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Ion beam induced liquid crystal alignment properties of 4-alkylphenoxymethyl-substituted polystyrenes

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The pretilt angles of liquid crystals (LCs) can be controlled over the range 0° to 90° using ion beam treated 4-alkylphenoxymethyl-substituted polystyrene films as alignment layers, where the alkyl group is $–(CH_2)_nH$ ($n = 1, 2$ or 4), by changing the ion beam irradiation time, incidence angle and energy. In general, LC cells made using a polymer film with a longer irradiation time, higher irradiation incidence angle with respect to the planar direction and higher irradiation energy exhibited lower pretilt angles relative to the planar direction. Furthermore, the LC cells produced using polymer films containing longer alkyl groups and a higher molar content of 4-alkylphenoxymethyl side groups exhibited greater pretilt angles under similar irradiation conditions. The LC alignment behaviour demonstrated good correlation with the wettability of the polymer films, due to fragmentation of the side groups on the polymer surfaces during ion beam irradiation. The electro-optical characteristics of the LC cells formed using these polymer films were similar to those produced using rubbed polyimide films, which are the LC alignment layers most commonly encountered.

Keywords: liquid crystal; alignment; ion beam; polystyrene

1. Introduction

Mechanical rubbing of polymeric substrates has been widely studied as a method of aligning liquid crystals (LCs) for applications in LC flat panel displays, even though the rubbing process has disadvantages such as generation of electrostatic charge, dust formation and physical damage to the LC alignment layer surfaces [1–22]. Furthermore, the pretilt angle of LCs on the alignment layer surfaces cannot readily be controlled using the rubbing technique. Non-contact LC alignment methods have therefore been investigated in order to overcome these disadvantages [23–27].

In particular, the ion beam alignment method offers a number of advantages; for example, it is a clean process free from dust generation and it allows continuous control of the pretilt angle by changing the irradiation time, incidence angle and energy of the ion beam. A number of organic and inorganic materials have been studied as ion beam LC alignment layers, for example:

- polyimides [28–32];
- polystyrene [33];
- polymers such as poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) [34] and 4-(*N*-methacryloylamino)phenylmethacrylate with 2,2,3,3,4,4,5,5-octafluoropentyl-methacrylate (MAPhM-F8) [35];
- acrylic overcoat material [36];
- diamond-like carbon [26, 27, 37–41];
- metal oxides, including high-*k* oxides [42–46]; and
- silicon compounds such as silicon dioxide [47–50], silicon carbide [51–53], silicon nitride [54] and silicon oxynitride [55].

Recently, we have found that polystyrene surfaces may be prepared at low temperatures, producing homogeneous planar and/or homeotropic LC alignment layers suitable for fabricating flexible plastic-based displays [56–63]. For example, the side chain structure, which consists of two phenyl groups and an alkyl group in the 4-position of the phenoxy groups of 4-alkylphenoxymethyl-substituted polystyrenes, can induce strong homeotropic LC alignment behaviour [62].

In the present paper, the LC alignment properties of LC cells fabricated using the ion beam treated films of 4-alkylphenoxymethyl-substituted polystyrenes (Figure 1) are examined in terms of ion beam irradiation time, incidence angle and energy. The electro-optical performance of the LC cells produced using ion beam treated 4-alkylphenoxymethyl-substituted polystyrene films is also included.

2. Experimental

2.1 Materials

4-Methylphenoxymethyl-substituted polystyrene (P4MP), 4-ethylphenoxymethyl-substituted polystyrenes (P4EP*x*,

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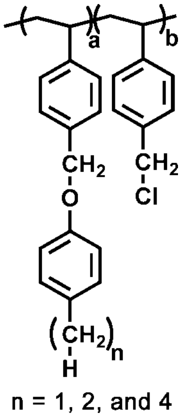


Figure 1. Chemical structure of 4-alkylphenoxymethyl-substituted polystyrenes.

where x is the molar content of 4-ethylphenoxymethyl side groups in per cent), and 4-butylphenoxymethyl-substituted polystyrene (P4BP) have been used, as reported in a previous paper [62]. Pre-imidised alignment agent AL60101 was supplied by Japan Synthetic Rubber Co. Ltd. All other reagents and solvents were used as received.

2.2 *Film preparation and LC alignment process*

Solutions of P4MP, P4EPx and P4BP in toluene (2 wt%) were prepared. The solutions were filtered using a **polytetrafluoroethylene (**PTFE) membrane with pore size of 0.45 μm. P4MP, P4EPx and P4BP films were prepared by spin-coating (2000 rpm, 30 s) on to 1.5 cm × 1.5 cm glass substrates coated with indium tin oxide (ITO). Films coated with pre-imidised alignment agent AL60101 were produced by spin-coating (3000 rpm, 20 s) on 1.5 cm × 1.5 cm ITO-coated glass substrates. The AL60101 films were pre-baked at 70°C for 5 min and then fully baked at 200°C for 60 min. The polymer films were treated using ion beam irradiation (Kaufman Ar ion gun), as shown in Figure 2.

The ion beam irradiation incidence angle varied from 30° to 75° relative to the planar direction. The ion beam irradiation energies ranged from 100 eV to 200 eV, and an ion beam current density of 0.75 μA cm^{-2} was used. The polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corporation, Korea). The rubbing density equation may be written as

$$L/l = N[(2\pi rn/60v) - 1]$$

where L is the total length of the rubbing cloth (mm), l is the contact length of the circumference of the rubbing roller (mm), N is the cumulative number of rubbings, n is the speed (rpm) of the rubbing roller, r is the radius (cm) of the rubbing roller and v is the velocity (cm s^{-1}) of the substrate stage [9, 11].

