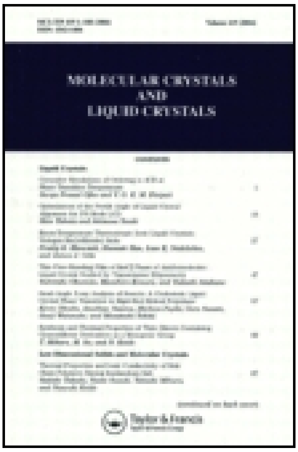

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Alignment of Diacrylate Polymer Network in 488 nM Wavelength Holographic Interference Field

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The crosslinking of a diacrylate mesogen was initiated in a holographic field created by 488 nm wavelength laser beam. The holographic irradiation provided both energy for crosslinking of acrylate groups and the driving force to align mesogenic groups in the diacrylate mesogen. A template with localized molecular ordering in the diacrylate mesogen layer in a mesophase can be created by the holographic field, and is frozen up by in situ *polymerization of the mesogen. The resultant polymer networks possess localized orientational order which was patterned by the holographic field.*

Keywords Diacrylate mesogen; diacrylate polymer network; orientation of polymer network; two-beam interference

1. Introduction

Polymeric systems with oriented molecular structures can possess highly anisotropic optical, electrical and mechanical properties, and have drawn a great deal of attention because of their potential use in various applications. A manipulation of an oriented structure into a polymer network locally to form an optical phase modulator template, which is particularly desirable for photonic applications, is a highly interesting research topic. In this context, at least two issues must be taken into account: firstly, a polymeric optical medium in which molecular alignment is feasible and the molecular orientational order can be locked in; secondly, a technique that provides means to drive polymer chains to orient in a desired direction and further to locate the orientational structures in predetermined positions. Mesogens comprising photopolymerisable acrylic end groups can form polymers with network-type structures consisting of a backbone with mesogenic units [1–3]. The photo-initiated bulk polymerization of diacrylate monomers in a mesophase leads to the formation of densely crosslinked networks and allows the molecular ordering in the mesophase to be permanently frozen in on the creation of the network. Owing to their mesogenic nature and anisotropic characters the mesogenic groups in diacrylate monomers in

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Address correspondence to Wenjun Zheng, Photonics Department, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 80424, R.O.C. Tel.: +886 7 5252000 ext 4445; Fax: +886 7 5254499; E-mail: wzheng@ymail.com the liquid crystalline phase can be aligned by either electric [4] or magnetic field [5], a mechanical shearing, and using a surface alignment layer. Oriented polymer networks with fibrous morphology can be produced by polymerisation of diacrylate monomers in an aligned low molar mass mesogen [6,7]. The induced orientational order can subsequently be frozen in by *in situ* isothermal polymerization of the diacrylate mesogen [8]. The distinctive characteristics of mesogenic diacrylate provide the possibility of the attainment of local oriented structures in a polymer. However, all above-mentioned methods for the alignment of mesogenic monomers are less applicable when patterning orientational order of a polymer is concerned.

Holography provides a way in which the optical field can be redistributed in the space through interference in a controllable manner. For example, holographic patterns can be produced by means of two-beam-interferometric technique in which two coherent beams with equal intensity and the same wavelength λ are allowed to intersect at an angle α in the space. The result of the coherent addition of the two beams is the formation of a spatial distribution of the optical field with a grating pattern. When both coherent beams electrically oscillated perpendicular to the incident plane, i.e., in the s-polarization, the interference fringes are parallel to the polarisation of the light beams, i.e., perpendicular to the incident plane, and the spatial period Λ of the fringes is given as [9]

$$\Lambda = \frac{\lambda}{2\sin(\alpha/2)}. \tag{1}$$

Thus, for a given wavelength, the spatial period of the gratings can be easily controlled by adjusting the angle between two beams. The two-beam-interferometric technique has been successfully used to induce molecular reorientation and polymer chain migration to create local holographic gratings in azo-based polymers for optical recording/storage [10–15]. The successfulness of holography in azo-based polymers inspired us to apply holography irradiation to pattern orientation of mesogenic groups in diacrylate monomers.

