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Alignment control of liquid crystals on surface relief gratings

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Alignment control of liquid crystals on surface relief gratings

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Liquid crystal alignment layers of a high T_g polymer containing an azobenzene moiety are prepared by photofabrication of a surface relief grating (SRG). The interference pattern of a circular and linearly polarized Ar^+ laser beam generated the surface relief grating and the morphology was detected by atomic force microscope. The optical anisotropy of the films was investigated by polarizing optical microscopy. The orientation of the optical axis of the film mainly depends on the direction of the initial polarization plane. Nematic liquid crystals were aligned parallel to the direction of the grating, but the pretilt angles of the liquid crystals were nearly zero. Irradiation with homogeneous linearly polarized light could also align liquid crystals, but this alignment capability was weaker than that of the SRG film.

1. Introduction

A liquid crystal display (LCD) is one of the typical examples of molecular electronics, and the alignment of liquid crystals has been of keen interest not only because of industrial applications, but also because of scientific curiosity. Though many devices are produced by a simple rubbing method, non-rubbing treatments have been studied for the surfaces of polymer films submitted to SiO evaporation [1], by the Langmuir-Blodgett method [2] and using photoalignment [3–16]. Among these, the photoalignment of liquid crystals, which controls the orientation of the LC with light, is becoming important in technology. Various methods of photocontrol have been reported. The liquid crystals have been aligned on the surfaces with photoisomerizable molecules [3–8], which undergo *cis-trans*-configurational changes on irradiating with light; and polymers doped with azo dye induce the orientation of liquid crystals using linearly polarized light [9–14]. Photoreactive polymers such as poly(vinyl cinnamate) could also induce the orientation of nematic liquid crystals using linearly polarized UV light [15, 16]. Another type of photo-orientation includes the photodegradation of high T_g polymers such as polyimide with linearly polarized UV light [17] and the generation of gratings by laser etching [18]. In recent years, the surface relief grating (SRG) on polymer films functionalized with azobenzene has become attractive for optical and electronic devices [19–21]. In this paper, the alignment control of nematic liquid crystals on polymer surfaces with a surface relief grating is discussed.

2. Experimental

A maleimide-based high T_g polymer (PMPD35, $M_n \sim 2.5 \times 10^4$) was used and details of the synthesis and chemical characterization of the PMPDs have been reported previously [22]. PMPD35 contains 35% dye chromophore relative to all the repeating units, that is, the *y* value in figure 1; this figure is the degree of dye functionalization. A 5 wt % solution of PMPD35 in chloroform was spin-coated at a speed of 700 rpm onto the glass substrate. The thickness of the film was measured by a mechanical stylus profiler (Tensor instruments, Alpha-step 300). The thickness of the coated films ranged from 0.9 to 1.0 μm. The optically induced surface gratings were recorded on the polymer film by exposing to an interference pattern. Figure 2 shows the experimental set-up for the generation of the surface relief grating. The interference pattern was produced by two coherent beams from an Ar^+ laser (488 nm) of intensity 40 mW cm^{-2}. Polarization of the Ar^+ laser beam was

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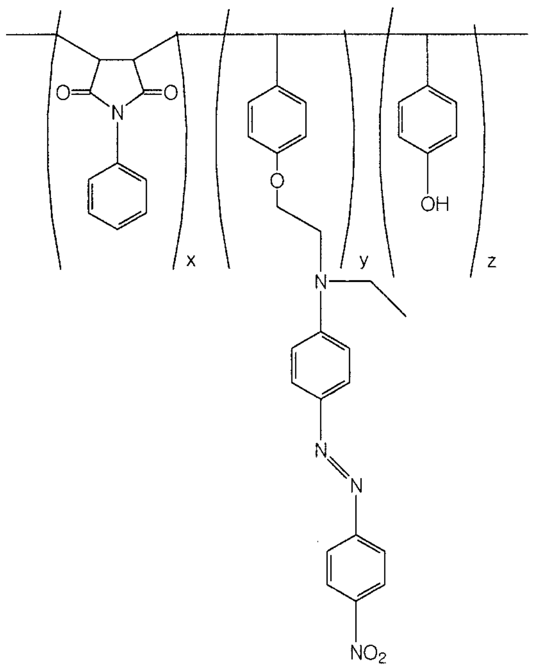


Figure 1. Molecular structure of the high T_g polymer PMPD.

varied by using a half-wave plate for linear polarization and a quarter-wave plate for circular polarization. The diffraction efficiency of the first order diffracted beam from the surface gratings in the transmission mode was probed with an unpolarized, low power, He-Ne laser beam at 633 nm. The systematic study of the photo-fabrication of SRGs with this polymer has been reported elsewhere [23].

