

# Lasing from a Stiff Chain Polymeric Lyotropic Cholesteric Liquid Crystal

P. V. Shibaev,<sup>\*,†</sup> K. Tang,<sup>‡</sup> A. Z. Genack,<sup>†,||</sup> V. Kopp,<sup>†,||</sup> and M. M. Green<sup>\*,‡</sup>

*Chiral Photonics Inc., 115 Industrial East, Clifton, New Jersey 07012; Herman F. Mark Polymer Research Institute, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201; and Department of Physics, Queens College of the University of New York, 65-30 Kissena Boulevard, Flushing, New York 11367*

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**ABSTRACT:** Lasing is reported at the edge and in the middle of the selective reflection band produced in the visible region of the spectrum for the cholesteric phase of a lyotropic liquid crystal formed from an optically active polyisocyanate in toluene. This is the first observation of lasing from a stiff polymer based lyotropic liquid crystal. Lasing was observed at a relatively low threshold when the selective reflection band overlaps with the emission peak of an incorporated dye molecule. The absence of fine structure of the selective reflection band at wavelengths near the edge of this band indicates that the cholesteric liquid crystal is not perfectly periodic. Lasing in these multidomain films may therefore be associated with defects in the periodic structure.

## Introduction

Cholesteric liquid crystals are unique in their ability to selectively reflect circularly polarized light<sup>1</sup> with the same handedness as the dielectric tensor of the crystal over a band of wavelengths. In the thick sample limit, the band lies between wavelengths  $n_e P$  or  $n_o P$ , where  $n_e$  and  $n_o$  are the extraordinary and ordinary indices of refraction, respectively, and  $P$  is the pitch of the cholesteric phase. In thin films, a sequence of well-defined reflection peaks is observed at the edges of a flat reflection band. In samples with multiple randomly oriented cholesteric domains, however, the fine structure at the reflection band is washed out because the wavelength of the reflected light depends on the orientation of the individual cholesteric domains and the viewing angle.

One-dimensional<sup>2</sup> photonic band gap (PBG)<sup>3,4</sup> materials are of considerable current scientific and technological interest because they are readily fabricated and exhibit a wide reflection band with a suppressed density of states. Typical one-dimensional PBG structures consist of multilayer stacks of dielectric material arranged in alternating layers with different refractive indices. Monodomain cholesteric liquid crystals, described above, are an example of one-dimensional photonic band gap materials, which exhibit a stop band for a single sense of circularly polarized radiation.

Lasing in dye-doped cholesteric liquid crystals was proposed almost 30 years ago and was discussed within the framework of distributed feedback theory, which is appropriate for structures in which the dielectric constant is weakly modulated.<sup>5–8</sup> It was argued that light emitted within the band gap would experience multiple reflections and hence experience a considerable delay before emerging from the material. It was therefore expected that the gain required to reach the lasing threshold would be lowest near the center of the

reflection band. Early observations of lasing in thermotropic cholesteric liquid crystals far from the center of the reflection band were consequently ascribed to distortions of the helical structure, which shifted the reflection band.

Recently, it was argued that emission and hence lasing from the planar texture<sup>9</sup> of cholesteric liquid crystal materials are prohibited in the center of the reflection band since the emission is proportional to the density of states for circularly polarized light, which vanishes within the reflection band. Rather, lasing occurs at modes near the band edge. Because the photon dwell time in these modes is enhanced, the lasing threshold at the band edge in thin films is low.<sup>9–11</sup> The photon dwell time increases rapidly with film thickness, which is why the materials that can potentially form large oriented cholesteric domains are of considerable interest.

Stiff polymer lyotropic cholesteric liquid crystals, although previously untested for their lasing potential, are interesting because their elastic constants, which control the domain structure, are affected by a large number of variables not accessible in thermotropic liquid crystals in addition to the fact that the phase boundary between the isotropic and liquid crystal states only weakly depend on temperature.<sup>12</sup> Variables include concentration (density) as well as molecular weight (contour length) and chain stiffness (persistence length), the latter a function of monomer structure.

Within the general class of stiff polymers, the polyisocyanates offer special access to these variables via living polymerization methods for their synthesis,<sup>13</sup> variability in chain stiffness arising from variation in side chain structure,<sup>14</sup> a wide concentration range in a variety of solvents for forming the liquid crystal state,<sup>15</sup> and interesting advances in material manipulations of this state.<sup>16</sup> Moreover, manipulation of the helical sense character of the backbone is exceptionally well studied in the polyisocyanates.<sup>14</sup> This is a key parameter controlling liquid crystal pitch,<sup>14,16–18</sup> which is essential for adjusting the reflection band of the cholesteric state to the dye emission wavelength necessary for lasing. An

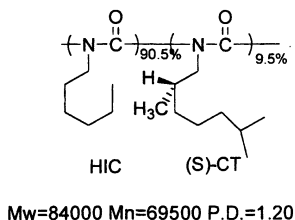
\* Corresponding authors.