We herein demonstrate that polymer networks with local orientational order can be produced by exposed a diacrylate mesogen in a liquid crystalline phase to a holography irradiation.

2. Experimental

The diacrylate mesogen used in the present study was RM257 (1,4-bis[3-(acryloyloxy)propyloxy]-2-methyl benzene), which was purchased from Merck. The details of this mesogen can be easily achieved in the current literature (for example, cf. references [1–3]). In the monomeric form, RM257 exhibits the nematic phase in a rather broad temperature range (70–127°C). The moderate clearing temperature of the mesogen at 127°C allows the monomer to be heated into isotropic state without thermally initiating the crosslink of the acrylic end groups. The cells were constructed to have a gap of 10 μm determined using glass substrates without any surface treatment other than a sonic cleaning operation. Samples were prepared by injecting RM257 into the cells at a temperature of 145°C where the diacrylate mesogen was in the isotropic phase. A particular mesophase of the diacrylate mesogen was obtained by properly controlling the temperature of the sample using a

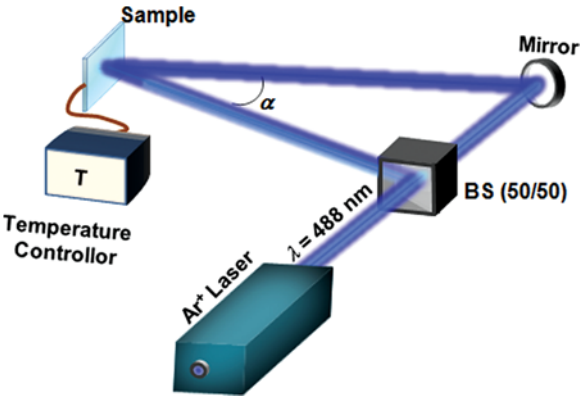

Figure 1. Optical setup of tow-beam interferometric holographic irradiation system. An s-polarized laser beam is divided by a 50/50 beam split BS, and the two coherent beams are allowed to interfere in the space where a sample of diacrylate layer whose temperature is controlled by a temperature system T. (Figure appears in color online.)

TMS93 temperature system (Linkam Scientific Instrument). The phase behaviour and the orientation states of the diacrylate mesogen were examined using a thermal polarising optical microscope (POM) system Axioscop40 (Zeiss). Photomicrographs of the optical textures of the samples were taken by the digital camera PowerShot A620 (Canon), which was installed in the polarising microscope.

Holographic patterns were produced using a two-beam-interferometric system (Fig. 1). The light source was an Ar+ laser (2060Beamlok, Spectra-Physics). A laser beam of 600 mW cm^{-2} radiant flux, operated at 488 nm, was split into two equal intensity s-polarized beams which were allowed to intersect in the space where the sample was installed. For convenience in observation and measurement we set $\Lambda = 30\,\mu$m by properly adjusting the angle α.

3. Results and Discussion

For a routine test, we mixed 0.5 wt% of a photo-initiator Irgacure 907 (Ciba Geigy) into RM257 and sandwiched the reactive mesogen between two untreated glass plates with a 5 µm gap. The mesophases of the compound can be easily observed and recognized by examining its optical textures using the POM. In its monomeric form, RM257 exhibits a nematic phase within the temperature range 70–127°C. The polymerization of the compound was carried out by exposing the sample to a UV radiation. After the UV curing of the sample, the RM257 layer became solid, and its optical texture did not change with temperature. The thermally unchangeable optical texture indicates the loss of the phase transition in the material in the sample and signals that the resin has been polymerized, and is the criterion we used for determining the polymerization of diacrylate mesogen. The optical texture of a RM257 thin layer in the polymeric form was found to be identical to that of the mesogen in the mesophase in which the crosslinking of diacrylate units was initiated, i.e., the molecular ordering of the mesogen in a particular mesophase has been locked up by polymerizing the compound in the mesophase.