The depth modulation and the pitch of the surface gratings were observed by atomic force microscopy (AFM) (Digital Instruments Inc., Nanoscope IIIa) using a contact mode. The optical anisotropy of the PMPD35 polymer films was investigated by a polarizing optical microscope (Nikon, Optiphot2-pol) with a monochromic filter and by polarized UV-Vis spectroscopy. The polymer coated glass substrates were assembled in an anti-parallel direction for all the experiments except for making a twisted nematic cell. The gap between the two substrates was fixed by inserting polystyrene particles of size 5 μm into the UV-curable adhesive. After curing the adhesive by irradiating with a UV lamp for 5 min, two nematic liquid crystal materials (E7 and MLC-6418-1R, E. Merck) were filled into the cell as the isotropic liquids by capillary forces. The texture and the optical anisotropy of the liquid crystal in the cells were observed by polarizing optical microscopy. The pretilt angles of the liquid crystals were measured by the crystal rotation method.

3. Results and discussion

3.1. *Surface morphology of the polymer*

Figure 3 shows the AFM images of the films of high T_g PMPD35 with the SRG of three different polarizations. The depth modulation of the samples with 40 mW cm^{-2} for 4000 s was about 130–140 nm, though the diffraction efficiencies were slightly different dependent upon the kinds of polarization. The depth resolution showed a linear relationship with photon dose or irradiated time, as reported previously [23].

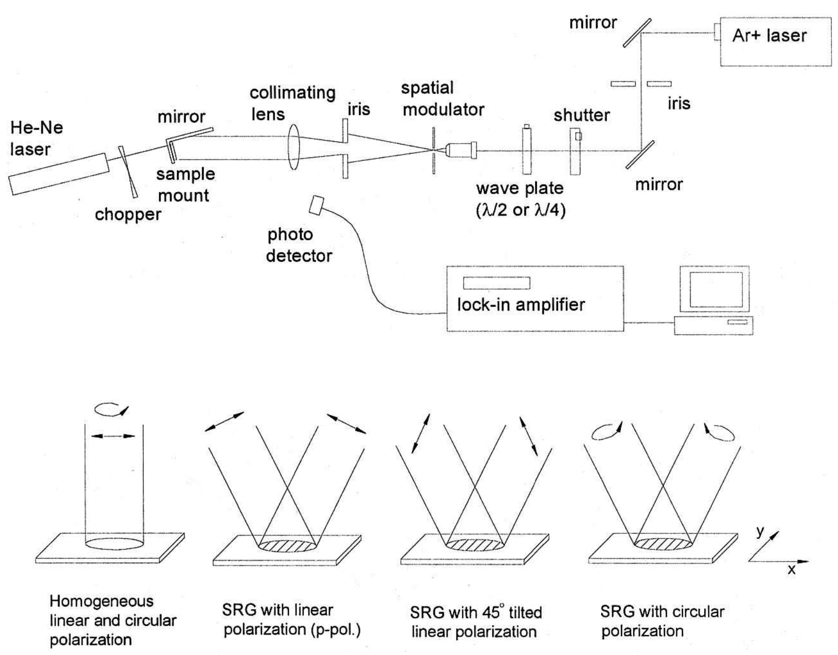
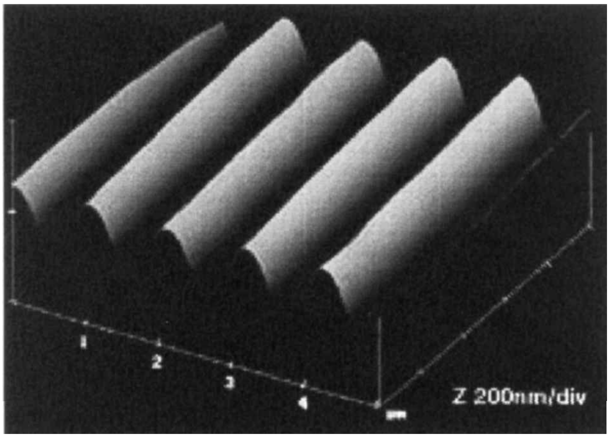


Figure 2. Experimental set-up for generation of the SRG.



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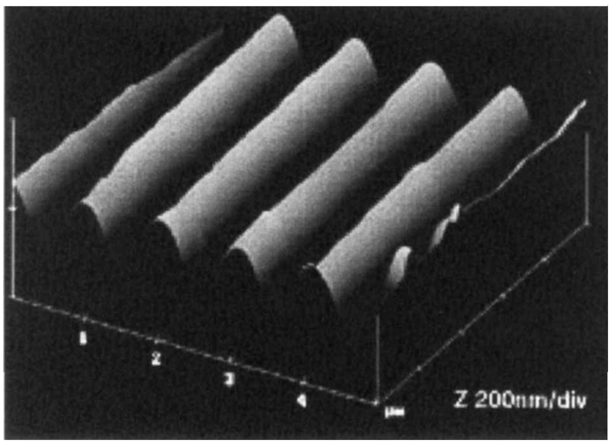

