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The influence of homogenization process on lasing performance in polymer-nematic liquid crystal emulsions

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A B S T R A C T

In this letter we report on the results of studies of amplified spontaneous emission in polymer – liquid crystal emulsions based on mixtures of poly(vinyl alcohol) and 5CB nematic liquid crystal doped with three luminescent dyes: DCM, Coumarin 504 and Coumarin 540. The mixture of dyes was used in order to extend the range of stimulated emission spectra. We have investigated the emission properties of four samples with different size and distribution of liquid crystal micro droplets, controlled by the length of time exposure on ultrasounds during the homogenization process. We have designated the threshold conditions for stimulated emission occurrence and compared the emission spectra obtained below as well as above threshold conditions.

1. Introduction

Liquid crystal (LC) is unusual physical state that is showing the features typical for liquids and crystalline solids. This phase is characterized by fluidlike behaviour and long range orientational order attributed to the crystal phase. The properties of LCs are very promising for science and technology, especially like: flexibility, high optical anisotropy and switching ability of their physical properties induced by an external electric field. These features make them advantageous in construction of different optical and photonic devices [1]. Nowadays nematic liquid crystals (NLC) are mainly used in display applications, in nanotechnology as memory or optical array devices [2]. They are also used as controllable phase retarders, logic gates, optical switches [3,4] and spatial light modulators, however the variety of LC types and their high optical damage threshold makes them also suitable to be used in devices strictly devoted to work with lasers. Some applications are based on the unique property of cholesteric liquid crystals (CLC) with the naturally occurring photonic band gap, which might be used to control e.g. waveguiding properties of liquid crystalline waveguides [5]. The occurrence of photonic band gap results in frequencies of light that are forbidden and the speed of light at the edges of bands becomes nearly stopped, therefore the light in the presence of gain material becomes strongly amplified. This strategy is commonly used to construct liquid crystalline lasers with tunable wavelength of emission depending on the helix pitch [6–9]. As it was shown in literature the wavelength tunability may be achieved via changing the concentration of chiral dopant [10], by the influence of external electric fields applied to the LC film [11], or by stress [12]. The role of dye embedded to the LC is to provide the gain and by the cleaver engineering of the LC mixture with dopants it could be possible to obtain multicolour laser emission [10]. The use of the photonic band-gap is not only the one possibility that allows to introduce the feedback that is distributed inside the liquid crystal gain medium. It has been shown that so called random lasing can also occur in LC systems. The random lasing phenomena and band edge lasing are based on two different mechanisms. Both of the lasing types are possible to achieve in the chiral liquid-crystalline system by changing the micro-droplets size. As it was shown in ref. [13] large droplets show the narrow linewidth which is typical for the band-edge lasing. Small droplets are not able to serve as the cavity for band edge-lasing. Instead of this, it forms good system for random lasing which relies on disorder induced light scattering. The feedback mechanism is provided by scatterers, which are randomly distributed in active medium - in opposite to the conventional lasers with external resonator [14–17]. The random laser feedback may occur in two types - the first one is energy or intensity feedback which is identified with non-resonant/incoherent random lasing. The second one is field or amplitude feedback which is

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known as resonant/coherent random lasing. The explanation of diffusive non-resonant random laser may be understood in terms of different type of cavity, which replaces the Fabry-Perot's one mirror. The scattering surface causes the multiply scattering in changing directions which results in amplification of the light. The light doesn't travel back to the original position. The incoherent random lasing phenomena is characterized by narrowing of the spectrum above the threshold, with the centered peak in the highest frequency. The coherent/resonant random lasing is the analogy of Fabry-Perot interference bringing light back to the position, from which the light started its travel – and it presents the multiple narrow peaks in the spectrum [18–23].

Composites based on liquid crystals and polymers are studied for many years and are very widely reported in the literature [24–26]. Polymers can serve as host for liquid crystals due to the their high optical transparency and ability to stabilize the liquid crystal phase [27]. There are few mechanisms reported and used in order to generate the phase-separation and to obtain the polymer dispersed liquid crystals (PDLC). The most commonly used technique is a polymerization-induced phase separation which occurs when homogenous mixture of polymer and liquid crystal undergoes polymerization reaction [28]. The liquid mixture might be placed between transparent electrodes in order to achieve electrically controlled optical properties of emulsion and then the process of polymerization can be initiated by the change of temperature or by UV light illumination [29]. Another approach of LC-polymer emulsion fabrication relies on utilization of dissolved polymeric matrix and doping it with LC. If the solvent does not dissolve the LC phase, the phase separation may occur. The crucial aspect for the quality of the obtained materials is the process of homogenization. Depending on the method and time of this process the LC domains sustained in polymeric matrix may change in their size and distribution.

In this paper we show and describe the influence of exposure time on ultrasonic waves on LC-Poli(vinyl alcohol) (PVA) emulsions quality, and their emissive properties after doping the LC phase with three laser dyes, DCM, Coumarin 504 and Coumarin 540.