In the present study, no photo-initiator has been added into the diacrylate mesogen. The crosslinking of RM257 in the solid state was found to be very difficult.

We were unable to have RM257 polymerized by exposing the diacrylate compound at room temperature to the holographic irradiation for a few hours. A low yield of free-radical due to an insufficient optical absorption of the mesogen at 488 nm [16] and the localized reaction of active polymer chains due to very low mobility of radicals in the solid state mesogen are thought to be major causes that are responsible for the failure of the holography irradiation in polymerization of the solid state RM257.

Figure 2 shows the optical texture of an irradiated RM257 sample. The sample was exposed to holographic irradiation for 30 min, and during holographic irradiation RM257 was kept in the nematic phase at 110°C. The photograph was taken at 160°C which was well above the clear temperature of the mesogen. The black appearance of the unexposed region indicates that the mesogen is in the isotropic state, whereas the exposed region exhibits an optical texture with the same features which were observed in the nematic phase where the crosslinking of diacrylate units was initiated. The thermally unchanged optical texture thus indicates the mesogen in the exposed region has been polymerized, and the molecular ordering of the mesophase where the crosslinking is initiated has been locked in. The optical texture also indicates that the polymer network has not been aligned, but with the polymer chains in the region randomly extended.

To initiate the crosslinking of RM257 in the isotropic phase, we kept the samples at 140°C while exposed it to the holographic irradiation. The diacrylate was found, confirmed by POM observation, to be polymerised after the irradiation. In the POM, a grating pattern can be seen in the irradiated region (Fig. 3). The spatial period of the fringes was measured to be 30 μm, and was consistent with that of the holographic irradiation. The optical appearance is a reflection of the optical characteristics in these regions and can be explained by considering optical phase retardation resulted from the birefringence due to molecular ordering in the regions. It is well known that a layer of homogeneously aligned mesogenic material can act like

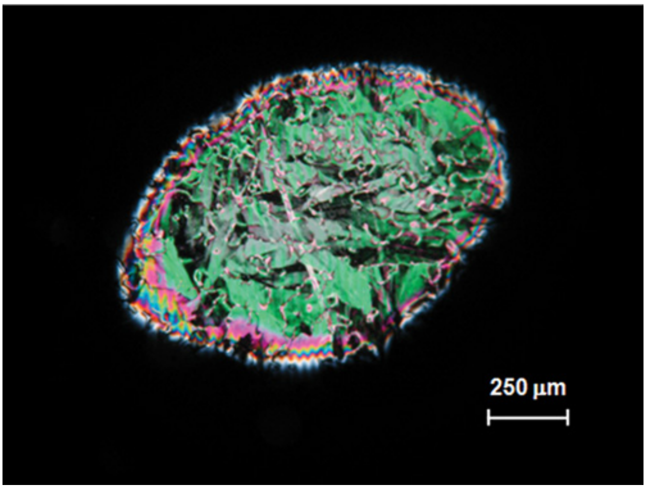

Figure 2. Photomicrograph of a layer of irradiated RM257. The holography irradiation was carried out while RM257 was kept in the nematic phase at 110°C. The photograph was taken when the sample was at 160°C. (Figure appears in color online.)

