Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 4068–4076

polymer

www.elsevier.com/locate/polymer

Rubbed films of isomeric poly(4-vinylpyridine) and poly(2-vinylpyridine): surface morphology, molecular orientation, and liquid crystal alignability

Seung Woo Lee, Boknam Chae, Seok Gyu Hahm, Byeongdu Lee, Seung Bin Kim*, Moonhor Ree*

BK21 Program and Division of Molecular and Life Sciences, Department of Chemistry, Center for Integrated Molecular Systems, Polymer Research Institute, Pohang University of Science and Technology, Pohang 790-784, South Korea

Received 19 September 2004; received in revised form 3 March 2005; accepted 6 March 2005
Available online 19 April 2005

Abstract

Films of poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) were characterized before and after they were rubbed with a rayon velvet, and their liquid crystal (LC) aligning abilities were investigated. Atomic force microscopy images showed that microgrooves developed along the rubbing direction in the surfaces of the rubbed films of both polymers. Retardation and linearly polarized infrared spectroscopy analyses revealed that in both polymers the vinyl backbones are oriented along the rubbing direction, while the pyridine side groups are oriented perpendicular to the rubbing direction; the *para*-directions of the pyridine rings in the P4VP film have a tilt angle of about 45° in the plane perpendicular to the rubbing direction but the *para*-directions of the pyridine rings in the P2VP film align nearly in the film surface. These rubbed films were found to induce uniform, homogeneous LC alignment along the rubbing direction. Both LC alignments were, however, found to have low anchoring energies that are due to the inherently weak interactions of the LCs with the film surfaces. Moreover, LC cells prepared using these films were found to have only limited stability. These results lead to the conclusion that the microgrooves generated along the rubbing direction play a critical role in governing the alignment of LCs that weakly interact with the parallel oriented vinyl main chains in competition with the perpendicularly oriented pyridine side groups, despite their dimensions, which are larger than the LC molecules and thus limit their effectiveness. In addition, the zero degree pre-tilting behavior of the LCs on these films was investigated in detail, taking into account both the rubbing-induced orientations of the polymer segments and their anisotropic interactions with the LC molecules.

Keywords: Polyvinylpyridines; Rubbing; Surface morphology

1. Introduction

In the liquid crystal (LC) display industry, the uniform alignment of LC molecules is currently obtained by rubbing polymer alignment layers with a velvet fabric, which plays important role in the optical and electrical performance of LC display devices [1]. Thus much research has been applied to the development of alignment layer polymers for the fabrication of LC display devices and to understanding the mechanism of the alignment of LC molecules on rubbed polymer surfaces [1–31]. Of the polymers used as alignment layers, polyimides (PIs) are widely used as LC alignment layers because of their advantageous properties [1–22]. Most rubbed PIs have been reported to align LCs parallel to the rubbing direction [1–20]. Recently two other PIs have, however, been discovered to align LCs in a direction perpendicular to the rubbing direction [19–22].

Unlike the PIs conventionally used in the LC display industry, rubbed polystyrene (PS) films have also been found to align LCs perpendicular to the rubbing direction, with zero pre-tilt [23]. It was found that rubbing of PS films generates microgrooves in the films along the rubbing direction and orients the polymer main chains parallel to the rubbing direction, as is also always observed for PI films,

---

* Corresponding authors. Tel.: +82 54 279 2120; fax: +82 54 279 3399. Tel.: +82 54 279 2106; fax: +82 54 279 3399.

E-mail addresses: sbkim@postech.edu (S.B. Kim), ree@postech.edu (M. Ree).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.03.085

while the phenyl side groups are oriented perpendicular to the rubbing direction [23–29]. These results for rubbed PS films have widely been cited as a clue that the microgrooves generated by the rubbing process are not necessarily involved in the alignment of LCs on surfaces.

