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Orientational Crosslinking of Mesogenic Diacrylates in Holographic Interference Field

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Abstract: Orientated acrylate-based polymer networks are produced in holographic field. The mesogenic groups of the diacrylate monomers in the isotropic phase are aligned locally by the holographic field and the polymerization of the monomers is then carried out in situ to lock up the orientational order. The holographic irradiation, created by means of two-beam-interferometry, acts double as the driving force to align mesogenic groups and the optical source for initiating the crosslinking of acrylate end groups.

Key words: diacrylate mesogen; polymer liquid crystals; two-beam interference; orientational order of liquid crystals

介晶双丙烯酸酯在全息干涉光场中的指向性交联

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摘 要: 通过在全息光场中聚合双丙烯酸酯形成具有指向性的分子网络, 所需全息辐射光场由双光束干涉方法产生。在全息光场作用下, 处于各向同性状态中的双丙烯酸酯单体中的介晶分子团被局域定向, 通过原位聚合具有指向状态的单体而形成高分子网络从而将该指向秩序锁定。在此过程中, 全息辐射同时具有两个功能: 既提供促成介晶分子团形成指向秩序的驱动力, 又是启动终端丙烯酸双键进行交联所需的光辐射。

关 键 词: 双丙烯酸酯介晶体; 高分子液晶; 双光束干涉; 液晶指向秩序

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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 in various applications. To manipulate an oriented structure into a polymer network locally to form an optical phase modulator tem-

plate, 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 oriented order can be locked in, and secondly a technique that provides means to drive polymer chains to orient in a desired direction and further to locate the orientational

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structures in predetermined positions. Mesogenic diacrylate consisting of photopolymerisable acrylic end groups can form polymers with network-type structures consisting of a backbone with mesogenic units^[1-2]. The photoinitiated 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 a crosslinked network. Due to their mesogenic nature and anisotropic characters the mesogenic groups in diacrylate monomers in the liquid crystalline phase can be aligned by an electric^[3], a magnetic field^[4], a mechanical shearing, or 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^[5-6]. The induced orientational order can subsequently be frozen in by in situ isothermal photo-polymerisation of the diacrylate mesogen^[7]. 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 is a way through 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 fringes of the interference are parallel to the polarisation of the light beams.

The spatial period Λ of the fringes is given as^[8]:

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

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^[9-14]. The successfulness of holography in azo-based polymers inspired us to apply holography irradiation to pattern orientation of mesogenic groups in diacrylate monomers.

2 Experiments

The polymer thin films were prepared using a commercial mesogenic diacrylate monomer-RM257(1,4-bis[3-(acryloyloxy)propyloxy]-2-methyl benzene) (E. Merck). In the monomeric form, RM257 exhibits the nematic phase in a rather broad temperature range (70 ~ 130 °C). The moderate clearing temperature of the mesogen at 130 °C allows the monomer to be heated into isotropic state without thermally initiating the crosslink of the acrylic end groups. The cells were constructed using glass substrates without any surface treatment other than a sonic cleaning operation. Samples were prepared by capillary injecting RM257 into the cells at an elevated temperature where the diacrylate mesogen was in the isotropic phase. All cells used have a gap of 10 μm . The diacrylate monomer films exhibited normal thermotropic phase transition which can be easily recognized from their optical textures. A particular mesophase of the diacrylate mesogen was obtained by properly controlling the temperature of the sample using a Linkam TMS93 temperature system (Linkam Scientific Instrument). The phase behaviour and the orientation states of the diacrylate mesogen were evaluated using a thermal polarising optical

microscope (POM) system (Axioscop40, Zeiss). Photomicrographs of the optical textures of the samples were taken using a Canon digital camera (PowerShot A620, Canon), which was installed in the polarising microscope.

To produce holographic patterns, a two-beam interferometry system, as schematically shown in Fig. 1, was used. The light source was an Ar^+ laser (2060 Beamlok, 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 $\Delta = 30 \mu\text{m}$ by properly adjusting the angle α .

