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## Liquid Crystal Assisted Replica Molding Method to Align Uniaxial Molecules in Patterned Polymer at Ambient Temperature

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In this paper, we demonstrate an easy approach—liquid crystal assisted replica molding method—to align uniaxial molecules in a patterned polymer at ambient temperature. During the replica molding process, the orientation of liquid crystals was parallel to the groove of the grating and the uniaxial molecules were aligned by liquid crystals. In order to confirm our observations, we had measured photoluminescence (PL) and polarized absorption spectra to quantify the degree of alignment. This approach to align uniaxial molecules in a polymer at ambient temperature opens up a simple way to manufacture optoelectronic and electronic devices. [DOI: [10.1143/JJAP.47.8606](https://doi.org/10.1143/JJAP.47.8606)]

KEYWORDS: liquid crystals, replica molding, molecular orientation

### 1. Introduction

To align molecules by nanoconfinement is an important and interesting issue nowadays because of the potential applications of aligned molecules. For example, molecular orientation in semiconducting polymers leads to anisotropic electronic conductivity;<sup>1)</sup> molecular orientation in polymers results in anisotropic optical devices such as optical polarizers; oriented molecules are used as an active layer in polymeric light-emitting diodes (PLEDs) to emit polarized light;<sup>2–4)</sup> second-order nonlinear optical properties stem from the alignment of molecules and they are frequently functioned in electro-optical modulator<sup>5)</sup> and frequency converter.<sup>6)</sup>

Several methods were used to align molecules in a polymer: (1) rubbing/stretching polymer films or polyimide (PI),<sup>3,7)</sup> (2) doping luminescent guest molecules in an aligned host matrix,<sup>8,9)</sup> (3) aligning molecules with magnetic, electric field, or photoirradiation,<sup>5,10–14)</sup> and (4) Langmuir–Blodgett deposition (self-assembly).<sup>15,16)</sup> However, there are certain kinds of problems existing in the methods above. The problem of rubbing/stretching is that rubbing can only align liquid crystals (LCs) or liquid crystal polymer (LCP) materials and the deformation by elongation can hardly be controlled easily when we stretch polymer films. Doping molecules in an aligned host matrix cannot cause good alignment because the molecules do not have strong interactions between each other. When applying fields or photoirradiation, we need very strong magnetic or electric field to align molecules well. Langmuir–Blodgett deposition can be applied only to specific molecules such as molecules with hydrophilic and hydrophobic polar. Those methods above are either hard to control or limited to certain molecules.

In this paper, we demonstrate an easy approach to align molecules in the plane of polymer films at ambient temperature. Here are the main advantages of this approach. First, the samples need not to undergo high temperature; that is, even non-heat-resistant molecules will not be destroyed throughout the process. Second, because LC assisted replica

molding method combines the aligning ability of LCs and the benefits of replica molding method together,<sup>17)</sup> we can use it to align many kinds of uniaxial molecules easily. The alignment of molecules was observed in the poly(dimethylsiloxane) (PDMS) films after we patterned the mixed PDMS by replica molding method, an efficient and effective way to duplicate the surface structure of a mold. The benefits of replica molding method are: low fabrication costs, high-throughput, simple fabrication, and the ability to copy nanometer scale structures over centimeters. In addition, the mold is reusable since that the curing and peeling of PDMS substrates does not destroy the original one. In other words, we can manufacture many PDMS films by only one mold. Therefore, the costs and time on producing molds can be decreased significantly in replica molding method. In short, the LC assisted replica molding method not only saves the costs of manufacturing but also broadens the applications of molecules.

### 2. Experiments

In this work, we used LC assisted replica molding method to fabricate flexible devices. Figure 1 is the flowchart of the LC assisted replica molding method fabrication process we have used in this paper. The LCs and molecules were mixed with PDMS; the mixed PDMS was then dropped on the silicon mold and deposited at ambient temperature. Right afterwards, the LCs were aligned by the grooves of the grating on the mold and the uniaxial molecules were aligned by LCs. About several hours later, the mixed PDMS could be readily converted into solid elastomers by cross-linking. After it was cured, we peeled PDMS against the rigid mold. To this point, the PDMS with aligned molecules was complete totally and the thickness was 594  $\mu\text{m}$ .