2.3 *LC cell assembly*

Twisted nematic (TN) and antiparallel LC cells were produced using untreated or treated ion beam polymer films on ITO-coated glass slides. The TN LC cells were formed by assembling the polymer films orthogonally with respect to the ion beam incidence direction using a spacer of 4.5 μm thickness. The antiparallel LC cells were constructed by assembling the polymer films antiparallel to the ion beam incidence direction using spacers of 4.5 and 50 μm thicknesses. The LC cells

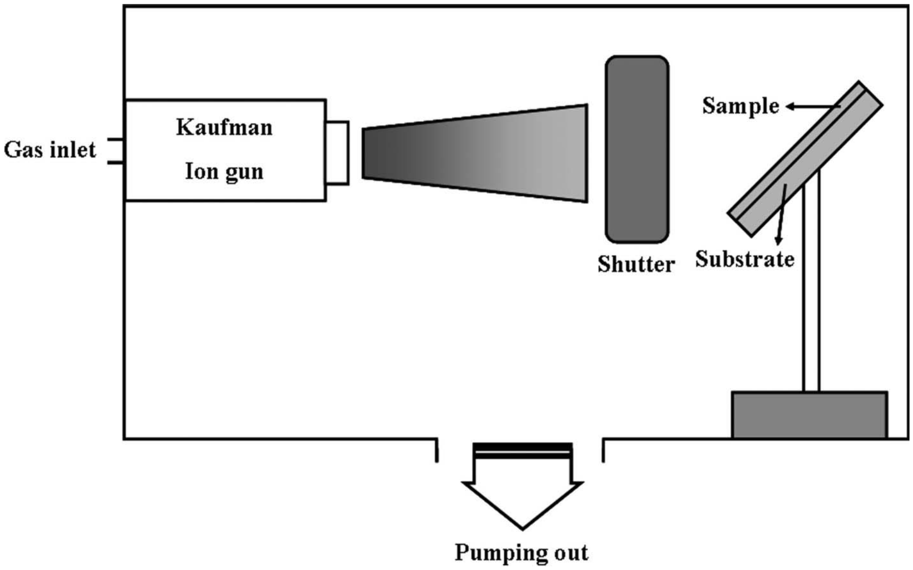


Figure 2. Ion beam irradiation system.

were filled with two nematic LCs, 5CB (Merck & Co. Inc., $n_e = 1.7360$, $n_o = 1.5442$ and $\Delta\varepsilon = 14.5$, where n_e, n_o and $\Delta\varepsilon$ represent extraordinary refractive indexes, ordinary refractive indexes and dielectric anisotropy, respectively), and MLC-7026-000 (Merck & Co. Inc., $n_e = 1.5577$, $n_o = 1.4755$ and $\Delta\varepsilon = -3.7$), in the isotropic state in order to avoid creating flow alignment by capillary action, and then sealed with epoxy resin.

2.4 Instrumentation

UV–Vis spectra were produced using an Agilent 8453 UV/VIS spectrophotometer. For the UV–Vis spectra of P4EP, the polymer films were prepared by spin-coating 2 wt% P4EP solutions in toluene on ITO-coated glass substrates at 2000 rpm for 30 s. The surface morphology of the ion beam untreated or treated polymer films in an area of 3 μm × 3 μm was examined using atomic force microscopy (AFM; XE-150, PSIA) in non-contact mode (spring constant of the cantilever: 0.6 N m^{-1}, scan rate 1 Hz). Static contact angles for 4 μL of distilled water on the polymer films were determined using a Kruss DSA10 contact angle analyser equipped with drop-shape analysis software. The electron spectroscopy for chemical analysis (ESCA) experiments was performed in an ultra-high vacuum multipurpose surface analysis system (Thermo Scientific, Sigma Probe, UK) operating at base pressures of less than 10^{-10} mbar. The photoelectron spectra were excited by an Al K_α (1486.6 eV) anode operating at constant power of 100 W (15 kV and 10 mA). During determination of the spectra the constant analyser energy mode was employed, at a pass energy of 40 eV and steps of 0.1 eV, at a take-off angle of 90°. Core peaks were analysed using a linear-type background, and peak positions and areas were obtained by a fitting programme (Thermo Scientific, Avantage Data System) using a least-square fit of model curves (70% Gaussian, 30% Lorentzian) to the experimental data. The cell gap was measured before LC filling using a spectrophotometer (Ocean Optics Inc., S2000). Polarised optical microscopy (POM) images of the LC cells were taken from an optical microscope (BX60, Olympus, Japan) equipped with polariser and digital camera (Olympus C–2020 Zoom). The electro-optical properties of the LC cells were investigated using optical apparatus equipped with a He–Ne laser, polariser, analyser and a photodiode detector. The LC alignment direction of the antiparallel LC cells was investigated by measuring the angular dependence of the absorbance of a dichroic dye (CI Disperse Blue 1, Aldrich) dissolved at 1 wt% in 5CB using an optical apparatus equipped with a He–Ne laser, a polariser, and a photodiode detector as a function of rotation angle of samples [11]. The pretilt angle of LCs with respect to the planar direction in an antiparallel LC cell was measured by a modified crystal rotation method using PAMS series (Sesim Photonics Technology, Korea) [64]. The voltage–transmittance (*V–T*) was measured from the TN LC cell made from polymer film and MLC-7026-000 using the method as reported elsewhere [65, 66]. The threshold voltage (V_{th}) and driving voltage (V_{on}) in the *V–T* curve are defined as the voltages at which the transmittance is decreased to 90% and 10% of the initial transmittance value, respectively [65, 66].

3. Results and discussion

Figure 1 shows the chemical structures of P4MP, P4EP and P4BP, respectively, for ion beam LC alignment. Detailed information on the synthesis and characterisation has been reported previously [62]. The polymer films were treated using an ion beam irradiation system (Kaufman Ar ion gun), as shown in Figure 2. The transmittance (87.2%) of the untreated P4EP film was shown to decrease compared to that (88.8%) of bare ITO at a specific wavelength of 550 nm, as shown in the supplementary material which is available via the multimedia link on the online article webpage. The transmittance (87.0%) of the ion beam treated P4EP film was similar to that of untreated P4EP film. The optical transparency in the visible region of the ion beam treated polymer films was still sufficient for them to be used as optical materials for flexible LC devices [67].

The orthoscopic and conoscopic POM images of the antiparallel LC cells made from the ion beam treated polymer films and 5CB were observed in order to investigate the effect on the LC alignment behaviour of the irradiation time, irradiation incidence angle, irradiation energy, and the side group length and molar content of the polymer side group (Figures 3–5). The Maltese cross pattern in conoscopic POM images of the LC cells made from ion beam treated P4EP films with an irradiation energy of 100 eV and irradiation incidence angle of 45° showed a significant difference in LC orientation with irradiation time (Figure 3). When the irradiation time was less than 14 s the LC cells showed homeotropic LC alignment, whereas the LC orientation on the P4EP films changed from homeotropic to a tilted LC alignment as the irradiation time increased from 14 s to 18 s.