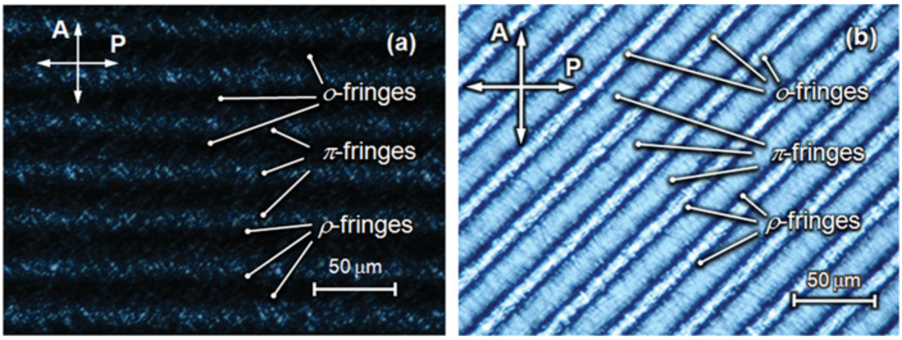

Figure 3. Photomicrographs showing the optical appearance of polymerized RM257 layer in a POM, with the fringes (a) parallel to and (b) making a 45° angle against the axis of the polarizer of the POM, respectively. The different types of fringes reflect the orientation of polymer chains in the sample. (Figure appears in color online.)

an optical plate, and when such a plate is laid between two crossed polarisers the intensity of light transmitted through the system can be described as [17]

$$T = T_0 \sin^2(2\varphi)\sin^2\left(\frac{\pi\Delta n d}{\lambda}\right), \tag{2}$$

where d is the thickness of the mesogen layer, λ is wavelength of incident light, Δn is the birefringence which arises due to a unidirectional orientation of the polymer chains, and ϕ is the azimuthal angle of the polarisation of the incident beam made against the optical axis, i.e., the director, of the mesogen. When the holographic irradiated sample was rotated, the intensity of the overall light transmitted through of the irradiated region T, as illustrated in Figure 4, varied sinusoidally and follows Eq. (2). The optical characteristics indicate that on the whole the mesogenic groups in the region orient in the same direction. The RM257 network is a main chain mesogenic polymer. The appearance of the fringes is resulted from the difference in light transmission due to the difference in orientational ordering of the polymer networks in different regions.

Carefully examining the grating pattern in the sample revealed that there were three types of fringes (Fig. 3), with each of them reflecting certain molecular ordering in the corresponding region, in the irradiated area. Upon rotating in the POM one group of fringes changed their appearance and became black and white alternately acting like optical wave plates whose light transmittance can be described by Eq. (2). We classify the fringes of this type as σ-fringes. The polymer networks in the striped regions corresponding to these fringes are, according to the previous discussion, thought to be well aligned. So the σ-fringe is an optical reflection of the aligned polymer networks. The second type of fringes, defined as π-fringes, are those whose visible appearance will not disappear in the black state of the sample [cf. Figure 3(a)] indicating that there is always light leaking from these striped regions. On rotating the sample, the brightness of the fringes varied periodically. The light leakage is an effect of the multi scattering of light due to a random extending of the polymer chains in the regions. The periodical variation in transmitted light intensity, though it is rather weak, indicates a partial orientation of the polymer chains in

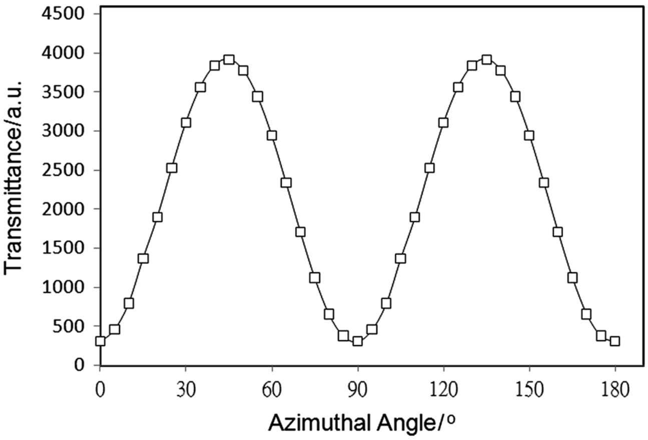

Figure 4. The azimuthal variation of light transmittance of the polymeric RM257 layer.

these regions. Therefore, the π-fringes reflect partial alignment of polymer chains in the regions. The appearance of the fringes of the third type, defined as ρ-fringe, in the POM was always black [cf. Figs. 3(a) and (b)], regardless the azimuthal position of the sample in the POM. This indicates that in the corresponding regions the polymer chains in the network system stretch randomly without a unique orientation, and form optically isotropic polymer stripes. Therefore, the orientational order of the polymer networks has been patterned spatially by the holographic irradiation.