During our research process, the mold was made up of silicon wafer with microgrooves patterned via traditional photolithography; the pitch of the grating was 1  $\mu\text{m}$  and the line-width of the grating was 700 nm with 270 nm in depth. As for PDMS, it was commercially available from Dow Corning Corporation and supplied as a two-part kit: a liquid silicone rubber base and a curing agent. Here, we mixed curing agent and liquid silicone rubber base at a ratio of 1 : 5. Since that the PDMS elastomer is isotropic and

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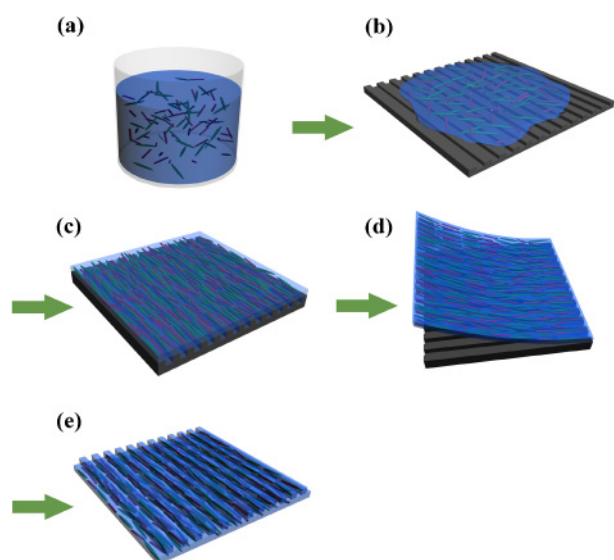


Fig. 1. (Color online) Flowchart of the fabrication process of PDMS substrates with uniaxial molecules and LCs. (a) Mixing uniaxial molecules and LCs with PDMS. (b) Dropping mixed PDMS on the silicon mold. (c) Depositing mixed PDMS at ambient temperature for several hours. (d) Peeling mixed PDMS against mold. (e) Flexible mixed PDMS substrate.

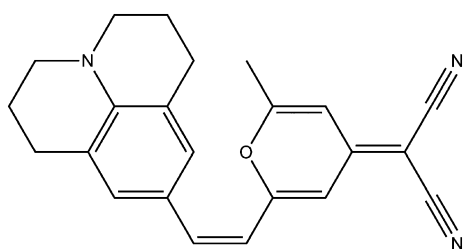


Fig. 2. Molecular structure of DCMII.

homogeneous with good thermal stability up to 186°C, substrates made from this material can be deformed mechanically to fit the patterns in the surfaces of molds. The formulation, application, and fabrication of PDMS elastomers have been extensively studied in ref. 18.

The uniaxial molecules and LCs were mixed with PDMS before PDMS was cured. We mixed 0.02 wt % uniaxial molecules with 2.00 wt % LCs and PDMS by stirring. The uniaxial molecule, 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyram II (DCMII), was offered by Exciton Corp. Figure 2 shows the molecule structures of DCMII. DCMII is an organic dye molecule and its dipole is oriented mainly along the molecular chain direction. The LC used here is nematic LC MJ9915, supplied by Chung-Hwa Picture Tube Co.

To measure the photoluminescence (PL) of LCs to make sure if the molecules had macroscopic anisotropic luminescence intensity, nematic LC MJ9915 was introduced into empty cells by capillary action in the isotropic phase. The empty cells with PI alignment layers for planar orientation were manufactured in a 180° antiparallel-nematic configuration where a cell gap of 4 μm was ensured by spacers. PL was carried out at room temperature and the excitation source was a 325 nm He–Cd laser. In order to measure the luminescence of different polarization, an optical polarizer