Homogeneous planar LC alignment was observed when the irradiation time was greater than 21 s. Figure 4 shows the change in the LC orientation with the irradiation incidence angle. The homeotropic LC alignment was changed to planar LC alignment when the incidence angle relative to the planar direction was increased from 30° to 75°. A change in LC orientation from homeotropic to planar was also observed with increasing ion

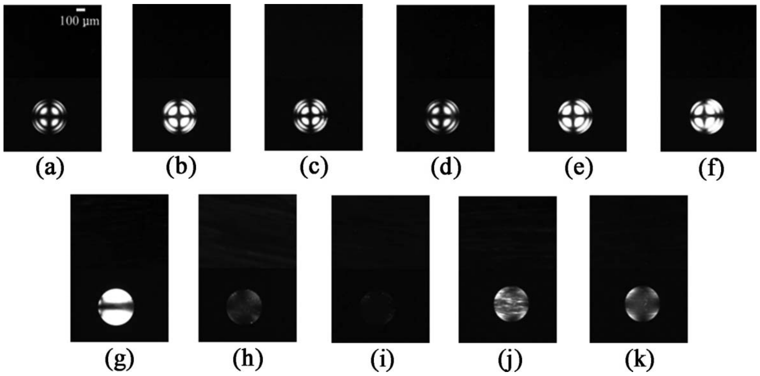


Figure 3. Orthoscopic and conoscopic POM images of the antiparallel LC cells made from ion beam treated P4EP films with an irradiation energy of 100 eV at an irradiation incidence angle of 45° and an irradiation time of (a) 0, (b) 3, (c) 6, (d) 12, (e) 14, (f) 16, (g) 18, (h) 21, (i) 24, (j) 30 and (k) 40 s.

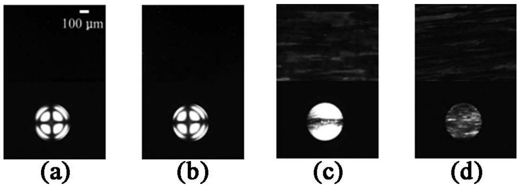


Figure 4. Orthoscopic and conoscopic POM images of the antiparallel LC cells made from ion beam treated P4EP films with an irradiation energy of 100 eV for 14 s and irradiation incidence angle of (a) 30°, (b) 45°, (c) 60° and (d) 75°.

beam irradiation energy, as shown in the supplementary online material. For comparison, the LC alignment behaviour of the LC cells made from a range of polymer films (P4EP, P4EP78, P4EP60, P4EP37, P4EP20, P4BP and P4MP), with different lengths and molar content of side groups, was also investigated under similar irradiation conditions (irradiation energy of 100 eV for 14 s at an irradiation incidence angle of 45°).

Figures 5(a)–5(e) show orthoscopic and conoscopic POM images of the LC cells made from these polymer films. Homeotropic LC alignment was observed with P4EP and P4EP78, whereas planar LC alignment behaviour was observed with P4EP60, P4EP37 and P4EP20. This suggests that under these conditions of ion beam irradiation the molar content of 4-ethylphenoxymethyl containing a monomeric unit should be above about 60% in order to induce homeotropic LC alignment. The P4BP film showed homeotropic LC alignment behaviour, whereas the P4MP film showed tilted LC alignment behaviour, as shown in Figures 5(f) and 5(g), respectively, indicating that longer alkyl groups increase the homeotropic LC alignment ability [60, 68, 69].

Polar diagrams of the absorbance of the dichroic dye, CI Disperse Blue 1, in the antiparallel LC cells fabricated using P4EP films were produced in order to investigate the effect of ion beam irradiation on the direction of LC alignment (Figure 6). As expected, the P4EP films showed the homeotropic LC alignment behaviour before ion beam irradiation. In contrast, the maximum absorbance along the 0° ↔ 180° direction was observed after irradiation with the 100 eV ion beam at an irradiation incidence angle of 45° for 40 s, indicating parallel LC alignment relative to the direction of ion beam incidence.

Figure 7 shows the effect of ion beam irradiation conditions on the pretilt angle of the antiparallel LC cells fabricated using P4EP films. Previously, when antiparallel LC cells were prepared using rubbed P4EP films with rubbing density increasing from 0 to 250 the pretilt angle changed hardly at all, from 90° to 88°, indicating that the rubbing process has little effect on the pretilt angle [62]. On the other hand, ion beam irradiation can change the homeotropic LC alignment

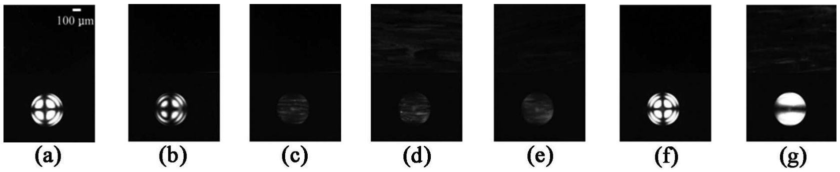


Figure 5. Orthoscopic and conoscopic POM images of the antiparallel LC cells made from ion beam treated polymer films of (a) P4EP, (b) P4EP78, (c) P4EP60, (d) P4EP37, (e) P4EP20, (f) P4BP and (g) P4MP, at an irradiation energy of 100 eV and irradiation incidence angle of 45° for 14 s.