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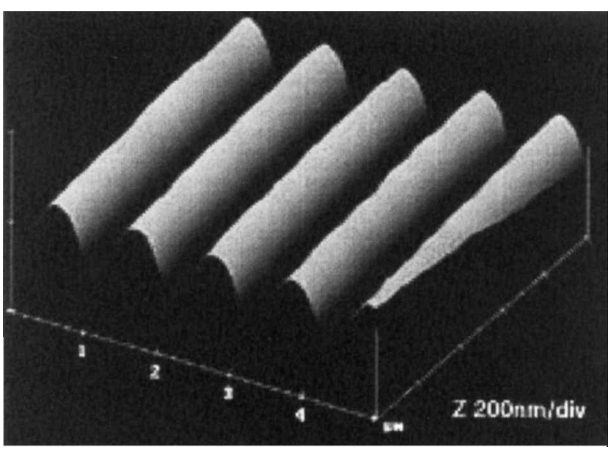

(*c*)

Figure 3. AFM images of SRG films: (*a*) SRG with p-pol., (*b*) SRG with 45° tilted linear pol., (*c*) SRG with circular pol.

3.2. *Optical anisotropy of the films*

We made five different films irradiated with the same laser intensity and investigated the optical anisotropies of the films. Figure 4 shows the optical anisotropy of

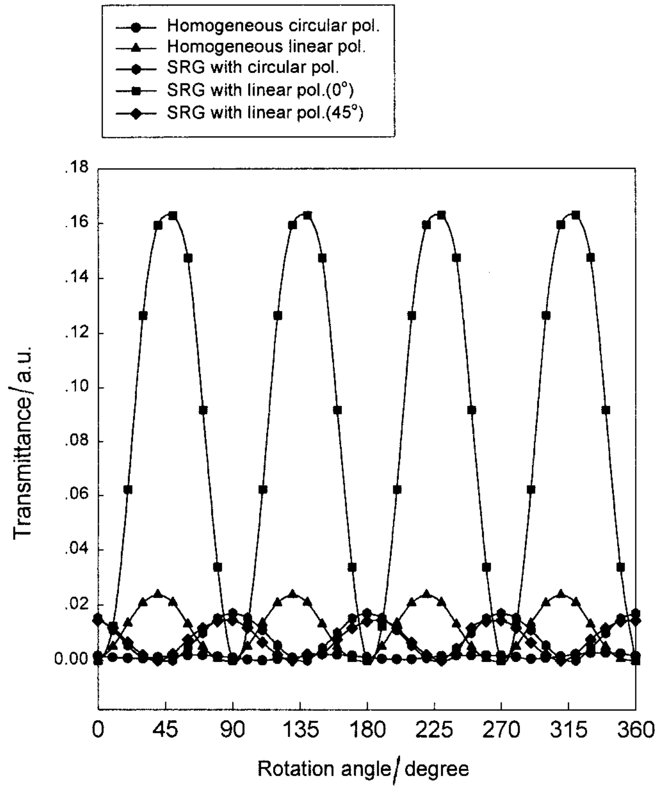

Figure 4. Optical anisotropy of the PMPD polymer films measured by polarizing microscopy.

the PMPD35 polymer films measured using crossed polarizers by polarizing microscopy. All the samples of SRG film except that having homogeneous circular polarization showed optical anisotropy mainly due to the selective response of the dye chromophore to the irradiating laser light. The transmittance changed periodically with a regular 90° separation of the rotation angle, which is in agreement with the following equation

$$T = \sin^2 2\Phi \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right). \tag{1}$$

The films with homogeneous irradiation of linear polarization and SRG with p-pol. showed that the alignment of the chromophore was in the same direction as that of the polarizers of the microscope. However, the SRG films with circular and 45° tilted linear pol. showed the 45° shifted maxima in figure 4, indicating that the optical axis of the polymer was rotated relative to the polarizers. It is interesting that the direction of the optical anisotropy is mainly dependent on the direction of the initial polarization plane. In the case of the SRG film with p-pol., the plot showed a large anisotropy compared with that of homogeneously irradiated film with linear polarization. This indicates that the orientation of the polymer was motivated by mass transport due to the gradient of the light during the SRG process [24]. All the SRG films showed diffraction efficiencies contributed to by an anisotropic (or birefringence) part and a surface relief part. Though the films showed a relaxation of the diffraction efficiencies when the laser was turned off, the relaxation of the induced birefringence grating was relatively slower than for other low T_g polymers with azo moeties.

