithana, H. K. M.; Genack, A. Z. *Opt. Lett.* **1998**, *23*, 1707.
(2) Kopp, V. I.; Zhang, Z. Q.; Genack, A. Z. *Phys. Rev. Lett.* **2001**, *86*, 1753.
(3) Finkelmann, H.; Kim, S. D.; Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Adv. Mater.* **2001**, *13*, 1069.
(4) Munoz, A.; Palffy-Muhoray, P.; Taheri B. *Opt. Lett.* **2001**, *26*, 11.
(5) Shibaev, P. V.; Kopp, V.; Genack, A. Z.; Green, M. *Macromolecules* **2002**, *35*, 3022.
(6) Shibaev, P. V.; Kopp, V. I.; Genack, A. Z. *J. Phys. Chem. B* **2003**, *107*, 6961.
(7) Shibaev, P. V.; Kopp, V.; Genack, A. Z.; Hanelt, E. *Liq. Cryst.* **2003**, *30*, 1391.
(8) Shibaev, P. V.; Genack, A. *Liq. Cryst.* **2003**, *30*, 1365.
(9) Chandrasekhar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, 1992.
(10) de Vries, H. *Acta Crystallogr.* **1951**, *4*, 219.
(11) Hikmet, R. A. M.; Zwerver, B. H. *Liq. Cryst.* **1993**, *13*, 561.
(12) Lub, J.; Broer, D. J.; Hikmet, K. R. A. M.; Njerop, G. J. *Liq. Cryst.* **1995**, *18*, 319.
(13) Plate, N. A.; Shibaev, V. P. *Comb Shaped Polymers and Liquid Crystals*; Plenum Press: New York, 1987.
(14) Kricheldorf, H. R.; Krawinkel, T. *Macromol. Chem. Phys.* **1998**, *199*, 783.
(15) Chen, S. H.; Shi, H.; Mastrangelo, J. C.; Ou, J. J. *Prog. Polym. Sci.* **1996**, *21*, 1211.
(16) Chen, H. P.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H.; Jacobs, S. D.; Hood, P. J. *Adv. Mater.* **2000**, *12*, 1283.
(17) Kreuzer, F.-H. Proceedings 11, Freiburger Arbetstagung Flusssigkristalle, 1981; p 5.
(18) Tamaoki, N. *Adv. Mater.* **2001**, *13*, 1135.
(19) Shibaev, P. V.; Schaumburg, K.; Plaksin, V. *Chem. Mater.* **2002**, *14*, 959.
(20) Lub, J.; Broer, D. J.; Hikmet, R. A. M.; Njerop, K. G. J. *Liq. Cryst.* **1995**, *18*, 319.

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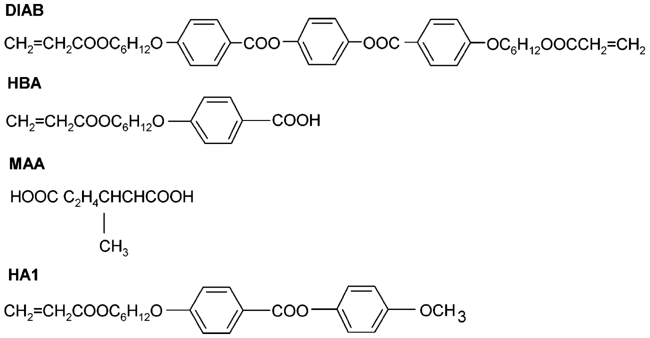

Figure 2. Chemical structure of monomers and chiral compounds (DIAB is nematic cross-linker, HBA is donor/acceptor moiety, MAA is chiral dopant, and HA1 is nematic monomer).

Monomer mixtures containing the compounds shown in Figure 2 displayed cholesteric state at elevated temperatures (ca. 70−90° C), with the SRB lying in a visible part of the spectrum when a concentration of methyladipic acid (MAA), a chiral dopant, exceeded 12−14%. Monomers were dissolved in toluene, doped with laser dyes, and cast from a solution onto a glass substrate covered by a rubbed polyimide layer. After evaporation of the toluene, the position of the SRB was tuned to the desired wavelength by changing the temperature. The laser dyes were the pyrromethenes 597, oxazine 725 supplied by Exciton, and Nile Blue purchased from Aldrich Chemical Co. All dyes are highly miscible with cholesteric material; however, to avoid aggregation of dye molecules and strong absorption of the pumping beam, only low dye concentrations were used.

The UV-induced polymerization of the cholesteric mixture with the SRB position at the desired wavelength was carried out in thin glass cells filled with the liquid-crystalline composition forming a planar texture. Typical composition of the cholesteric mixture was 20−30% of DIAB, 15−25% of HBA, 12−16% of MAA, and the rest HA1. Sample thickness (from 8 to 50 μm) was controlled by two plastic strips and/or glass beads. After polymerization, one of the glasses was removed and the film surfaces were released for further treatment in water solution subject to pH changes. Free-standing films could also be obtained by simply peeling the cholesteric film off the glass substrate.