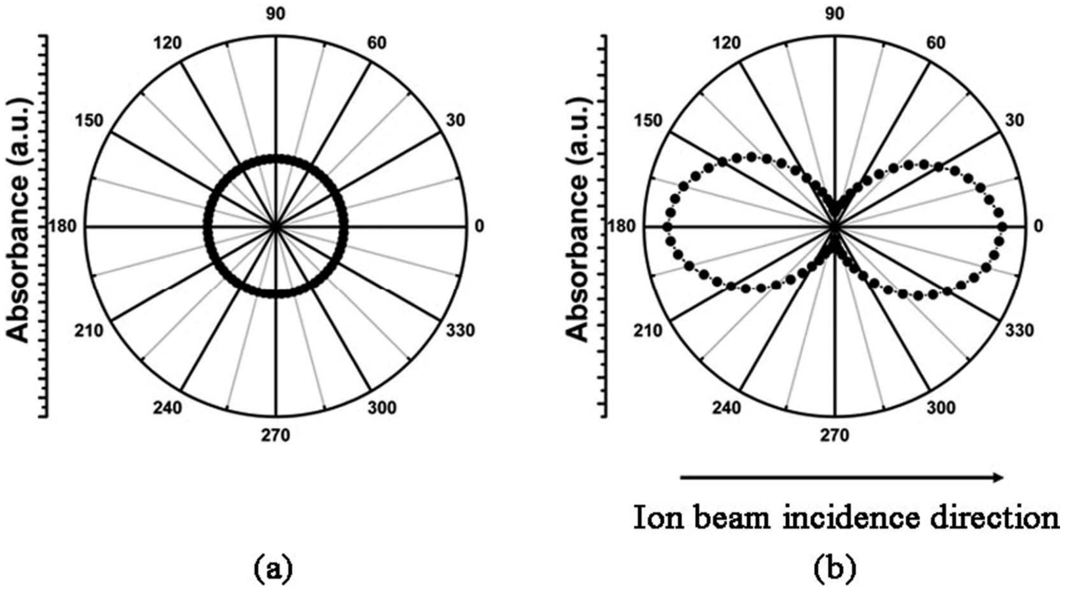


Figure 6. Polar diagrams of the absorbance of a dichroic dye (CI Disperse Blue 1) in the antiparallel LC cells fabricated using P4EP films for (a) 0 s and (b) 40 s with an irradiation energy of 100 eV and an irradiation incidence angle of 45° as a function of rotation angle of the samples.

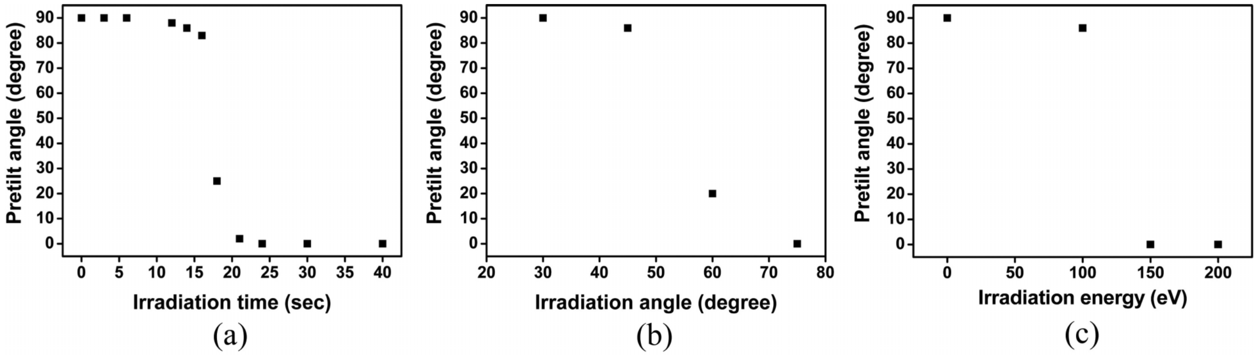


Figure 7. Pretilt angles of the antiparallel LC cells fabricated with ion beam treated P4EP films as a function of (a) irradiation time (45° incidence angle and 100 eV irradiation energy), (b) irradiation incidence angle (14 s irradiation time and 100 eV irradiation energy), and (c) irradiation energy (14 s irradiation time and 45° irradiation incidence angle).

to planar LC alignment if a longer irradiation time, larger irradiation incidence angle or increased irradiation energy is used. For example, as the irradiation time was increased from 0 to 14 s, the pretilt angles on the ion beam treated P4EP film with an incidence angle of 45° and irradiation energy of 100 eV decreased gradually from 90° to 86°. When the irradiation time was increased to 18 s, the pretilt angle decreased sharply to approximately 25°. Moreover, when the irradiation time was greater than 21 s, the pretilt angle became almost constant (approximately 0°), indicating that the LC alignment direction had changed to planar. The pretilt angles were approximately 90°, 86°, 20° and 0° when the irradiation incidence angles of the ion beam with an irradiation time of 14 s and an irradiation energy of 100 eV were 30°, 45°, 60° and 75°, respectively (Figure 7(b)). The pretilt angle decreased from 86° to 0° as the irradiation energy of the ion beam (14 s irradiation time and 45° irradiation incidence angle) was increased from 100 to 200 eV.

AFM (shown in the supplementary online material) was used to investigate the effect of surface morphology on the pretilt angle. Surfaces of both ion beam treated and untreated P4EP films had no groove-like structure and gave very low surface roughness values (R_a), less than about 1 nm, indicating that the ion beam irradiation process did not change the surface topography of these polymer films, as previously described for an ion beam treated polyimide surface [32]. It is concluded that a change in LC

Table 1. Water contact angle and pretilt angle of LCs on the ion beam treated polymer films.

	Irradiation condition				
Polymer designation	Energy (eV)	Time (s)	Angle (°)	Water contact angle (°)[a]	Pretilt angle (°)[b]
P4EP	100	0	45	87	90
P4EP	100	3	45	87	90
P4EP	100	6	45	87	90
P4EP	100	12	45	87	88
P4EP	100	14	45	87	86
P4EP	100	16	45	86	83
P4EP	100	18	45	84	25
P4EP	100	21	45	82	2
P4EP	100	24	45	82	0
P4EP	100	30	45	82	0
P4EP	100	40	45	82	0
P4EP	100	14	30	87	90
P4EP	100	14	60	83	20
P4EP	100	14	75	82	0
P4EP	150	14	45	82	0
P4EP	200	14	45	82	0
P4EP78	100	14	45	86	84
P4EP60	100	14	45	82	0
P4EP37	100	14	45	82	0
P4EP20	100	14	45	82	0
P4MP	100	14	45	85	62
P4BP	100	14	45	90	90

[a] Measured from static contact angles.
[b] Measured by crystal rotation method.