In order to determine the orientational direction of the chromophore, the absorbance using polarized UV-Vis spectroscopy was observed. Figure 5 shows the polarized UV-Vis absorbances of a PMPD35 film with homogeneous irradiation of linear polarization. The cell axis is defined as the direction of the polarization plane of an irradiating laser. The SRG film with linear p-pol. also showed dichroism of the polarized UV-Vis absorbance as shown in figure 6. To check the angular orientation of the chromophore, the absorbances of the dye at 488 nm were measured as a function of the rotation angle. Figure 7 shows the polar plot of the polarized absorbance spectra of the homogeneously irradiated PMPD35 film, and figure 8 that for the SRG film with p-polarization. The dichroism showed that the chromophore was oriented perpendicular to the direction of the irradiated light, which is the same as that observed for a photosensitive azo-dye polymer. The dichroic ratio ($A_{\|}/A$) of the SRG film with p-pol. was 0.975, lower than that of the film with homogeneous linear pol., 0.989, agreeing with the results from polarizing microscopy.

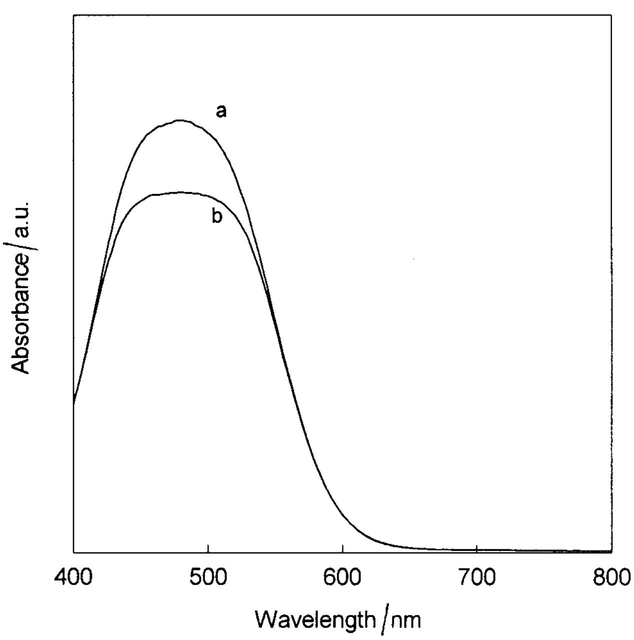

Figure 5. Polarized UV-Vis absorbance of PMPD film with irradiation by homogeneous linear polarization: (*a*) light is perpendicular to pol., (*b*) light is parallel to pol.

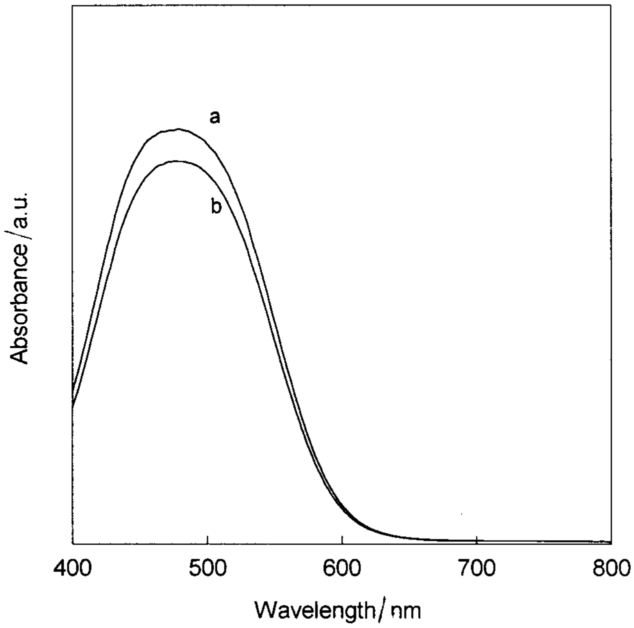

Figure 6. Polarized UV-Vis absorbance of SRG film with linear pol. (*a*) light is perpendicular to pol., grating is parallel to pol. (*b*) light is parallel to pol., grating is perpendicular to pol.

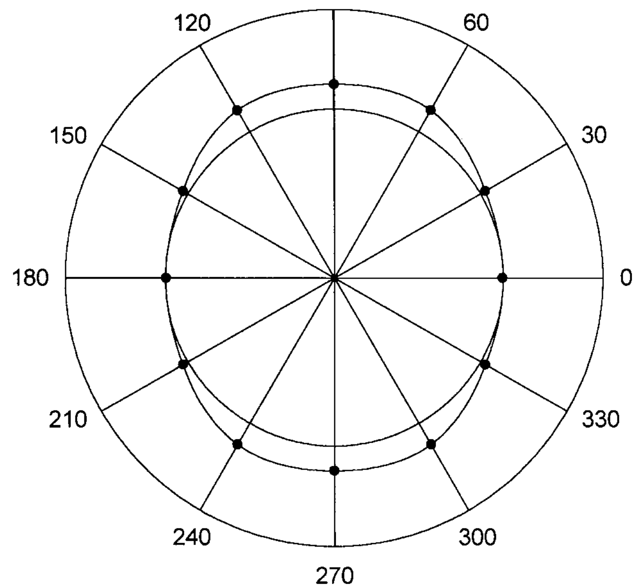

Figure 7. Polar plot of the polarized absorbance spectra at 488 nm of PMPD films with irradiation of linear polarization; polarizer is parallel to the direction of irradiating polarization.