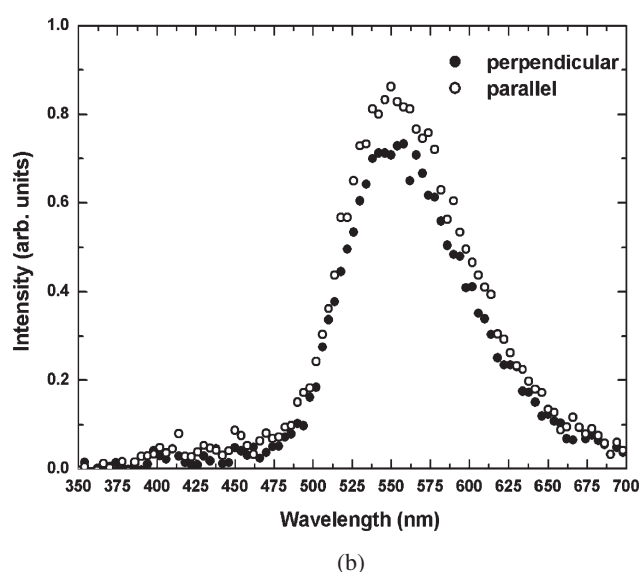
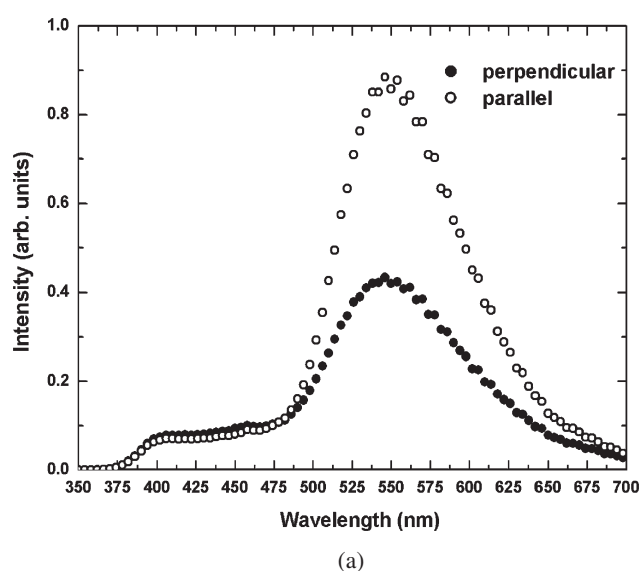


Fig. 3. Polarized PL measurement results of samples with DCMII. PDMS/DCMII patterned by grating mold (a) with LCs and (b) without LCs.

was inserted in front of the spectrometer (Horiba iHR320) for us to select the signal polarization direction precisely. The spectrometer was used to measure spectrum with wavelengths from 350 to 700 nm and a lock-in amplifier (Stanford SR830 DSP) was used to lock the signals to a computer.

We also conducted optical absorption spectrum to confirm the good anisotropic property of DCMII in the LC-assisted sample. Optical absorption was carried out at room temperature and an optical polarizer was inserted in front of the light source for us to produce light with different polarizations. In order to analyze the outcomes of different wavelengths, we measured the absorption versus the wavelengths from 400 to 700 nm by spectrometer (PerkinElmer Lambda 900).

### 3. Results and Discussion

Figure 3 shows the PL results of samples measured by the spectrometer. Figure 3(a) is the PL of DCMII assisted by LC alignment in the patterned PDMS grating mold while

Fig. 3(b) shows the PL result of DCMII in the patterned PDMS grating mold without the assistance of LCs. According to the results of Fig. 3(a), it is found that the luminescence intensity was strongest when the grating vector of the samples was parallel to the polarization direction of polarizer; the luminescence intensity was weakest when the grating vector of the samples was perpendicular to the polarization direction of polarizer. Since that DCMII has stronger PL spectrum along the molecular chain direction, we could find that the DCMII was parallel to the LCs in the PDMS rather than orthogonal to them from the result above. The dichroism ratio at wavelength 550 nm of the DCMII sample with LCs was 2.02 in Fig. 3(a) while the dichroism ratio of the DCMII sample without LCs was about 1.27 in Fig. 3(b), which means the DCMII molecules could only be aligned slightly by the groove of grating mold without the assistance of LCs. From the macroscopic view, the PDMS film with only uniaxial molecules was almost an isotropic one. Therefore, we have known from Fig. 3 that the mixed PDMS films with LCs presented a very good anisotropic property.

