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Controllable-gradient microscale PDLC electro-optical materials formed by nanosecond laser photopolymerization

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Nanosecond UV laser photopolymerization is employed to fabricate a polymer dispersed liquid crystals (PDLC) monolayer. The PDLC system contains droplets with a gradient size distribution. The formation of the PDLC structure, as well as the droplet gradient, are fully controlled by the PDLC cell geometry and UV laser. The electro-optical switching of the produced PDLC is probed.

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1. Introduction

Polymer dispersed liquid crystals (PDLC) [1-3] consisting of liquid crystal (LC) droplets dispersed in an optically transparent polymer matrix, are special advanced materials for electro-optical (EO) applications [4]. Since the EO properties of PDLC materials strongly depend on the LC droplets characteristics, such as shape, size and size distribution [1,3,5], it is of importance the PDLC morphology to be controllable formed and modified. The PDLC morphology is mainly determined by LC/monomer mixture, temperature and polymerization method. For instance, by changing the polymerization rate, one can obtain various droplet sizes and shapes. Furthermore, by photopolymerization, variable-intensity photo-masks are capable of forming PDLC with regular gradients, e.g. nanoscale PDLC with refractive index gradient [6]. Recently, such nano-PDLC EO materials have been applied for tunable-focus electronic microlens arrays [7].

In general, for PDLC produced by phase separation between polymer and LC, there are difficulties in controlling the size and size distribution of LC droplets. Here, we used a phase separation by a high-power nanosecond UV laser photopolymerization of a wedge-confined LC/monomer mixture to design a droplet-gradient PDLC for light control. It was of interest to prepare a stable PDLC monolayer of relatively large LC microdroplets which sizes vary linearly along the sample. As demonstrated, the EO properties of this PDLC wedge can be spatially well controlled.

2. Experimental

PDLC wedge was prepared by UV polymerization-induced phase separation (photo-PIPS) method [8,9]. A mixture of UV-curable NOA-65 (Norland) and nematic LC E7 (BDH) in 50 : 50 wt. % ratio was used as precursor of the PDLC material. Such a ratio was chosen because it leads to better separation of LC and the polymer. The PDLC wedge cell was made as is usual with PDLC devices [1-4]. The mixture was heated to 60˚ C to achieve a homogeneous mixing in isotropic phase. The mixed material was then injected into a wedge-like cell assembled from two 1 mm-thick glass substrates with inner surfaces coated with conductive indium-tin-oxide (ITO) (Fig. 1). The wedge was 17.5 mm long from one edge to the other, a 25 μm-thick Mylar spacer was used.

The photopolymerization was performed at room temperature with coherent irradiation of nitrogen laser (ZWG IGL 300/2) operating at wavelength 337.1 nm. Laser pulses with 40 kW power (energy of 100 μJ and duration of 2.5 ns fwhm) were used at 1 Hz repetition rate. The laser beam was expanded to an aperture 1 × 1.5 cm where the intensity distribution was uniform. Reduced from the transmittance (75 %) of ITO-coated glass plates at 337 nm, the irradiation intensity within the cell was ~ 20 kW/cm^2. The curing time was set at 30 min.

The sample morphology was monitored through optical microscope NU-2 Universal Research Microscope (Zeiss) and recorded by Hitachi VK-C150ED video camera and computer. The EO response of the PDLC wedge was probed by measurement of voltage dependence of the transmittance of a linearly polarized light of He-Ne laser HNA25/10 (633 nm ≅ 10 mW ≅ 1 mm spot) at room temperature. The light passed through the PDLC wedge was registered by a photodiode and a power multimeter To the wedge cell electrodes sinusoidal voltage of 0 to 20 V_{rms} at 350 Hz was applied.