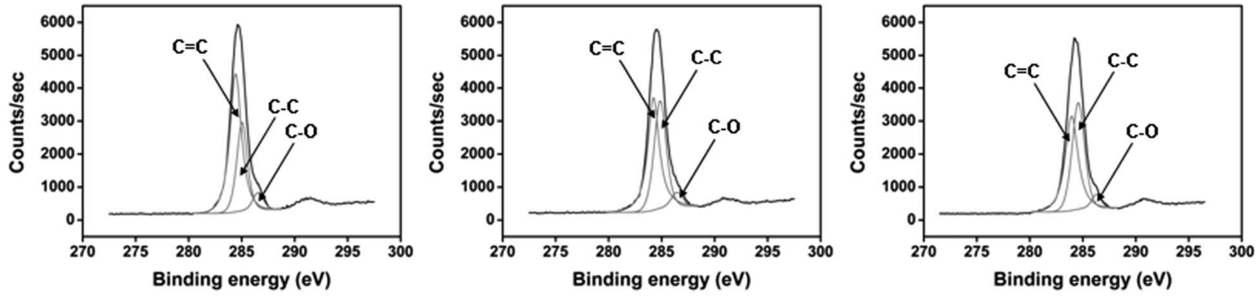
alignment direction following ion beam irradiation is not affected by surface morphology.

The effect of ion beam conditions on irradiation water contact angles on the polymer films was measured in order to assess the effect of wettability on the pretilt angle of LCs (Table 1). Water contact angles were determined in static mode and were found to decrease with increasing irradiation time, confirming that changes in pretilt angle were strongly affected by changes in wettability of the polymer films, as described previously [39, 70, 71]. The water contact angles of the polymer films decreased with increasing irradiation energy and incidence angle. Furthermore, under similar irradiation conditions an increasing water contact angle was observed on the polymer films with higher molar content and length of side groups: 86°, 86°, 82°, 82°, 82°, 85° and 90° for P4EP, P4EP78, P4EP60, P4EP37, P4EP20, P4MP and P4BP, respectively. The pretilt angle of the ion beam treated polymer films thus depends strongly on the wettability of the polymer surface.

ESCA was carried out to investigate the effect of chemical composition on the LC alignment behaviour of the polymer surface treated with the ion beam. Figure 8 shows the ESCA spectra of C_{1s} recorded at a 90° take-off angle for P4EP films irradiated with an ion beam for (a) 0 s, (b) 18 s and (c) 40 s, using an irradiation energy of 100 eV and an irradiation incidence angle of 45°.

Three signals in the C_{1s} ESCA spectra were assigned by curve-fitting to the C=C, C–C and C–O components at 284.5 eV, 285.1 eV and 286.6 eV, respectively. The two O_{1s} peaks in the ESCA spectra were assigned to the C=O and C–O component at 531.9 eV and 533.2 eV, respectively. The oxygen to carbon ratio in polymer films, calculated from the O_{1s} and C_{1s} peaks in the ESCA spectra at a take-off angle of 90°, was 0.086 at an irradiation time of 40 s, which is higher than the values (0.061 and 0.071) obtained at irradiation times of 0 s and 18 s, respectively. This indicated that the ion beam irradiation process decreased the carbon content on the polymer surface, possibly due to fragmentation of the 4-ethylphenoxy side groups on the polystyrene surface. Similar fragmentation of side groups has been reported following ion beam treatment of a polyimide alignment layer [72]. This demonstrates that ion beam irradiation increases the oxygen:carbon ratio on the surface of polystyrene derivatives, which in turn decreases the pretilt angles of LC and the water contact angle on these polymer films.

The electro-optical performance of the TN LC cells fabricated using ion beam- treated P4EP film (14 s irradiation time, 45° irradiation incidence angle



(a) (b) (c)

Figure 8. ESCA spectra of P4EP films for (a) 0 s, (b) 18 s and (c) 40 s at an irradiation energy of 100 eV and irradiation incidence angle of 45° in the C_{1s} recorded at 90° take-off angle.

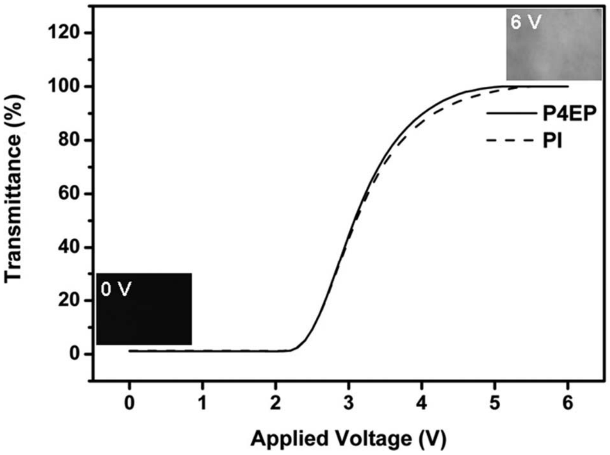


Figure 9. *V–T* curves of the TN LC cells fabricated with ion beam treated P4EP film at an irradiation energy of 100 eV and an irradiation incidence angle of 45° for 14 s, and rubbed polyimide film with a rubbing density of 150.

and 100 eV irradiation energy) and rubbed polyimide film (AL60101 from Japan Synthetic Rubber Co., Ltd.) with a rubbing density of 150, was determined by measuring the *V–T* curve (Figure 9).

In the present study a nematic LC with negative dielectric anisotropy, MLC-7026-000, was used. This gives a suitable switching behaviour in vertical alignment (VA) mode. The electro-optical performance of the LC cell made from the ion beam treated P4EP was at least as good as that produced from the rubbed polyimide film, which suggests that the ion beam technique in this polymer system is suitable for practical LC display applications. We therefore believe that these polymer films are good candidates as alignment layers for flexible LC display applications in VA mode.

The thermal stability of the antiparallel LC cells made from ion beam treated P4EP films was estimated from POM images of an LC cell at room temperature and after heating for 10 min at 100, 150, 200 and 250°C (Figure 10).