2. Materials and methods

2.1. Materials

In our studies, we have focused our attention on a system, based on PVA host matrix into which we embedded micro-droplets of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) nematic LC doped with three laser dyes, in 1:1:1 wt to weight ratio to each other. The used laser dyes were: DCM (4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran), Coumarin 504 (2,3,6,7-tetrahydro-11-oxo-1H,5H,11H- [1]benzopyrano[6,7,8-ij]quinolizine-10-carboxylic acid) and Coumarin 540 (3-(2-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one). The DCM, Coumarin 504 Coumarin 540 are well-known laser dyes which emit light in the visible region of light between 440 and 680 nm [30]. For the investigation we have also used commercially available poly(vinyl alcohol) (M_w = 85–124 kDa, 99% hydrolyzed, ALDRICH®).

2.2. Methods

The goal of experiment was to create different emulsions of LC and PVA with varying size distribution of LC domains, depending on time of exposure on ultrasound waves during homogenization process. The procedure of sample preparation is relatively easy because we do not use polymerization reaction, initiators and auxiliary compounds. In order to prepare four thin films based on PVA matrix and varied by the size of liquid crystals micro droplets we have used the mentioned above materials – luminescent dyes, liquid crystals and the ultrasonic water bath. The homogenization procedure is schematically shown in Fig. 1. Firstly we dissolved PVA powder in water in 9% concentration. The next step was to mix the 5CB liquid crystal with the dyes (DCM, Coumarin 504, Coumarin 540) in relation 1:1:1 with 0.9% weight to weight concentration of total dye amount, resulting in concentration 0.3% of each laser dye. The PVA solution as well as LC mixtures were distributed in equal quantities to four vials and exposed on ultrasonic waves generated by the ultrasound bath Polsonic, Sonic 3 ($P = 160$ W, $f = 40$ kHz) for varied time. Different time ($t_1 = 10$ min, $t_2 = 15$ min, $t_3 = 20$ min, $t_4 = 30$ min) of exposition on ultrasound waves resulted in the formation of different LC micro-droplets size distributions.

As a source of photoexcitation we have used the Horizon Parametric Oscillator (Continuum) pumped by the third harmonic of Surelite II Continuum nanosecond pulsed Nd:YAG laser (time duration 6 ns, repetition rate 10 Hz). The pumping wavelength in experiment was set to 446 nm to ensure that all of used dyes will be excited (see Fig. 2(a)). The laser beam was driven through the half-wave plate and Glan-Laser polarizer system, serving as an output energy controller. The excitation area was formed in a circular

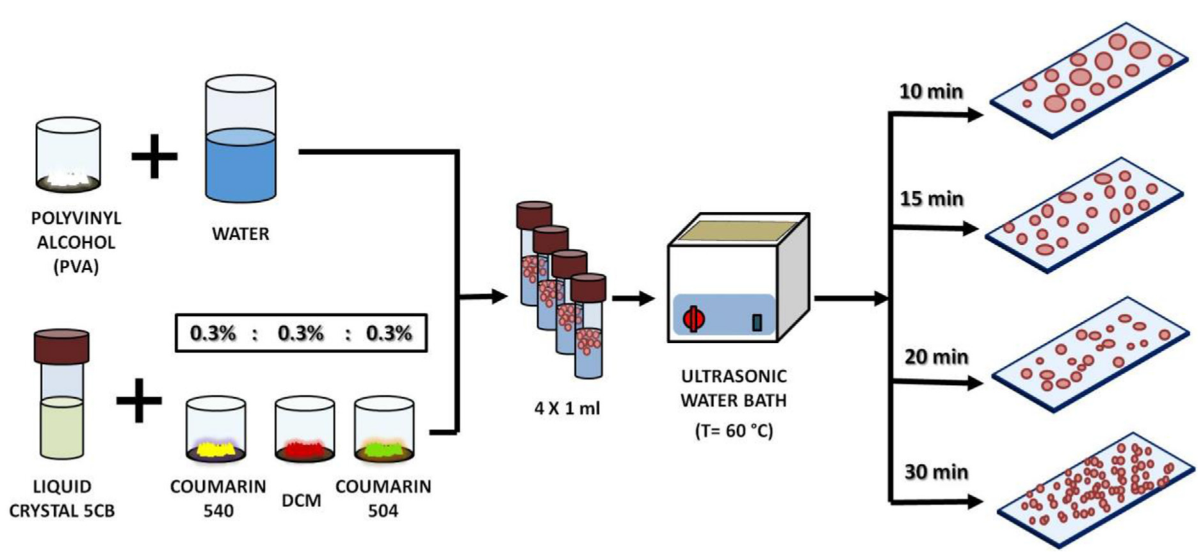

Fig. 1. The scheme of emulsion and samples preparation based on PVA matrix with embedded liquid crystal droplets.