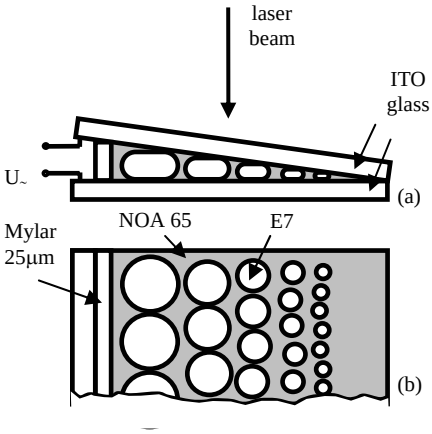

Fig. 1. Sketch of the PDLC wedge cell: (a) – side view; (b) – top view. Single droplets within PDLC wedge are illustrated.

3. Results and discussion

NOA-65 is a mixture of aliphatic thiols, vinyl monomers and photoinitiator, and the UV irradiation leads to a polymer network formation due to thiol-radicals addition to the double bond of vinyl component [10,11]. According to the NOA-65 data sheet, the recommended energy required for full cure is 4.5 J/cm^2 at long wavelength UV light (380 nm). Taking into account the relatively low (30 %) absorption of NOA-65 at the cured laser wavelength 337 nm, the efficiently used UV laser pulse energy density in our experiment was 15 μJ/cm^2. Since the photopolymerization was implemented by using of 1500 – 1800 laser pulses, the cumulative effect from nitrogen laser irradiation appeared to be at least two orders of magnitude more efficient than the photopolymerization with CW light sources, e.g. 100 Watt Mercury Spot Lamp at 6 inches. Obviously, that is due to the much higher laser irradiation intensity.

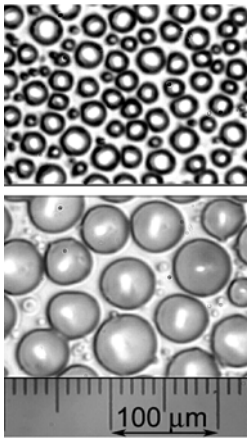

Fig. 2. The optical microscope images of E7 droplets dispersed in NOA-65 in equal wt. % amounts. Average droplet diameters: 20.2 μm (upper) and 52 μm (lower). Magnification: 25×.

Optical microscope observations indicate that a monolayer configuration of well-formed PDLC droplets was created within the wedge cell. Observing perpendicular to the wedge plane, the LC droplets have circular shapes (Fig. 1 (b)) with average diameters ranging between 10 to 52 μm along the wedge. Locally, they are well-dispersed and quite regularly distributed (Fig. 2), similarly to homogeneous PDLC structure formed by low-intensity UV lamp illumination [9,12]. The droplets form is determined by the photo-PIPS dynamics [8,9,13,14].

The use of single and short (nanosecond) high-power UV laser pulses allows the photo-PIPS process to be slow, which results in a higher mobility and intensive coalescence of the initial LC droplet creatures. During the slow PIPS, the relatively free diffusion of both mixed components (LC molecules and prepolymer) leads to a complete separation of LC and polymer [9,12] and does form the final structure of PDLC confined in the wedge. On this way, the cell gap does format the LC droplet sizes and determines the droplet size distribution. Since the uniform UV laser irradiation imposes identical photo-PIPS condition across the whole wedge, PDLC with a linear-gradient droplet size distribution was produced along the wedge slope. This was confirmed by optical microscope measurements. Fig. 3 presents the dependence of the average longitudinal droplet size on their transversal size. The latter is equal to the PDLC wedge thickness. The linear relation in Fig. 3 means that the use of a wedge geometry combined with nanosecond UV laser photopolymerization allows to be made well formed microscale PDLC of any desired droplet sizes, as well as any droplet size gradient.

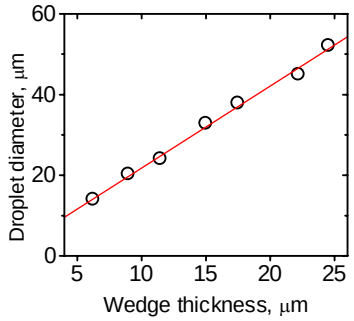

Fig. 3. Average droplet size vs the wedge thickness. Linear fit to data is also given.