In order to ensure that the anisotropic PL behavior at wavelength 550 nm was produced by DCMII, we measured the PL of PDMS and LCs. Figure 4(a) is the PL of pure flat PDMS while Fig. 4(b) is the PL of pure PDMS with grating structure. In both cases, there was a peak at 435 nm, but with no obvious anisotropic PL. In other words, either the flat or structured PDMS did not have anisotropic PL behavior. Likewise, Fig. 4(c), there was also no obvious anisotropic PL behavior as well in the PL result of 180° antiparallel LC cell with a peak at 415 nm. Furthermore, we can know that, in Fig. 3(a), the peak of 415 nm produced by LCs and the peak of 435 nm produced by PDMS were overlapped to form a slight hill between 375 and 475 nm; the high dichroism ratio at 550 nm was caused by the good anisotropic property of DCMII in the sample. From the results above, we can see that patterned PDMS and DCMII mixture with the assistance of LCs possesses a very good dichroism ratio. Because the dichroism ratio is in proportion to the anisotropic degree, we can figure out that LCs have very good microscopically orientation along the grating vector and the uniaxial dye molecules are oriented by LCs.

Figure 5 presents the optical absorption spectrum of mixed PDMS. The absorption of LCs and DCMII mixed PDMS patterned by the grating mold [Fig. 5(a)] had a larger absorption when polarized light parallels to the grating vector and the average absorption ratio was about 2.48. In Fig. 5(b), the difference between different polarized absorption of the DCMII sample without LCs was rather slight; the DCMII molecules were aligned almost randomly without the help of LCs. Also, in order to ensure that the absorption difference from wavelength 400 to 700 nm was mainly produced by DCMII, we measured the absorption spectrum of both PDMS and LCs. Figure 6(a) is the absorption spectrum of pure flat PDMS and Fig. 6(b) is the absorption spectrum of pure PDMS with grating structure. We could find that neither the flat nor the structured PDMS had obvious absorption difference and they were not optically birefringent. Figure 6(c) is the absorption spectrum of structured PDMS with LCs only; an average absorption ratio about 1.27 existed but it was less than that of structured