The effect of holographic irradiation on the polymerisation of RM257 in a thin film form was evaluated by examining phase behaviour of the mesogen: the irradiated mesogen was thought to retain its monomeric form if the phase transition occurred upon the mesogen thermally crossing relevant phase transition temperature, or to be polymerized if no phase transition can be observed upon heating or cooling the mesogen.

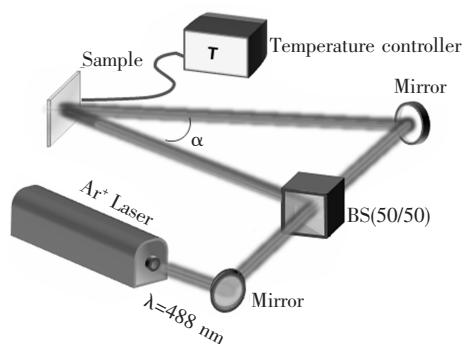


Fig. 1 Optical setup for two-beam interferometry. An s-polarized laser beam is divided by a 50/50 beam split BS, and the two coherent beams are allowed to interfere in the space where a sample is installed. A temperature controller T is used to control sample temperature.

3 Results and Discussion

The crosslinking of the mesogenic diacrylate

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. A low yield of free-radical due to an insufficient optical absorption of the mesogen at 488 nm ^[15] 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.

Fig. 2 shows the optical texture of RM257 sample which was exposed to the holographic irradiation for 30 min. 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 colourful image of the spot results from the difference in the optimum transmitted wavelength for different regions due to the variation in phase retardation, originated from the orientational ordering of the polymer chains, from one region to the other in the exposed spot (cf. equation (2) in a following section). The thermally unchanged optical texture thus indicates, although the degree of the transition of the monomers has not yet been determined, the mesogen in the exposed region has been polymerized to a sufficient high rate, and the molecular ordering of the mesophase where the crosslinking is initiated has been locked in. The optical texture also indicates that an aligned polymer network has not been achieved.

In general, a small amount of a photoinitiator, which provides the free-radicals for initiating chain crosslinking polymerization on exposure to ultra violet irradiation, is demanded. In the

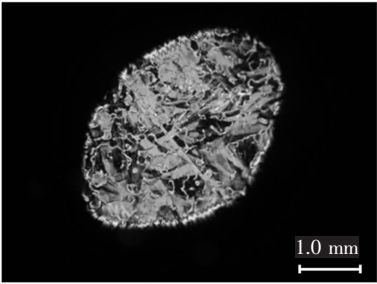


Fig. 2 Photomicrograph of a layer of RM257, which was exposed to the holography irradiation while it was kept in the nematic phase at 110 °C. The photograph was taken while the sample was at 160 °C. The region exhibited the colour texture was exposed to the irradiation, whereas the black region in the picture was unexposed.

present study, no photoinitiator has been added into the diacrylate monomer. The fact that the RM257 thin film has been polymerised in our experiment indicates that the mesogenic monomers has been activated by the holography irradiation operated at wave length $\lambda = 488\text{ nm}$. The optimum exposure period for the polymerization of RM257 has not yet been determined. To guarantee good polymerization of the diacrylate mesogen, all samples discussed in this article were irradiated for 30 min.

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, confirmed by POM observation, found 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 $30\text{ }\mu\text{m}$, and was consistent with that of the holographic irradiation. When the sample was rotated, it can be clearly seen in the POM that there were stripes whose appearance becomes white and black alternately as illustrated in Fig. 3. It is well known that a layer of homogeneously aligned mesogenic material can act like an optical plate, and when such a plate is laid between two crossed polarisers the intensity of light transmitted