The POM images of the LC cells fabricated with ion beam treated P4EP films (14 s irradiation time, 45° irradiation incidence angle and 100 eV irradiation energy, illustrated in Figure 10 as 14 s/45°/100 eV) indicate that the homeotropic LC aligning ability was maintained when heated for 10 min at 150°C. This is well above the glass transition temperature of P4EP (Figure 10(b)), even though DSC showed that molecular motion of P4EP occurred at approximately 48°C [62] and defects were observed above 200° C. The homogeneous planar LC aligning ability of the LC cell made from a different ion beam treated P4EP film (shown as 14 s/45°/200 eV) was maintained up to 125°C (Figure 10(h)), but defects began to appear from 150°C. This confirmed that the temperature at which the uniformity of a LC cell made from the ion beam treated P4EP film (14 s/45°/200 eV) with planar LC aligning ability deteriorated was somewhat lower than that of the P4EP film (14 s/45°/100 eV) with homeotropic LC aligning capability.

4. Conclusions

The pretilt angle of a LC on 4-alkylphenoxymethyl-substituted polystyrene films can be controlled between 90° and 0° by varying the ion beam irradiation time, incidence angle, irradiation energy, and the length and molar content of the side groups. A lower pretilt angle was observed for LC cells made from ion beam treated polymer films with a longer irradiation time, higher irradiation incidence angle and larger irradiation energy, and from polymer films with shorter side group length and a lower molar content in the polymer. The pretilt angle correlated well with the wettability of the polymer films, due to fragmentation of the side group on the polymer surfaces caused by the ion beam irradiation process. Good electro-optical

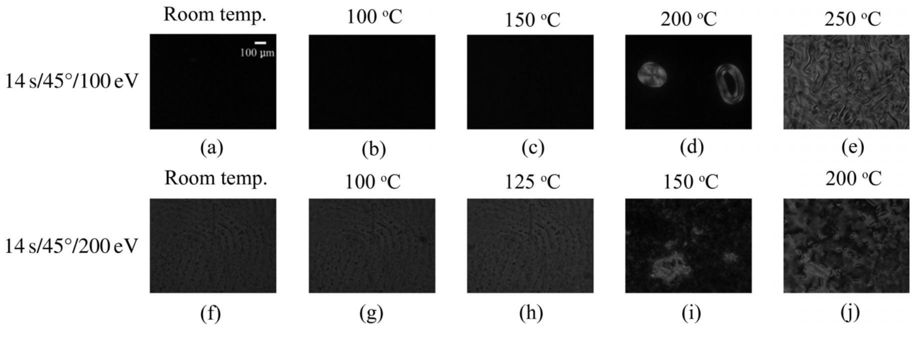


Figure 10. Orthoscopic POM images of the antiparallel LC cells made from ion beam treated P4EP films at an irradiation energy of 100 eV and an irradiation incidence angle of 45° for 14 s at (a) room temperature, (b) 100°C/10 min, (c) 150°C/10 min, (d) 200°C/10 min and (e) 250°C/10 min, and with an irradiation energy of 200 eV at an irradiation incidence angle of 45° for 14 s at (f) room temperature, (g) 100°C/10 min, (h) 125°C/10 min, (i) 150°C/10 min and (j) 200°C/10 min.

properties were observed for LC cells made from ion beam treated polymer films. For example, the V_{th} and V_{on} of the LC cell fabricated with the polymer film were 2.50 V and 4.00 V, respectively, indicating that the LC cell could be used for practical LC display applications, including flexible displays.