To determine orientation direction of the mesogenic groups in the aligned regions, i.e., in those stripes corresponding to the σ-fringes, we placed the sample in the POM, aligned the stripes parallel to the transmission axis of the polarizer, i.e., making $\phi = 0$ [cf. Eq. (2)], and then slightly lifted the sample at one edge while kept the opposite edge of the sample firmly in touch with the surface of the stage of the POM. This causes the sample to rotate a small angle θ about an edge of the cell. For an ordinary incident beam, the rotation will not create any change in the light transmission. For an extraordinary incident beam, however, a rotation about the optical axis will cause no change in $\Delta n = n_e - n_o$ when the optical axis is parallel to the rotation axis, and thus nor change in T, whereas a rotation of the polymer film about an axis which is perpendicular to the optical axis will cause changes in extraordinary refractive index and the optical birefringence Δn in Eq. (2) is replace by an effective refractive index difference $\Delta n_e = n_{eff} - n_o$, with $n_{eff} = n_o n_e / \sqrt{n_o^2 \sin^2\theta + n_e^2 \cos^2\theta}$, leading to a change in T (c.f. Fig. 5). Using this technique, we revealed that the orientation of polymer chains in the aligned regions is perpendicular to the fringes. As the fringes are parallel to the polarization of the s-polarized light beams, we thus infer that the holography irradiation drives the mesogenic groups oriented perpendicular to the polarization of the writing beam.

The effects of initiating diacrylate in different mesophases on the orientational order in the resultant networks may be explained based on the consideration of a competition between the rate of polymerization and the response time of the mesogen to an external field. Radical photopolymerization is a fast process, and polymer chains can form via chain addition reaction in a fraction of a second. The period for

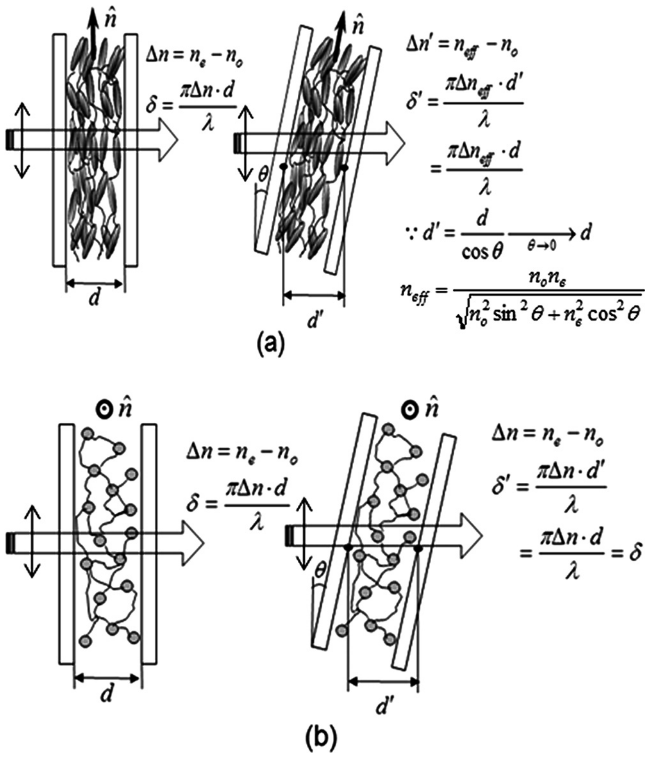

Figure 5. Schematically showing changes in phase retardation caused by a change in birefringence due to sample rotation. (a) For an extraordinary incident beam whose polarization is parallel to the polymer chains, a rotation of the sample about the optical axis of the polymer networks will not cause any change in birefringence, whereas a rotation of the sample about an axis perpendicular to the optical axis will cause changes in birefringence. (b) For an ordinary incident beam, the rotational operates described in picture (a) will not cause any changes in optical birefringence.