† Chiral Photonics Inc.

‡ Polytechnic University.

|| Queens College of the City University of New York.

**Scheme 1 Chemical Structure, Molecular Weight, and Polydispersity of the Polyisocyanate Used To Make the Cholesteric Liquid Crystal Solution**



additional important aspect of stiff polymer lyotropic liquid crystals exemplified in the polyisocyanates<sup>12,19</sup> is spontaneous formation of planar textures without surface manipulation for relatively thick cells. Because of the unique properties of the cholesteric liquid crystals formed by polyisocyanates (see Scheme 1) and the example they pose for other stiff chain lyotropic liquid crystals that might also be used to explore this phenomenon, we have produced and made an initial investigation of lasing from this class of liquid crystals.

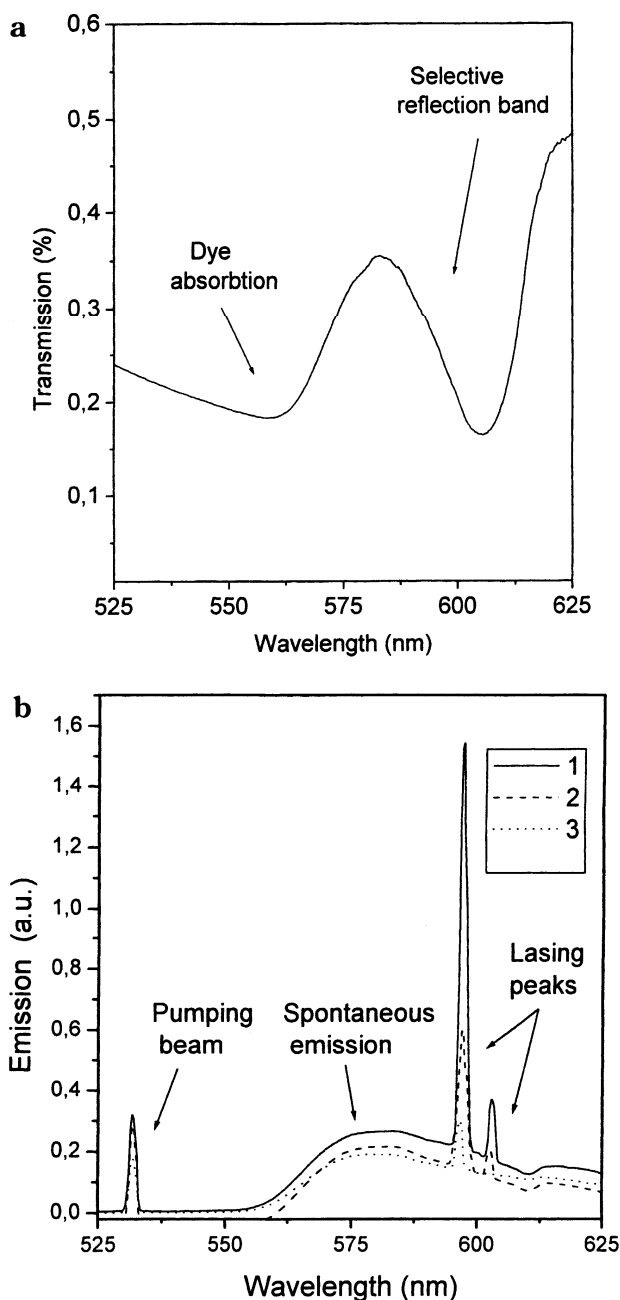
### Results and Discussion

The work reported here is based on the "sergeants and soldiers" copolymer<sup>18</sup> **1** formed from 90.5% of hexyl isocyanate and 9.5% of (*S*)-2,6-dimethylheptyl isocyanate by weight, which were copolymerized with a method allowing moderate control of molecular weight.<sup>20</sup> The synthesized copolymer formed the lyotropic cholesteric liquid crystal as a concentrated solution in toluene (see Experimental Section).