The OPO laser (EKSPLA Ltd.) was used to excite the dye molecules trapped in the polymer film near the absorption maximum. The pump pulse was approximately 10 ns in duration. The pump beam was focused on a polymer to a spot with a diameter of ca. 50−100 μm. The emission from the polymer sample was collected in the direction perpendicular to the polymer surface in a small cone angle and was focused on the monochromator's entrance slit. Spectrally resolved emission was recorded with a CCD detector attached to the monochromator (CVI Digikrom). The details of experimental setup were discussed in refs 1, 2, 5, and 6.

In our recent work, the SRB position in cholesteric materials containing noncovalently bonded (hydrogen-bonded) nematic molecules was shown to depend on the pH of the chemical environment.[19] In the present work, the novel cholesteric mixture does not have nematic molecules noncovalently linked to the polymer matrix. This resulted in improved optical properties of the films, that is, diminishing phase separation between the components of the polymer film and lowered light scattering. The quality of the SRB, measured in terms of the percentage of circularly polarized light reflected from the sample, is also better in novel cholesteric materials. Moreover, the new cholesteric polymer composition displays a new property: It may be prepared as a free-standing film by simply peeling off the glass substrate. The free-standing film has a larger surface area, and therefore basic water solutions have better access to the film than in the case of a film deposited on a single glass substrate.

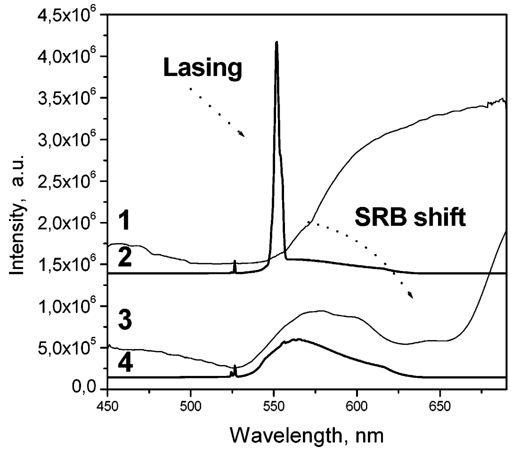

Figure 3. Cholesteric film with pyrromethene dye. Transmission of left circularly polarized light before (1) and after (3) treatment in basic solutions, emission before (2) and after (4) treatment in basic solution.

Fine structure at the SRB edges, the indicator of sample quality,[6,8,21] is observed in samples as thin as 8−20 μm. In freshly prepared samples with MAA concentration of about 16%, the selective reflection band lies at 580 nm (Figure 3). In thicker samples, fine structure could not be observed at the band edges. The multidomain structure of the planar cholesteric material washed out the sharp edges of the SRB, as well as oscillations near the band edge observed in planar monodomain samples.[6−8,21] A slight nonuniformity in the pitch across the sample also tends to wash out the fine band-edge structure.

In freshly prepared samples, lasing was always observed at the SRB edges when the emission band of laser dye overlapped the edge of the selective reflection band.

The wavelength of lasing and the SRB position can be shifted by placing the sample into aqueous solution subject to pH changes. Concentrations of base (KOH) as high as 20% were used to change the pH of the solution. A shift of as much as 80 nm was found after 2-min treatment in 5% KOH solution. The shift of the SRB is detectable in reflection mode even at a much lower concentration of base. However, a low concentration of base requires a much longer time for cholesteric pitch to change through the sample. The position of the shifted SRB depends on a diffusion rate of water and base molecules into cholesteric film. The mechanism of changes of the selective reflection is based on the breakage of hydrogen bonding between components of the cholesteric mixture. The detailed quantitative model

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(21) St. John, W. D.; Fritz, W. J.; Lu Z. J.; Yang, D.-K. *Phys. Rev. E* **1995**, *51*, 1191.

describing the changes of the selective reflection with time will be presented elsewhere. The changes in the SRB position were partially reversible: After treatment in acidic solutions (HNO_3), the SRB shifts toward the shorter wavelengths. However, the SRB deteriorated after several cycles of treatment in basic/acidic solutions.

The pyrromethene dyes did not degrade in basic solutions at moderate exposures to basic solutions, so it was possible to shift the SRB and still had a significant emission from the dye. Nile Blue and oxazine 725 changed their color in basic solution but retained some emission shifted toward the shorter wavelengths. The changes in emission could be reversed in acidic solutions where the dye color and its emission properties were restored.

Switchable lasing was achieved in the cholesteric films doped with the Nile Blue, oxazine 725, and pyrromethene 597 dyes.