That is, actually, the advantage of the PDLC forming in the wedge, compared to other methods of droplets size control, e.g. by changing the amount of LC in the LC/monomer mixture, temperature or UV dose [9]. Indeed, the creation of arbitrary large droplets by photopolymerisation with CW light source (conventional UV lamp) is strongly limited because the large droplets formation needs a weaker UV exposure, but the UV dose has to be also sufficient for an initiation of photochemical reactions of the polymerization. Note, there is no such a problem by photo-polymerization with nitrogen laser used in present work. As mentioned above, the photopolymerization in our case proceeds by discrete nanosecond steps at intensity levels which are 5 – 6 orders of magnitude higher than the ones usually available from the CW UV lamps. In addition, the cumulative effect of the UV portions and

photopolymerization rate can be controlled by the UV laser exposure rate. The latter can be set by both laser pulse energy and repetition rate. Thus, the formation of the PDLC wedge structure can be finely controlled.

To test the produced gradient PDLC wedge, we probed its electro-optics. As known, the mechanism responsible for EO response of PDLC is the change of the effective refraction index of the dispersed LC molecules with the applied voltage [4]. Due to the droplet gradient, the induced refractive index change should vary along the wedge slope, so that the EO properties of the PDLC wedge will depend on its thickness. We measured the voltage-dependent transmittance at 633 nm for various wedge thicknesses. Results are depicted in Fig. 4. As seen, the PDLC wedge exhibits a low threshold voltage, as well as low saturation voltage (the state-on voltage). In fact, the low switching voltages are due to the relatively large droplet sizes. For comparison, the required switching voltages for nanoscale gradient PDLC are greater than 100 V_{rms} at room temperature [6]. The threshold voltages of PDLC wedge are also considerably lower than the ones of submicron PDLC systems, e.g. E7/PMMA [15] and E7/Epoxy [16] (~ 10 V and ~ 20 V, respectively). The switching voltages of the present PDLC wedge are in the range typical for PDLC prepared with monodisperse micron-sized polymer/LC particles, e.g. PMMA/E7 with large E7 amount and size of 4 μm in a 25 μm-thick cell [5, 17], as well as close to the ones of the microscale UV-cured PDLC, e.g. E7/Epoxy [18] and the well-studied 50 : 50 % E7/NOA-65 system [19] (droplet size 1 – 5 μm, film thickness 20 – 30 μm) at room temperature.

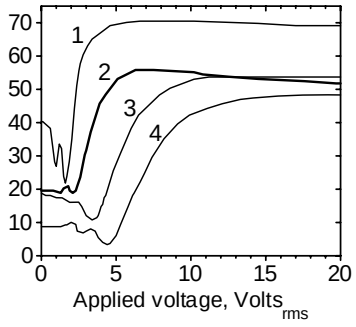

Fig. 4. Transmission at 633 nm versus applied voltage measured at various positions on the PDLC wedge. Wedge thickness: 6 μm (curve 1); 8.5 μm (2); 13 μm (3) and 17 μm (4).

Fig. 4 shows that the switching voltages of PDLC wedge depend significantly on its thickness. This feature can be practically used: the regime of the PDLC EO wedge can be appropriately set by simple wedge translation.

4. Conclusions

In conclusion, we adopted a simple technique to form a monolayer of micro-PDLC with controlled droplet size. Using standard LC/monomer mixture confined in a wedge-shaped cell and UV laser curing upon nanosecond regime, we have produced a PDLC wedge with relatively large droplets and easily controllable droplet size gradient. The light transmission EO switching of the formed PDLC was probed. The result shows that by simple moving of the wedge across the incident light, one can finely tune its EO switching behavior.

The proposed PDLC wedge can be applied like typical photonic and EO devices which are electrically and spatially commanded, for example, as switchable attenuator for light control, light modulator/discriminator, etc. Using various appropriate LC/monomer mixtures, it would be possible to develop various phase separation kinetics and corresponding microscopic structures, i.e. various EO characteristics can be obtained and the potential applicability of this device can be extended.

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