3.3. *Optical anisotropy of the LC cell*

After assembling the LC cell with an anti-parallel structure, the textures of the liquid crystals were observed by the polarizing microscope. The SRG region was hemispherical with a diameter of 1 cm. The texture of both

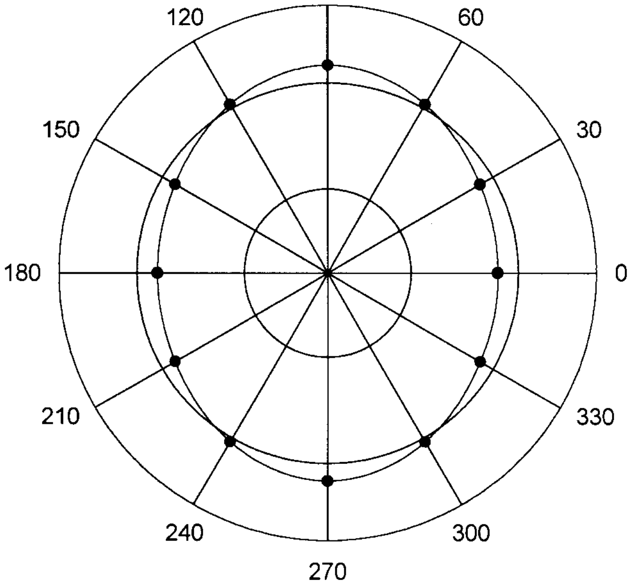

Figure 8. Polar plot of the polarized absorbance spectra at 488 nm of PMPD SRG films with irradiation of p-polarization; polarizer is parallel to the direction of irradiating polarization and perpendicular to the grating.

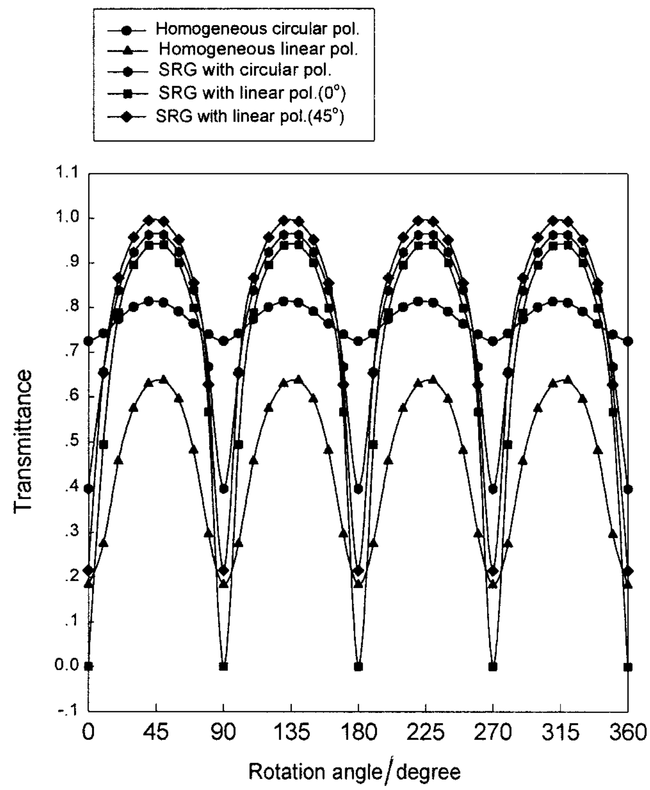

Figure 9. Optical anisotropy of LC cell (MLC-6418-1R) by polarizing microscopy.

nematic liquid crystals in the SRG region showed a homogeneous alignment, but the orientation of the liquid crystal between the films showed a random orientation when irradiated with homogeneous circular polarization. The nematic liquid crystals in the SRG region were aligned along the direction of the surface gratings, as detected by a pretilt angle measurement set-up. The LC cell with homogeneous irradiation of linear pol. could also align the liquid crystal in a homogeneous orientation due to the orientation effect of the azo moiety. The alignment of the nematic liquid crystals with homogenous irradiation of linear polarization was perpendicular to the direction of the polarization plane. Figures 9 and 10 show the transmittances of the LC cells between two crossed polarizers obtained by polarizing microscopy. Though the transmittance curve shows that the LC molecules align uniaxially to give a homogeneous alignment, some samples transmitted light with a 90° rotation angle periodicity. The low contrast in the LC cells of the SRG films with circular and 45° tilted linear pol. was caused by the optical anisotropy of the bare polymer, because their optic axes were tilted with respect to the axis of the polarizers in the microscope. This result can be seen in the figure for the polarizing microscopy of the bare polymer. The pretilt angles of the liquid crystals were measured by the crystal rotation method as shown in figure 11. The values were nearly zero, because there was no anisotropy in the direction of orientation of the liquid crystals.