The properties of pyrromethene dye were not significantly affected by basic solutions, and lasing wavelength depended only on the SRB position. Transmission and emission spectra of responsive polymer film doped with the pyrromethene 597 dye before and after treatment in basic solution are shown in Figure 3. When the edge of the SRB (Figure 3: 1) overlapped the emission band of laser dye, lasing (Figure 3: 2) occurred at the edge of the SRB. After treatment in aqueous basic solution, the SRB (Figure 3: 3) shifted toward longer wavelengths; emission band did not overlap the SRB (Figure 3: 4), and lasing was switched off. Lasing could be switched on again after the film was treated with acidic solution. The treatment in basic and acidic solutions could be repeated several times before lasing properties were lost. The loss of lasing properties was caused by deteriorating quality of the SRB and decreasing transparency of cholesteric films during the cycles of treatment in basic and acidic solutions. Indeed, the light scattering by the sample treated several times in basic and acidic solutions increased significantly (by 40%), as did the width of the SRB. In the best samples, lasing occurred at the lowest energy of the pumping beam, about 0.01 mJ. This corresponds to a lasing threshold of ca. 10×10^4 W/mm^2. The intensity of lasing emissions rose nonlinearly with the energy of the pumping beam and displayed a clear threshold. The lasing threshold was also several times higher in samples treated in basic and acidic solutions than in fresh samples. The only narrowing of spontaneous emission was observed at the low energy of the pumping beam (0.2−0.01 mJ) and/or after many cycles of treatment.

In samples containing Nile Blue dyes, with the SRB overlapping the dye emission band, the treatment in basic solution also resulted in a shift of the SRB and loss of lasing properties. The cause for losing lasing properties is not only a change in the position of the SRB but also the degradation of the lasing properties of the dye. The consequent treatment of samples containing Nile Blue dyes in basic and acidic solutions resulted in restoring the properties of lasing dye and SRB and led to narrowing of spontaneous emission but not lasing.

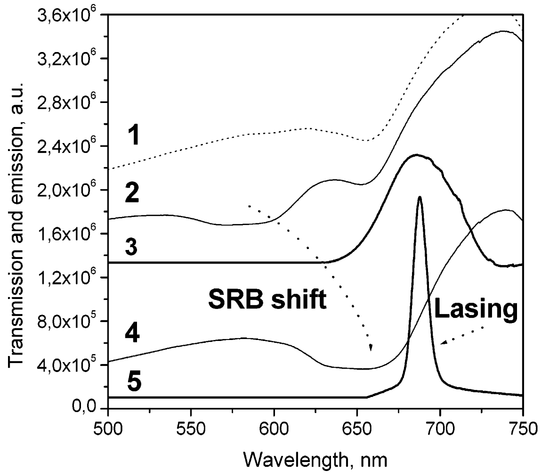

Figure 4. Cholesteric film with oxazine 725, composition 30% of DIAB, 25% of HBA, 16% of MAA, 29% HA1, and 0.9% oxazine 725. Transmission of right (1) and left (2) circularly polarized light before treatment in basic aqueous solutions, transmission of left circularly polarized light after treatment in basic 5% KOH solution (4), emission before any treatment (3), and emission after treatment in basic/acidic solutions and exposure in chloroform containing oxazine 725 (5).

Lasing could be achieved in films containing the oxazine 725 or Nile Blue dyes after their subsequent exposure in aqueous basic solutions and organic solvents (dichlorethane, chloroform) containing the same dyes. The treatment in basic aqueous solutions changes the position of the selective reflection band, while the brief exposure of polymer film in organic solvents containing laser dyes does not change the position of the SRB, but replenishes the amount of dye molecules in the films. For example, films containing oxazine 725 were first treated in 5% KOH and then in weak HNO_3 aqueous solutions. The latter did not restore completely the lasing properties of the film and additional treatment in chloroform/oxazine solution was needed to replenish the amount of dye. Transmission and emission spectra of the polymer film containing oxazine 725 before and after treatment in 5% KOH basic solution are shown in Figure 4. Transmission spectra of fresh sample for right (Figure 4: 1) and left (Figure 4: 2) circularly polarized light indicate that the right edge of the SRB is at 600 nm. No narrowing of spontaneous emission or lasing is observed in films before treatment in basic solutions (Figure 4: 3) since the SRB edge is too far from the emission band. Treatment in basic solution results in the SRB shift (Figure 4: 4) toward the emission band of laser dyes, which leads to lasing at the edge of the selective reflection band after a brief exposure of polymer films in chloroform containing oxazine 725 dye (Figure 4: 5).

The reported cholesteric films may find applications as new sensors for high concentrations of base and acid. Lasing from cholesteric thin films sensitive to changes in the chemical environment may be a powerful tool for studying the details of interaction of chiral photonic band gap materials with chemical agents. The approach outlined here may be used in a future synthesis of responsive low-threshold lasing polymers.

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