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References

[1] Kohki, T.; Masaki, H.; Mitsuhiro, K.; Nobuyuki, I.; Ray, H.; Masanori, S. *Alignment Technologies and Applications of Liquid Crystal Devices*; Taylor & Francis: New York, 2005.
[2] Feller, M.B.; Chen, W.; Shen, T.R. *Phys. Rev. A: At., Mol., Opt. Phys.*1991, *43*, 6778–6792.
[3] Van Aerle, N.A.J.; Tol, A.J.W. *Macromolecules (Washington, DC, U. S.)* **1994**, *27*, 6520–6526.
[4] Lee, K.-W.; Paek, S.-H.; Lien, A.; Durning, C.; Fukuro, H. *Macromolecules (Washington, DC, U. S.)* **1996**, *29*, 8894–8899.
[5] Kim, J.-H.; Acharya, B.R.; Kumar, S.; Ha, K.R. *Appl. Phys. Lett.* **1998**, *73*, 3372–3374.
[6] Stohr, J.; Samant, M.G.; Cossy-Favre, A.; Diaz, J.; Momoi, Y.; Odahara, S.; Nagata, T. *Macromolecules (Washington, DC, U. S.)* **1998**, *31*, 1942–1946.
[7] Yaroshchuk, O.; Zakrevskyy, Y.; Kumar, S.; Kelly, J.; Chien, L.-C.; Lindau J. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2004**, *69*, 011702/1–011702/7.
[8] Gu, M.; Smalyukh, I.I.; Lavrentovich, O.D. *Appl. Phys. Lett.* **2006**, *88*, 061110/1–061110/3.
[9] Yi, Y.; Nakata, M.; Martin, A.R.; Clark, N.A. *Appl. Phys. Lett.* **2007**, *90*, 163510/1–163510/3.
[10] Chae, B.; Kim, S.B.; Lee, S.W.; Kim, S.I.; Choi, W.; Lee, B.; Ree, M.; Lee, K.H.; Jung, J.C. *Macromolecules (Washington, DC, U. S.)* **2002**, *35*, 10119–10130.
[11] Hahm, S.G.; Lee, T.J.; Chang, T.; Jung, J.C.; Zin, W.-C. *Macromolecules (Washington, DC, U. S.)* **2006**, *39*, 5385–5392.
[12] Lee, Y.J.; Choi, J.G.; Song, I.-K.; Oh, J.M.; Yi, M.H. *Polymer* **2006**, *47*, 1555–1562.
[13] Kang, H.; Park, J.S.; Sohn, E.-H.; Kang, D.; Rosenblatt, C.; Lee, J.-C. *Polymer* **2009**, *50*, 5220–5227.
[14] Geary, J.M.; Goodby, J.W.; Kmetz, A.R.; Patel, J.S. *J. Appl. Phys.* **1987**, *62*, 4100–4108.
[15] Ishihara, S.; Wakemoto, H.; Nakazima, K.; Mastuo, Y. *Liq. Cryst.* **1989**, *4*, 669–675.
[16] Seo, D.-S.; Muroi, K.-I.; Isogomi, T.-R.; Matsuda, H.; Kobayashi, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 2165–2169.
[17] Seo, D.-S.; Yoshida, N.; Kobayashi, S.; Nishikawa, M.; Yabe, Y. *Jpn. J. Appl. Phys.* **1995**, *34*, 4876–4879.
[18] Schwab, A.D.; Agra, D.M.; Kim, J.-H.; Kumar, S.; Dhinojwala A. *Macromolecules (Washington, DC, U. S.)* **2000**, *33*, 4903–4909.
[19] Oh-e, M.; Hong, S.-C.; Shen, Y.R. *Appl. Phys. Lett.* **2002**, *80*, 784–786.
[20] Lee, S.W.; Chae, B.; Kim, H.C.; Lee, B.; Choi, W.; Kim, S.B.; Chang, T.; Ree, M. *Langmuir* **2003**, *19*, 8735–8743.
[21] Lee, S.W.; Yoon, J.; Kim, H.C.; Lee, B.; Chang, T.; Ree, M. *Macromolecules (Washington, DC, U. S.)* **2003**, *36*, 9905–9916.
[22] Hahm, S.G.; Lee, T.J.; Lee, S.W.; Yoon, J.; Ree, M. *Mater. Sci. Eng. B* **2006**, *132*, 54–58.
[23] Chigrinov, V.G.; Kozenkov, V.M.; Kwok, H.-S. *Photoalignment of Liquid Crystalline Materials: Physics and Application*; John Wiley & Sons: New York, 2008.
[24] Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847–1874.
[25] O'Neill, M.; Kelly, S.M. *J. Phys. D: Appl. Phys.* **2000**, *33*, R67–R84.
[26] Chaudhari, P.; Lacey, J.; Doyle, J.; Galligan, E.; Lien, S.-C.A.; Callegari, A.; Hougham, G.; Lang, N.D.; Andry, P.S.; John, R.; Yang, K.-H.; Lu, M.; Cai, C.; Speidell, J.; Purushothaman, S.; Ritsko, J.; Samant, M.; Stohr, J.; Nakagawa, Y.; Katoh, Y.; Saitoh, Y.; Sakai, K.; Satoh, H.; Odahara, S.; Nakano, H.; Nakagaki, J.; Shiota, Y. *Nature (London, U. K.)* **2001**, *411*, 56–59.
[27] Stohr, J.; Samant, M.G..; Luning, J.; Callegari, A.C.; Chaudhari, P.; Doyle, J.P.; Lacey, J.A.; Lien, S.A.; Purushothaman, S.; Speidell, J.L. *Science (Washington, DC, U. S.)* **2001**, *292*, 2299–2302.
[28] Gwag, J.S.; Park, K.-H.; Kang, D.J.; Jhun, C.G.; Kim, H.; Cho, S.J.; Yoon, T.-H.; Kim, J.C. *Jpn. J. Appl. Phys.* **2003**, *42*, L468–L471.
[29] Gwag, J.S.; Jhun, C.G.; Kim, J.C.; Yoon, T.-H.; Lee, G.-D.; Cho, S.J. *J. Appl. Phys.* **2004**, *96*, 257–260.
[30] Seo, J.-H.; Lee, S.P.; Yoon, T.-H.; Kim, J.C. *Jpn. J. Appl. Phys.* **2007**, *46*, 6057–6061.
[31] Kang, D.-H.; Kim, S.-H.; Kim, B.-Y.; Kim, J.-Y.; Ok, C.-H.; Kim, Y.-H.; Han, J.-W.; Kim, J.-H.; Hwang, J.-Y.; Oh, B.-Y.; Han, J.-M.; Lee, S.-K.; Lee, J.-W.; Moon, B.-M.; Kim, J.-H.; Seo, D.-S. *Jpn. J. Appl. Phys.* **2007**, *46*, 6601–6603.
[32] Oh, B.-Y.; Lee, K.-M.; Kim, B.-Y.; Kim, Y.-H.; Han, J.-W.; Han, J.-M.; Lee, S.-K.; Seo, D.-S. *J. Appl. Phys.* **2008**, *104*, 064502/1–064502/5.
[33] Fulghum, J.E.; Su, L.; Artyushkova, K.; West, J.L.; Reznikov, Y. *Mol. Cryst. Liq. Cryst.* **2004**, *412*, 361–368.
[34] Pylypenko, S.; Artyushkova, K.; Fulghum, J.E.; Buluy, O.; Aryasova, N.; Reznikov, Y. *Mol. Cryst. Liq. Cryst.* **2006**, *454*, 167–177.
[35] Wu, H.-Y.; Wang, C.-Y.; Lin, C.-J.; Pan, R.-P.; Lin, S.-S.; Lee, C.-D.; Kou, C.-S. *J. Phys. D: Appl. Phys.* **2009**, *42*, 155303/1–155303/6.
[36] Ok, C.-H.; Kim, B.-Y.; Oh, B.-Y.; Kim, Y.-H.; Lee, K.-M.; Park, H.-G.; Han, J.-M.; Seo, D.-S.; Lee, D.-K.; Hwang, J.-Y. *Liq. Cryst.* **2008**, *35*, 1373–1377.
[37] Hwang, J.-Y.; Jo, Y.-M.; Rho, S.J.; Baik, H.K.; Seo, D.-S. *Jpn. J. Appl. Phys.* **2002**, *41*, L992–L995.
[38] Ahn, H.J.; Rho, S.J.; Kim, K.C.; Kim, J.B.; Hwang, B.H.; Park, C.J.; Baik, H.K. *Jpn. J. Appl. Phys.* **2005**, *44*, 4092–4097.
[39] Ahn, H.J.; Kim, J.B.; Kim, K.C.; Hwang, B.H.; Park, J.S.; Kang, D. *Appl. Phys. Lett.* **2007**, *90*, 253505/1–253505/3.

[40] Ahn, H.J.; Kim, K.C.; Kim, J.B.; Hwang, B.H. *Jpn. J. Appl. Phys.* **2007**, *46*, 3521–3523.