However, the surface morphology of rubbed PS film was recently found to significantly depend on the molecular weight; microgrooves develop along the rubbing direction in rubbed films of PS with low molecular weight (<9800), while for rubbed films of PS with high molecular weight (>9800), meandering groove-like structures develop perpendicular to the rubbing direction [30,31]. The unusual meandering groove-like surface morphology is a significant departure from the surface topographies observed so far for rubbed PS and other polymer films, for which grooves are usually only found parallel to the rubbing direction. The director of the LC alignment was found to always coincide with the orientation direction of the generated microgrooves [30,31]. On the rubbed PS surfaces, LCs were found to anchor with a very low anchoring energy, which results in limited stability (less than 1 day) of the LC alignment [30,31]. These results suggest that the strength of the interactions of the LCs with the oriented vinyl main chains seems to be very close to that of the interactions of the LCs with the oriented phenyl side groups. Moreover, the anisotropic interactions of the LCs with the microgrooves in the film surface are also very weak. Of these three different anisotropic interactions between the LCs and the rubbed surface, none seems to dominate in the determination of the alignment of the LCs. Therefore, the alignment of LCs with only weak molecular interactions with the rubbed PS film surface is governed by the favorable cooperation of the interaction with the microgrooves with one of the interactions with the oriented main chain segments and side groups, all of whose directionally anisotropic interactions compete to align the LC molecules.

Poly(4-vinylpyridine) (P4VP) has the same vinyl backbone as PS and a similar aromatic side group except that its six-membered ring includes one nitrogen atom; its rubbed films have also been reported to induce LC alignment with zero pre-tilt perpendicular to the rubbing direction [32]. Poly(2-vinylpyridine) (P2VP) is an isomeric polymer of P4VP, but in contrast its rubbed films have been reported to induce LC alignment with zero pre-tilt parallel to the rubbing direction [32]. However, despite their interesting reported LC alignment behavior, the films of these polymers have rarely been studied. In this paper, we conclude that rubbed P4VP films align LCs along the rubbing direction, which contradicts the previously reported result.

To elucidate the mechanism of alignment of LCs by the P4VP and P2VP surfaces, in the present study, we quantitatively investigated the surface orientational distributions of the main chains and the side groups of the P4VP and P2VP films, both before and after rubbing, using linearly polarized Fourier transform infrared (FTIR) spectroscopy and optical retardation analysis. We also examined the films' surface topography using a high-resolution atomic force microscope (AFM). In addition, anti-parallel and 90°-twisted LC cells were assembled from the rubbed films, injected with a nematic LC, 4-*n*-pentyl-4′-cyanobiphenyl (5CB), and the alignment behavior and anchoring energy of the LC molecules were characterized. We discuss the observed LC alignment and anchoring behaviors by taking into account the interactions between the oriented polymer segments and the LC molecules. In addition, the contributions of the films' surface topographies to LC alignment are discussed.

2. Experimental

2.1. Film and LC cell preparation

P4VP (50,000 weight average molecular weight $\bar{M}_w$; 143 °C glass transition temperature T_g) and P2VP (40,000 $\bar{M}_w$; 100 °C T_g) were purchased from scientific polymer products (Ont., NY, USA). Isopropyl alcohol (IPA) and a nematic LC 5CB (n_e (extraordinary refractive index) $=$ 1.717 and n_o (ordinary refractive index) $=1.530$) [33] were purchased from Aldrich Chemical Company. Solutions of P4VP and P2VP were prepared in isopropyl alcohol (IPA) (2.0 wt% solid). These solutions were spin-coated onto calcium fluoride windows for the FTIR spectra, onto gold-coated silicon wafers for the AFM measurements, and onto indium tin oxide glass substrates for the optical retardation measurements and LC cell assembly. The films were dried at 120 °C for 12 h. The resulting films were measured to have a thickness of around 200 nm using a spectroscopic ellipsometer (Woollam Co., model M2000) and an alpha-stepper (Veeco Co., model Tektak3). The polymer films were rubbed using a laboratory rubbing machine (Wande Co.) with a roller covered by a rayon velvet fabric (Yoshikawa Co., model YA-20-R). The rubbing density was varied by changing the cumulative rubbing time for a constant rubbing depth of 0.15 mm; the rubbing density (L/l) is defined by $L/l=N[(2\pi rn/60v)-1]$ where L is the total length of the rubbing cloth which contacts a certain point of the polymer film (mm), l is the contact length of circumference of rubbing roller (mm), N is the cumulative number of rubbings, n and r are the speed (rpm) of and the radius (cm) of rubbing roller (rpm), respectively, and v is the velocity (cm/s) of the substrate stage [3,8–18]. Some of the rubbed polymer films on glass substrates were cut into 2.5×2.5 cm^2 pieces and then used for assembling two different LC cells as follows. First, paired pieces cut from each glass substrate were assembled together anti-parallel with respect to the rubbing direction by using 50 μm thick spacers, injected with LC, and then sealed with epoxy glue, giving anti-parallel nematic LC cells. Second, paired pieces from each glass substrate were assembled together orthogonally with respect to the rubbing direction by using silica balls of 4.0 μm diameter as spacers, injected with LC, and then sealed with an epoxy glue, giving 90°-twisted nematic LC cells (TN cells). In addition, a solution of the LC in ethyl ether (10 wt% LC) was directly spin-coated onto some of the rubbed films, and dried at room temperature for 3 h; the thicknesses of the coated LC layers were measured with the spectroscopic ellipsometer to be around 300 nm.