the completion of the whole process depends on many conditions. Thiem *et al.* 15]. showed that the polymerization of RM257 was faster in the nematic phase, 50 sec for 80% conversion, than in the isotropic phase, 180 sec for 80% conversion. These conversion times can be much longer in our case as there was no added photo initiator. Furthermore, RM257 is a slow electrically response mesogen, and the response time of the mesogen will be increased drastically as crosslinking proceeding. Therefore, the nematic phase RM257 has less chance to be aligned by the holography irradiation before the completion of the crosslinking of the diacrylate units. In the isotropic state, however, the mesogen might have enough time to be aligned by the holography irradiation before it is polymerized.

4. Conclusion

We demonstrate that crosslinking of diacrylate mesogen RM257 can be initiated by the holography irradiation operating at 488 nm. The holography irradiation acts double as an optical source providing energy for producing free-radicals for the crosslinking of the acrylate units and the driving force for the alignment of mesogenic groups in the diacrylate mesogen. In the holographic field, the mesogenic groups are driven to form a template with a localized molecular ordering, which is determined by the features of the holographic field. The molecular template can be permanently locked up through *in situ* polymerization of the diacrylate mesogen which is initiated by the holography irradiation. Due to the competing of the speed of the polymerization to the time required for the mesogen group to response to the field provided by the holographic irradiation, the diacrylate mesogen should be exposed to holographic irradiation in the isotropic state to obtain the alignment template.

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References

[1] Broer, D. J., Finkelmann, H., & Kondo, K. (1988). *Makromol.*, *189*, 185.

[2] Broer, D. J., Boven, J., Mol, G. N., & Challa, G. (1989). *Makromol. Chem.*, *190*, 2255.

[3] Hikmet, R. A. M., & Broer, D. J. (1991). *Polymer*, *32*, 1627.

[4] Huisman, B. H., Valeton, J. J. P., Nijssen, W., Lub, J., & ten Hoeve, W. (2003). *Adv. Mater.*, *15*, 2002.

[5] Assender, H. E., & Windle, A. H. (1997). *Polymer*, *38*, 677.

[6] Rajaram, C. V., Hudson, S. D., & Chien, L. C. (1995). *Chem. Mater.*, *7*, 2300.

[7] Rajaram, C. V., Hudson, S. D., & Chien, L. C. (1998). *Polymer*, *39*, 5315.

[8] Hikmet, R. A. M., & Broer, D. J. (1991). *Polymer*, *32*, 1627.

[9] Viswanathan, N. K., Balasubramanian, S., Li, L., Tripathy, S. K., & Kumar, J. (1999). *Jpn. J. Appl. Phys.*, *38*, 5928.

[10] Rochon, P., Batalla, E., & Natansohn, A. (1995). *Appl. Phys. Lett.*, *66*, 136.

[11] Kim, D. Y., Tripathy, S. K., Li, L., & Kumar, J. (1995). *Appl. Phys. Lett.*, *66*, 1166.

[12] Kawatsuki, N., Hasegawa, T., Ono, H., & Tamoto, T. (2003). *Adv. Mater.*, *15*, 991.

[13] Ramanujam, P., Pedersen, M., & Hvilsted, S. (1999). *Appl. Phys. Lett.*, *74*, 3227.

[14] Egami, C., Kawata, Y., & Aoshima, Y. (2000). *Jpn. J. Appl. Phys.*, *39*, 1558.

[15] Neumann, J., Wieking, K., & Kip, D. (1999). *Appl. Opt.*, *38*, 5418.

[16] Zheng, W. J., & Yu, S. W. (2009). *Mol. Cryst. Liq. Cryst.*, *511*, 1.

[17] Khoo, I. C., & Wu, S. T. (1993). *Optics and Nonlinear Optics of Liquid Crystals*, World Scientific: Singapore.