[41] Kim, J.B.; Kim, K.C.; Ahn, H.J.; Hwang, B.H.; Hyun, D.C.; Kim, J.T.; Lee, S.J.; Baik, H.K. *Jpn. J. Appl. Phys.* **2007**, *46*, 5213–5217.

[42] Wu, H.-Y.; Pan, R.-P. *Appl. Phys. Lett.* **2007**, *91*, 074102/1–074102/3.

[43] Kim, J.-Y.; Oh, B.-Y.; Kim, B.-Y.; Kim, Y.-H.; Han, J.-W.; Han, J.-M.; Seo, D.-S. *Appl. Phys. Lett.* **2008**, *92*, 043505.

[44] Park, H.-G.; Kim, Y.-H.; Oh, B.-Y.; Lee, W.-K.; Kim, B.-Y.; Seo, D.-S.; Hwang, J.-Y. *Appl. Phys. Lett.* **2008**, *93*, 233507/1–233507/3.

[45] Oh, B.-Y.; Lee, W.-K.; Kim, Y.-H.; Seo, D.-S. *J. Appl. Phys.* **2009**, *105*, 054506/1–054506/7.

[46] Lee, W.-K.; Oh, B.-Y.; Lim, J.-H.; Park, H.-G.; Kim, B.-Y.; Na, H.-J.; Seo, D.-S. *Appl. Phys. Lett.* **2009**, *94*, 223507/1–223507/3.

[47] Kim, K.C.; Ahn, H.J.; Kim, J.B.; Hwang, B.H.; Baik, H.K. *Langmuir* **2005**, *21*, 11079–11084.

[48] Kim, K.C.; Ahn, H.J.; Kim, J.B.; Hwang, B.H.; Baik, H.K.; Lee, S.J. *Jpn. J. Appl. Phys.* **2005**, *44*, 8071–8076.

[49] Son, P.K.; Park, J.H.; Cha, S.S.; Kim, J.C.; Yoon, T.-H.; Rho, S.J.; Jeon, B.K.; Kim, J. S.; Lim, S.K.; Kim, K.H. *Appl. Phys. Lett.* **2006**, *88*, 263512/1–263512/3.

[50] Kim, K.C.; Ahn, H.J.; Kim, J.B.; Hwang, B.H.; Kim, J.T.; Baik, H.K. *Mater. Chem. Phys.* **2007**, *106*, 54–57.

[51] Moon, H.-C.; Kang, H.-K.; Hwang, J.-Y.; Park, Y.-P.; Lim, S.-H.; Jang, J.; Seo, D.-S. *Jpn. J. Appl. Phys.* **2006**, *45*, 7017–7019.

[52] Son, P.K.; Park, J.H.; Kim, J.C.; Yoon, T.-H.; Rho, S.J.; Jeon, B.K.; Shin, S.T.; Kim, J.S.; Lim, S.K. *Appl. Phys. Lett.* **2007**, *91*, 103513/1–103513/3.

[53] Koo, W.H.; Kim, J.B.; Hwang, B.H.; Kim, J.T.; Jo, S.J.; Kim, C.S.; Lee, S.J.; Baik, H.K. *Jpn. J. Appl. Phys.* **2008**, *47*, 4617–4619.

[54] Lee, S.-K.; Kim, J.-H.; Oh, B.-Y.; Kang, D.-H.; Kim, B.-Y.; Han, J.-W.; Kim, Y.-H.; Han, J.-M.; Hwang, J.-Y.; Ok, C.-H.; Seo, D.-S. *Jpn. J. Appl. Phys.* **2007**, *46*, 7711–7713.

[55] Oh, B.-Y.; Kim, Y.-H.; Kim, B.-Y.; Lee, S.-K.; Seo, D.-S.; Han, J.-M.; Hwang, J.-Y. *Mater. Chem. Phys.* **2009**, *117*, 355–358.

[56] Kang, H.; Kwon, K.-S.; Kang, D.; Lee, J.-C. *Macromol. Chem. Phys.* **2007**, *208*, 1853–1861.

[57] Kang, H.; Kang, D.; Lee, J.-C. *Liq. Cryst.* **2008**, *35*, 1005–1013.

[58] Kang, H.; Park, J.S.; Kang, D.; Lee, J.-C. *Macromol. Chem. Phys.* **2008**, *209*, 1900–1908.

[59] Kang, H.; Park, J.S.; Kang, D.; Lee, J.-C. *Liq. Cryst.* **2009**, *36*, 479–485.

[60] Kang, H.; Park, J.S.; Kang D.; Lee, J.-C. *Polym. Adv. Technol.* **2009**, *20*, 878–886.

[61] Kang, H.; Kang, D.; Lee, J.-C. *Polymer* **2009**, *50*, 2104–2112.

[62] Kang, H.; Kim, T.-H; Kang, D.; Lee, J.-C. *Macromol. Chem. Phys.* **2009**, *210*, 926–935.

[63] Kang, H.; Lee, J.-C.; Kang, D. *Macromol. Res.* **2009**, *17*, 506–515.

[64] Sprokel, G.J. *The Physics and Chemistry of Liquid Crystal Devices*; Springer: New York, 1980.

[65] Wu, S.-T.; Yang, D.-K. Fast response liquid crystals. In *Reflective Liquid Crystal Displays*; J. Wiley & Sons: New York, 2001.

[66] Boer, W.D. *Active Matrix Liquid Crystal Displays: Fundamental Applications*; Elsevier: Amsterdam, 2005.

[67] Crawford, G..P. *Flexible Flat Panel Displays*; John Wiley & Sons: Chichester, England, 2005.

[68] Malone, S.M.; Schwartz, D.K. *Langmuir* **2008**, *24*, 9790–9794.

[69] Chiou, D.-R.; Chen, L.-J. *J. Phys. Chem. C* **2009**, *113*, 9797–9803.

[70] Price, A.D.; Schwartz, D.K. *Langmuir* **2006**, *22*, 9753–9759.

[71] Oh, S.-K.; Nakagawa, M.; Ichimura, K. *J. Mater. Chem.* **2001**, *11*, 1563–1569.

[72] Seo, J.-H.; Hwang, S.W.; Song, D.H.; Shin, J.H.; Yoon, T.-H.; Kim, J.C. *J. Phys. Chem. B* **2009**, *113*, 2001–2005.