3.4. *UV bleaching effect of the SRG film*

To investigate the effect of UV bleaching of the SRG film, a low pressure mercury lamp (365 nm) of 1.7 mW cm^{-2} was used to irradiate the polymer for 2 h. The unpolarized UV light bleached the polymer resulting from the disturbance of the SRG structure. Just as irradiation with unpolarized laser light disturbed the SRG structure, the UV treatment of the SRG film changed the holographic colour of the film to pale yellow. AFM images of the films showed that there were no gratings on the films after UV irradiation. Also, the liquid crystals between the substrates showed a random orientation.

3.5. *Heating effect on the SRG film*

To detect the effect of temperature, the SRG films were heated. The T_g of the polymer is 177°C, and samples were heated to 250°C, and held there for 20 min. The relaxation of the polymer caused the orientation of the liquid crystals to randomize with vanishing of the original colour, a similar effect to that in the UV bleaching experiment. Figure 12 shows how the optical anisotropy of the LC cell (MLC-6418-1R) is affected by the UV bleaching and heating, as measured by polarizing microscopy.

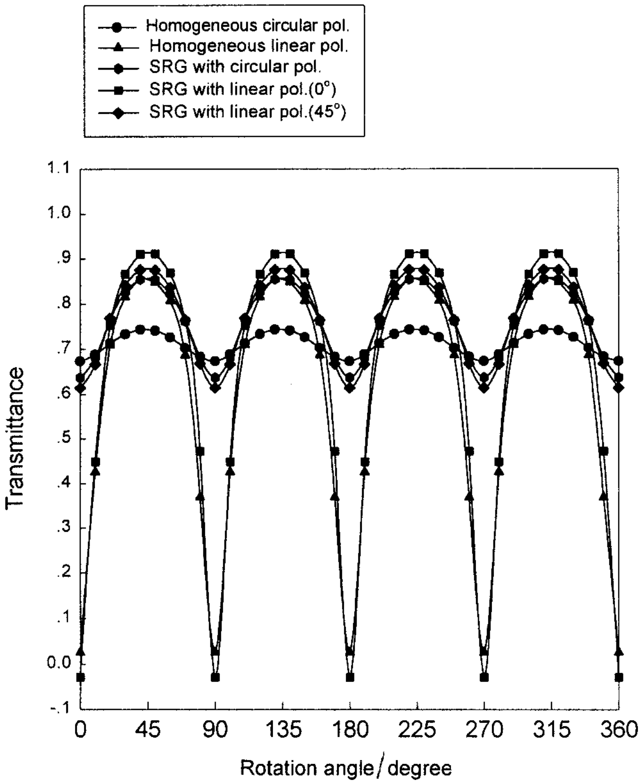

Figure 10. Optical anisotropy of LC (E7) cell by polarizing microscopy.

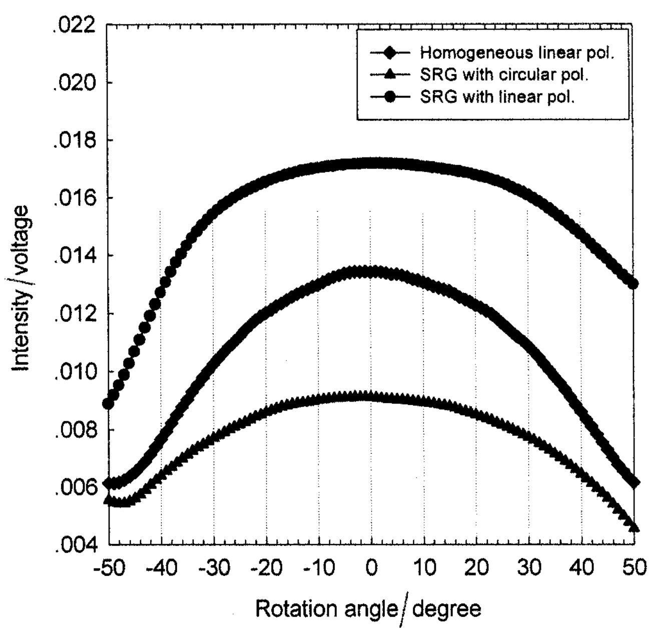

Figure 11. Pretilt angle of LC cell with PMPD polymer by the crystal rotation method.