In the experiments reported here, the cell width, in the range of 180  $\mu\text{m}$ , is near the maximum cell width for observation of the planar texture for the system studied.<sup>15,19</sup> We observe selective reflection bands in the visible region of the spectrum<sup>1</sup> with wavelengths that are sensitive to polymer concentration.<sup>15,16</sup> Thus, selective reflection bands were produced from a series of different solutions of **1** in toluene, with higher polymer concentrations yielding a tighter pitch, corresponding to selective reflection bands at shorter wavelengths. The selective reflection band is also sensitive to temperature. Lowering the temperature shifts the selective reflection band toward shorter wavelengths,<sup>15,16</sup> while observations recorded at different angles show wavelength shifts,<sup>16</sup> the latter consistent with a planar orientation of the sample. At the same time the multidomain structure of the sample is evidenced by the absence of fine structure at the band edge. A typical selective reflection band in the present study (Figure 1a) is rather smooth and has a narrow width of 25–35 nm, implying that the optical anisotropy of each cholesteric layer is small.

The cholesteric solutions produced from a concentrated solution of **1** in toluene were doped with a laser dye with an emission band in the wavelength region of the reflection band of the liquid crystal. A Nd:YAG beam was used to excite the dye near its absorption maximum, and the emission was focused on the entrance slit of a monochromator. The details are found in the Experimental Section.

Two lasing peaks were typically observed, the highest one at the low wavelength edge and the other near the middle of the selective reflection band (Figure 1a,b). Lasing was only observed when the selective reflection band overlapped the wavelength range of the dye emission. Certain regions of the sample showed selective



**Figure 1.** (a) Transmission spectrum of the cholesteric solution for **1**. (b) Emission spectrum and lasing at the edge and in the middle of the selective reflection band of the cholesteric solution for **1** at different pumping energies (1, 1.1 mJ; 2, 0.7 mJ; 3, 0.2 mJ).

reflection bands shifted slightly to shorter wavelengths than shown in Figure 1a. This variation in wavelength of the reflection band center is associated with a slight shift of the lasing wavelength. Lasing was not observed when the wavelength of the selective reflection band was displaced significantly (more than 40 nm) from the peak of the dye emission line.

The emission intensity of the lasing peak is shown in Figure 2 as a function of pump energy. The lasing threshold was estimated to be about  $8 \times 10^4 \text{ W/mm}^2$ . The lasing threshold for the emission peak at the low wavelength edge of the selective reflection band was compared to that for a 40  $\mu\text{m}$  thick thermotropic liquid crystal film formed with a nearly perfect planar texture using a rubbed polyimide alignment layer. The lasing

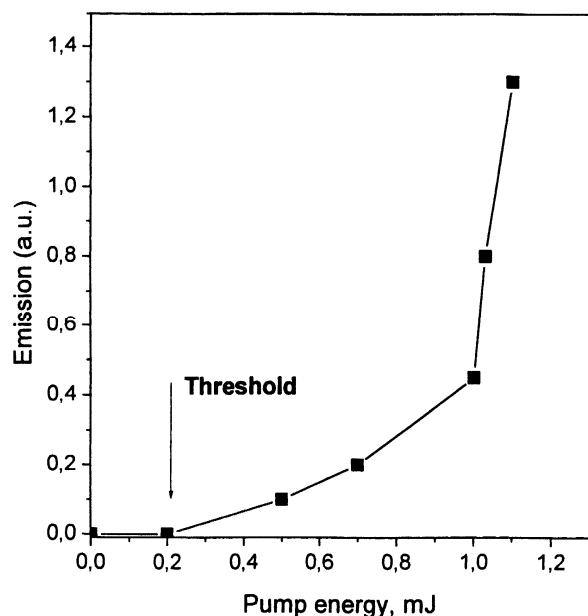


Figure 2. Intensity of lasing as a function of input energy.

threshold was higher by a factor of 8 in the lyotropic sample. This is likely the result of the formation of multiple domains within the lyotropic liquid crystal, which is consistent with microscopic observations of the lyotropic samples studied showing approximately planar multidomain structures. In such samples lasing is initiated in the largest and most uniform domains where the lasing threshold can be expected to be lowest. The thickness and width of the monodomain are crucial factors determining the lasing threshold.<sup>10</sup>

Optically pumped lasing in a perfectly periodic cholesteric liquid crystal occurs at the first mode at the edges of the selective reflection band of the cholesteric phase, that is, within the fine structure referred to above. The narrowest mode is the first mode on the high frequency side of the band. In the samples studied here, these oscillations at the band edge were greatly suppressed<sup>21</sup> by the multidomain structure so that it was impossible to assign band edge lasing to a specific mode of a periodic structure. The physical characteristics of defects and the role of defects<sup>22</sup> in fostering spatially localized states within the structure are under investigation, as is the question of the coherence properties of the lasing beam and the relationship of the coherence length to the domain characteristics of the liquid crystal.