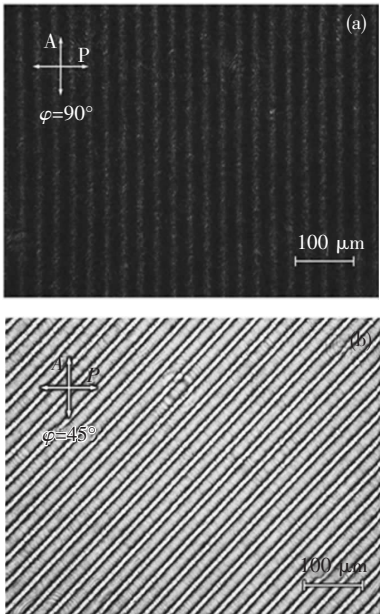


Fig. 3 Photomicrographs showing the gratings pattern recorded in a RM257 polymer plate, with (a) the fringes perpendicular to and (b) making an angle of 45° with respect to the axis of the polariser of the microscope, respectively.

through the system can be described by the following well known equation:

$$T = T_0 \sin^2(2\varphi) \sin^2(\pi \Delta n d / \lambda) \tag{2}$$

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. Fig. 4 shows azimuthal changes in the light transmittance as the sample is rotated, and to follow equation (2). The optical characteristics indicate that the mesogen groups in the regions whose light transmitting intensity vary periodically orient in a unique direction. As the RM257 network is a main chain polymer, we infer that the polymer chains in the regions orient in the same direction. Thus the appearance of the fringes is resulted from a difference in light transmission due to a difference in orientational ordering of the polymer networks in different regions.

In the grating pattern, the appearance of those stripes which always exhibit milky white is resulted from light scattering from the regions due to a random extending of the polymer chains with a short range of orientational ordering. The polymer networks in the striped regions whose light transmittance is described by equation (2), as described previously, are well aligned. Therefore, the orientational order of the polymer networks has been patterned spatially by the holographic irradiation.

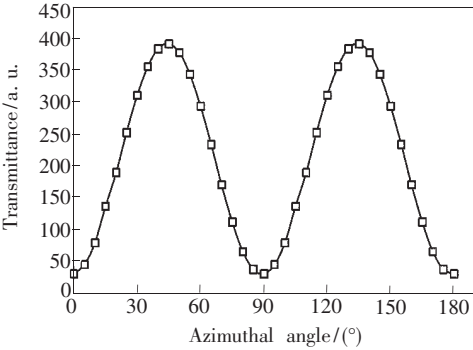


Fig. 4 Azimuthal variation of light transmittance of the RM257 polymer network irradiated by the holographic irradiation when the sample is rotated in the polarising microscope

At this stage, we are unable to map the respective constructive and destructive interference regions of the holography irradiation on the polymer network film. However, knowledge of the orientation of the polymer chains in those aligned regions is important. To determine the orientation of the polymer chains, we placed the sample in the POM, successively aligned the stripes parallel and perpendicular to the transmission axis of the polarizer, i. e. making $\varphi=0$ and $\varphi=\pi/2$, respectively (cf. equation (2)), and then slightly lifted the two adjoining edges of the sample in succession while kept respective opposite edges firmly in touch with the surface of the state of the POM. This causes the sample to rotate a small angle θ about respective edges of the cell in two mutually perpendicular directions. For a uniaxial polymer film, when the polarization of the incident light is parallel to the optical

axis of the polymer film, a rotation about the optical axis will not cause change in $\Delta n=n_e-n_o$ for linearly polarised incident light, and thus nor change in T , whereas any rotation of the polymer film about an axis which is not parallel to the optical axis will cause changes in extraordinary refractive index and the optical birefringence Δn in equation (2) is replaced by an effective refractive index difference $\Delta n_e=n_{\text{eff}}-n_o$, with $n_{\text{eff}}=n_on_e/\sqrt{n_o^2\sin^2\theta+n_e^2\cos^2\theta}$, leading to a change in T . Our measurements revealed that the orientation of mesogenic groups in those aligned regions is perpendicular to the fringes. As the fringes generated by s-polarised light beams are parallel to the polarisation of the light beams, we thus infer that the holography irradiation drives the mesogenic groups oriented perpendicular to the polarization of the writing beam.