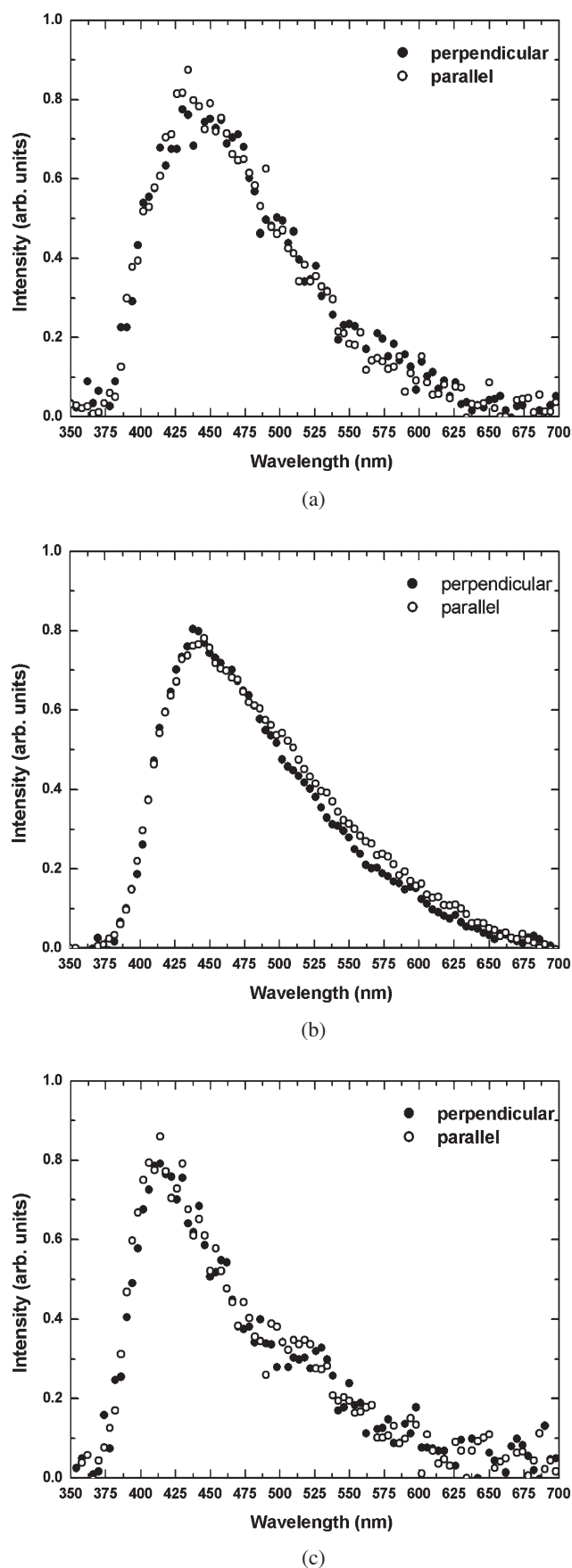


Fig. 4. Polarized PL measurement results of PDMS and LCs. (a) Flat pure PDMS. (b) Pure PDMS patterned by grating mold. (c) Pure LCs in 180° antiparallel cell.