### Summary and Conclusions

The first observation of lasing from a stiff chain polymer lyotropic cholesteric liquid crystal with lasing at the edge and in the middle of the selective reflection band is reported. Lasing occurring at modes within the reflection band is hypothesized to be introduced by disorder. Lyotropic cholesteric liquid crystal planar structures, essential for the observation of lasing, are formed without surface treatment because of the large axial dimension of the optically active polyisocyanate and the absence of polar end groups. The latter would anchor the chain ends at the surface, favoring therefore a homeotropic texture. The lasing threshold is less than an order of magnitude higher than in thermotropic liquid crystals subject to domain manipulation by surface treatments,<sup>23</sup> which we prepared for comparison. This relatively low threshold occurs without adjustment

of any of the numerous parameters that may be varied in liquid crystals formed from stiff chains in solution, as discussed above, and suggests that the threshold could be further reduced. In addition, this experiment forms a model system suggesting parallel lasing studies of cholesteric states formed from other stiff polymers if the necessary pitch values overlapping with appropriate dye emission wavelengths can be attained.

Finally, new experiments on temperature control of the helical properties of the polyisocyanates may offer unusual temperature dependent lasing properties.<sup>24</sup>

### Experimental Section

**Materials.** Poly(*n*-hexyl isocyanate-co-(*S*)-2,6-dimethylheptyl isocyanate) (HIC-co-(*S*)CT), **1**, was prepared and polymerized to the moderately narrow range of molecular weights necessary for the liquid crystal work as follows.<sup>20</sup> The polymerization was carried out in a 6 in. test tube with sidearm equipped with magnetic bar and rubber septum under an atmosphere of dry argon. The *n*-hexyl isocyanate (HIC) (Aldrich Chemical Co.) was dried overnight over calcium hydride and distilled under vacuum (50 °C at 7 mm) just before use. The (*S*)-2,6-dimethylheptyl isocyanate (*S*-CT) was prepared as described.<sup>18</sup> To form the initiator solution, sodium cyanide (120 mg) was dried under vacuum and dissolved in dimethylformamide (5 mL), which was freshly distilled under vacuum from phosphorus pentoxide (45 °C at 10 mm). Toluene was distilled with sodium under argon just before use. Dry syringes were used to transfer the exact amount of the two monomers and solvent to the reaction tube. After cooling the reaction tube in dry ice/methanol medium to -78 °C, the initiator was added with a syringe. The transfers and the polymerization were conducted in an argon atmosphere in a drybox. After several hours, a small volume of methanol was added to precipitate the polymer. Purification was carried out by precipitation from chloroform into methanol. The resulting cottonlike polymers were dried under vacuum.

In a typical polymerization there was used 878.1 mg of *n*-hexyl isocyanate (6.914 mmol), 122.4 mg of (*S*)-2,6-dimethylheptyl isocyanate (0.724 mmol), and 200  $\mu$ L of initiator solution. The yield of purified polymer was 0.74 g (74%). The molecular weight and polydispersity were determined by gel permeation chromatography using poly(*n*-hexyl isocyanate) standard samples for calibration.

**Cholesteric Solutions and Lasing.** Cholesteric solutions were prepared by dissolving the polymer in toluene, so as to obtain about 0.30 mL of solution in a 2 mL ground glass stoppered test tube and stirring overnight with a magnetic stirrer as follows: In a 2 mL ground glass stoppered test tube, 173.5 mg of **1**, 173.5 mL (200  $\mu$ L) of toluene, and 0.7 mg of the dye were dissolved. Samples were prepared by placing the solution between two glass plates with a gap of about 180  $\mu$ m. The formed cell was sealed with epoxy resin to prevent evaporation of the toluene.

The typical selective reflection band observed from the planar texture of the cholesteric solution produced above has a width in the range of 35 nm. We determined that the observed band in the transmission data in Figure 1a is a selective reflection band by carrying out experiments with left and right circularly polarized light, which showed that the handedness of the reflected light corresponds to the handedness of the cholesteric structure.

The laser dye pyromethene-597 has absorption and emission peaks in toluene solution as shown in Figure 1. Lasing was observed and studied by pumping samples with a frequency-doubled Nd:YAG laser at the absorption maximum of the dye. The pump light pulse duration was approximately 45 ns. The pump beam was focused to a spot with a diameter of approximately 140  $\mu$ m. A 20 cm focal length lens was used to collect light and to focus it on the entrance slit of the monochromator. Spectrally resolved emission was recorded with a CCD detector attached to the monochromator.

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