3.6. *Anchoring energy of the SRG films*

The anchoring of the liquid crystal molecules to the grating-aligned surface was investigated by measuring

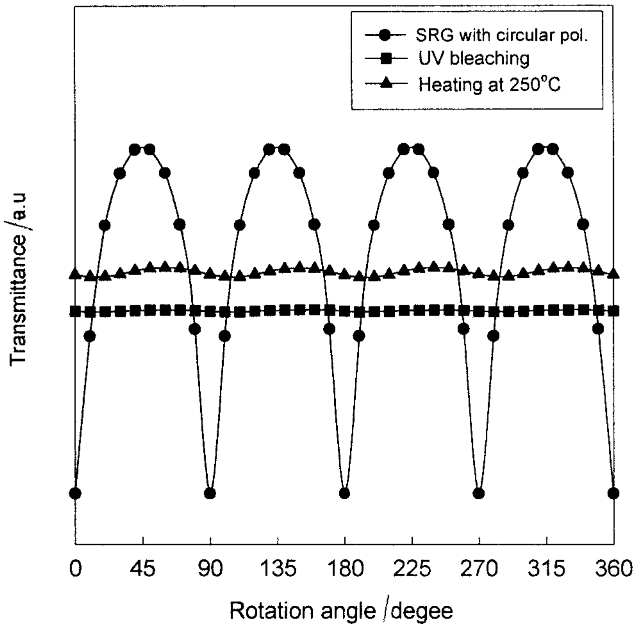

Figure 12. Optical anisotropy of LC cell (MLC-6418-1R) measured by polarizing microscopy and showing the effect of UV bleaching and heating.

the azimuthal anchoring energy of the twisted nematic cells with one rubbed polyimide surface and one SRG film. The twist angles were determined by polarizing microscopy by rotating the analyser. The azimuthal anchoring energy can be obtained from the equation [25]

$$E = \frac{2K_{22}\phi}{d \sin 2\phi} \tag{2}$$

where K_{22} is the twist elastic constant and d is the cell gap. The anchoring energy of the E7 cell of 5 μm cell gap was calculated for SRG films with circular and p-polarization. The SRG film of p-pol. showed 85.1° of twist angle, ϕ, giving the anchoring energy 1.82×10^{-5} J m^{-2}. The SRG film with circular polarization gave 84.5°, giving the value 1.61×10^{-5} J m^{-2}.

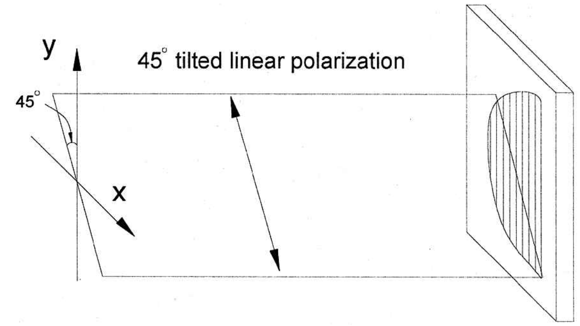

Figure 13. Irradiation of 45° tilted homogeneous linear polarization on SRG films with circular polarization.

The elastic constants of splay (K_{11}), twist (K_{22}), and bend (K_{33}) for E7 liquid crystal are 1.1×10^{-11}, 5.2×10^{-12}, and 1.7×10^{-11} N, respectively. The surface anchoring energy at the grating is expressed by the equation [26]

$$E = \frac{2Ku^2\pi^3}{\Lambda^3} \quad (3)$$

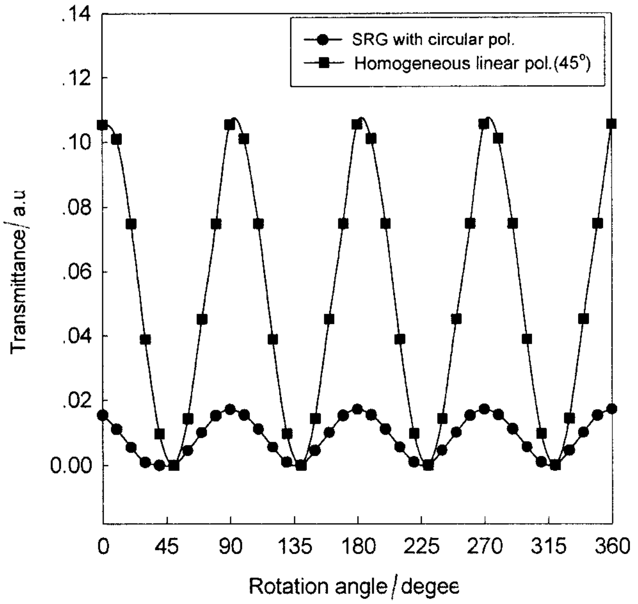

Figure 14. Optical anisotropy of PMPD films by polarizing microscopy.

where u is the depth modulation, Λ is the pitch of the grating, and K is the mean of the splay and bend elastic constants. The SRG film of p-pol. with 1.0 µm of pitch and 140 nm of depth modulation gave the value 1.70×10^{-5} J m^{-2}, and the SRG film of circular pol. with 1.0 µm of pitch and 130 nm of depth modulation gave 1.47×10^{-5} J m^{-2}. The measured values were higher than those calculated, because of the extra energy caused by the orientational effect of the azo-dye polymer. In the case of SRG film with linear pol., the orientation of the chromophore can effect the orientation of the liquid crystals.