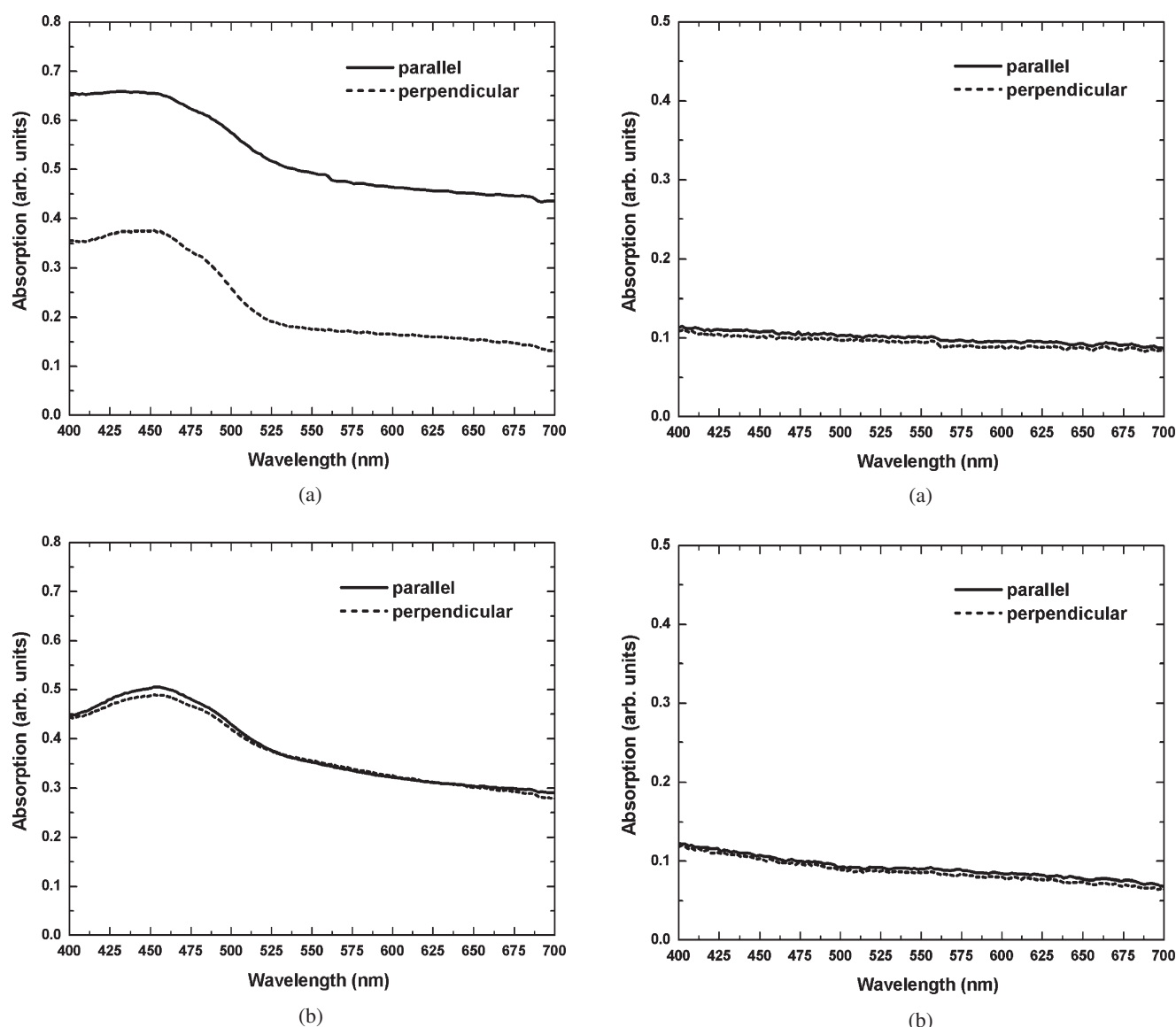


Fig. 5. Polarized absorption measurement results of samples with DCMII. PDMS/DCMII patterned by grating mold (a) with LCs and (b) without LCs.

PDMS with LCs and DCMII. Therefore, the absorption results above indicate that the absorption difference from wavelength 400 to 700 nm was mainly produced by well-aligned DCMII. In short, the measurement of optical absorption spectrum can also support that the good anisotropic property of DCMII in the LC-assisted sample. The measurement results of PL and optical absorption spectrum were basically consistent with each other. In experiments, we have also tried other uniaxial dye molecules like LDS698 (Exciton) and LD700 (Exciton) and found their preliminary results were consistent with those related to DCMII. Many other related experiments are still in progress.

#### 4. Conclusions

In conclusion, LC assisted replica molding method with grating molds is a simple and inexpensive method when we align uniaxial molecules in a patterned polymer. With the assistance of LCs, uniaxial molecules can be aligned well along the grooves of molds. Also, unlike nanoimprint

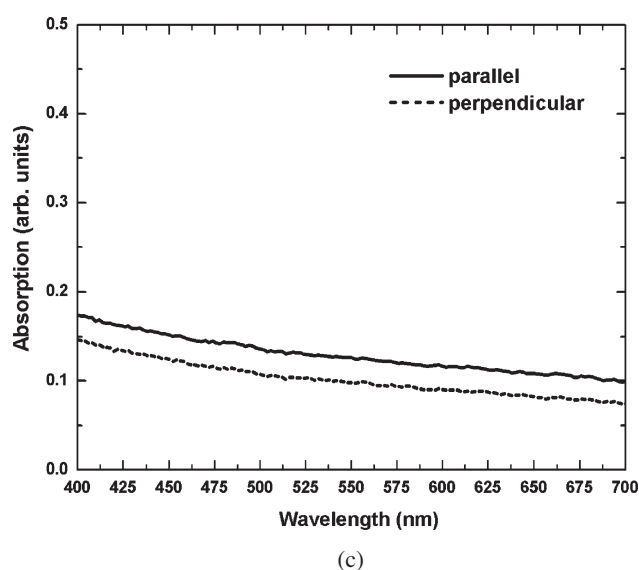


Fig. 6. Polarized absorption measurement results of PDMS and LCs. (a) Flat pure PDMS. (b) Pure PDMS patterned by grating mold. (c) PDMS patterned by grating mold with LCs.

method,<sup>19)</sup> this method does not need to function with high temperature. Therefore, it can be applied to more kinds of uniaxial molecules. Moreover, it can be extended to other polymers and uniaxial molecules for further applications. To sum up, it is undoubtedly that this method will have important applications on the fields of optoelectronics, molecular electronics, and optical devices.

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