4 Conclusion

Crosslinking of diacrylate mesogen RM257 can be initiated by the holography irradiation operating in visible band (e. g. $\lambda=488\text{ nm}$). The structures with orientational molecular ordering can be formed in the diacrylate based polymer network. The holographic irradiation acts double as an optical source providing energy to activate reacting groups for crosslinking of acrylate units and the driving force for the alignment of mesogenic groups in the diacrylate mesogen. The orientational order of the polymer chains can be patterned in the polymer networks by means of holography. To achieve oriented polymer networks the crosslinking of diacrylate should be carried out in the isotropic phase of the mesogen. The results attained show that the diacrylate mesogen RM257 is a promising material can be used for optical storage and in photonic applications. Besides, the holography irradiation induced polymerisation of diacrylate monomers provides a way for producing orientational polymer networks and can be a useful tool in processing polymeric photonic materials.

References:

- [1] Broer D J, Finkelmann H, Kondo K. In-situ photopolymerization of an oriented liquid-crystalline acrylate [J]. *Makromol.*, 1988, 189(1):185-194.
- [2] Broer D J, Boven J, Mol G N, *et al.* In-situ photopolymerization of oriented liquid-crystalline acrylates, 3. Oriented polymer networks from a mesogenic diacrylate [J]. *Makromol. Chem.*, 1989, 190(9):2255-2268.
- [3] Huisman B H, Valetton J J P, Nijssen W, *et al.* Oligothiophene-based networks applied for field-effect transistors [J]. *Adv. Mater.*, 2003, 15(23):2002-2005.
- [4] Assender H E, Windle A H. Domain structures in magnetically orientated liquid crystalline polymers [J]. *Polymer*, 1997, 38(3):677-688.
- [5] Rajaram C V, Hudson S D, Chien L C. Morphology of polymer-stabilized liquid crystals [J]. *Chem Mater.*, 1995, 7(12):2300-2308.
- [6] Rajaram C V, Hudson S D, Chien L C. Morphology of diacrylate copolymer networks formed in liquid crystalline media [J]. *Polymer*, 1998, 39(22):5315-5319.
- [7] Hikmet R A M, Broer D J. Dynamic mechanical properties of anisotropic networks formed by liquid crystalline acrylates [J]. *Polymer*, 1991, 32 (9): 1627-1632.
- [8] Viswanathan N K, Balasubramanian S, Li L, *et al.* A detailed investigation of the polarization-dependent surface-relief-grating formation process on Azo polymer films [J]. *Jpn. J. Appl. Phys.*, 1999, 38(10):5928 -5937.
- [9] Rochon P, Batalla E, Natansohn A. Optically induced surface gratings on azoaromatic polymer films [J]. *Appl. Phys. Lett.*, 1995, 66(2):136-138.
- [10] Kim D Y, Tripathy S K, Li L, Kumar J. Laser-induced holographic surface relief gratings on nonlinear optical polymer films [J]. *Appl. Phys. Lett.*, 1995, 66(10):1166-1168.
- [11] Kawatsuki N, Hasegawa T, Ono H, *et al.* Formation of polarization gratings and surface relief gratings in photocrosslinkable liquid crystals by polarization holography [J]. *Adv. Mater.*, 2003, 15(12):991-994.
- [12] Ramanujam P, Pedersen M, Hvilsted S. Instant holography [J]. *Appl. Phys. Lett.*, 1999, 74 (21):3227-3229.
- [13] Egami C, Kawata Y, Aoshima Y. Two-stage optical data storage in azo polymers [J]. *Jpn. J. Appl. Phys.*, 2000, 39(3B):1558-1361.
- [14] Neumann J, Wieking K, Kip D. Direct laser writing of surface reliefs in dry, self-developing photopolymer films [J]. *Appl. Opt.*, 1999, 38(25):5418-5421.
- [15] Thiem H, Strohriegl P, Shkunov M, *et al.* Photopolymerization of reactive mesogens [J]. *Macromol. Chem. Phys.*, 2005, 206(21):2153-2159.