To compare the ability to align the liquid crystals, homogeneous linear polarization was applied to the 45° tilted direction from the grating on the SRG of circular polarization in figure 13, because the 45° tilted homogeneous irradiation of linearly polarized light does not change the diffraction efficiency of the SRG film. In figure 14, the transmittance of the polarized light showed that the direction of the optical anisotropy of the film rotated to 45° from the direction of the grating was increased by the irradiation with homogeneous linear polarization. Assembling the LC cell anti-parallel to the grating direction, we observed the texture of the LC by polarizing microscopy. In figure 15, the liquid crystals in the hemispherical SRG region showed a homogeneous alignment parallel to the gratings, while the other region showed the twisted nematic structure caused by the orientational effect of the dye chromophore. If the orientational effect of the dye chromophore exceeds the effect

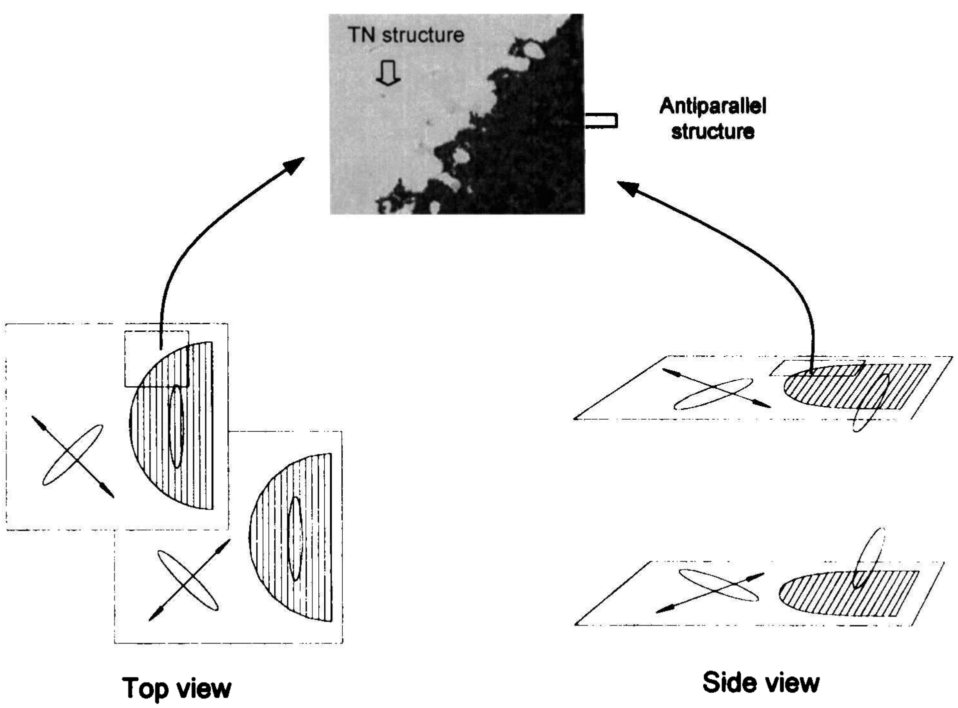

Figure 15. Polarizing microscopic image of the LC cell and the structure of the cell.

of the grating, all the regions of the cell must have the TN structure. This result clearly indicates that the liquid crystals were aligned mainly due to formation of gratings, which agrees with the result of the lower anchoring energy value calculated for PVCi without relief [25, 27].

4. Conclusions

Liquid crystal alignment layers of a maleimide-based high T_g polymer containing an azobenzene moiety have been prepared by photofabrication of a surface relief grating. The depth modulations of the samples with 160 J cm^{-2} of photon dose were in the range of 130–140 nm. The optical anisotropy of the films with homogeneous irradiation of linear polarization and SRG with p-pol. showed the direction of the chromophore perpendicular to the direction of the irradiated polarization plane, while the SRG films with circular and 45° tilted linear polarization showed 45° shifted maxima from the polarizers. The orientation of the optical axis of the film mainly depends on the direction of the initial polarization plane. Nematic liquid crystals were aligned parallel to the direction of the grating, but the pretilt angles of the liquid crystals were nearly zero. Irradiation with unpolarized UV light and heating of the polymer to 250°C disturbed the SRG structure and the liquid crystals between the substrates showed a random orientation. The measured surface anchoring energies of the SRG films with linear p-pol. and circular polarization were 1.70×10^{-5} and 1.47×10^{-5} J m^{-2}, respectively. Irradiation with the homogeneous linearly polarized light could also align the liquid crystals, but the ability to orient the liquid crystals was weaker than that of the SRG film. As a result, the liquid crystals were aligned mainly due to formation of gratings and the SRG technique is therefore a useful method for orienting liquid crystals in the field of optical devices.

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