2.2. Measurements

Surface images were obtained using a tapping mode AFM (Digital Instruments, model Multimode AFM Nanoscope IIIa). An ultralever cantilever (with 26 N/m spring constant and 268 kHz resonance frequency) was used for scanning. Optical phase retardations were measured using an optical set-up described elsewhere [31]. FTIR spectroscopic measurements were carried out on a FTIR spectrometer (Bomem, model DA8) equipped with a polarizer for the transmission FTIR spectra and a Seagull attachment (Harrick Scientific Co.) for the external reflection FTIR spectra. For samples installed perpendicular to the incident beam direction, transmission FTIR spectra were recorded at 4 cm^{-1} resolution under vacuum as a function of the angle of rotation of the polarizer. The external reflection IR spectra were obtained with *p*-polarized radiation at an incidence angle of 82°. Reflection IR spectra were also recorded at 4 cm^{-1} resolution as a function of the angle of rotation of the film sample with respect to the surface normal. For the anti-parallel LC cells, the polar anchoring energy and pre-tilt angle were measured using a polar anchoring energy apparatus [34,35] and a crystal rotation apparatus [31], respectively. For the TN LC cells, the azimuthal anchoring energy was measured by using the spectroscopic technique previously reported [31].

3. Results and discussion

3.1. Surface topography

Fig. 1(a) and (c) show a representative AFM image of P4VP films and of P2VP films, respectively, which were rubbed at a rubbing density of 50. The AFM images clearly show microgrooves that have developed along the rubbing direction. In the P4VP films, the microgrooves are somewhat different in shape and size to those observed in the PS films [25–27,30,31] and in the films of the PIs currently used in the LC display industry [2–18,21–23]. The microgrooves in the P2VP film are similar to those observed in the films of the PIs currently used in the LC display industry [2–18,21–23] but different to those observed in the PS films [25–27, 30,31]. In addition to these microgrooves, scratch lines, which are known to be created during the rubbing process where the surface is met by adjacent fiber pairs, are also present in the surfaces of both polymers (not shown in the AFM images), as are always observed for other polymer layers, including those of PS [30,31] and PIs [2–18,21–23].

The rubbed P4VP film surface shows 0.69 nm root-mean-square (rms) roughness over the entire area of the image in Fig. 1(a); the rms roughness is 0.74 nm rms along the $x1$–$x2$ line, across the rubbing direction, which is relatively larger than that (0.37 nm) along the $y1$–$y2$ line, parallel to the rubbing direction (Fig. 1(b)). The P2VP film reveals 1.95 nm rms roughness over the entire area of the image in Fig. 1(c); the rms roughness is 1.64 nm rms across the rubbing direction and 0.78 nm along the rubbing direction (Fig. 1(d)). These results indicate that the rubbed P4VP film shows relatively smaller roughness, compared to the rubbed P2VP film. The rubbed films overall reveal rougher surface that their unrubbed films showing smooth surface (only 0.18 nm rms roughness).

Collectively, the surface morphology of the rubbed P4VP film is somewhat different to that of the rubbed P2VP film, although P2VP and P4VP are structurally isomeric polymers and their films have similar surface topographies prior to rubbing. These differences in the surface morphologies of the rubbed P4VP and P2VP films might result from difference in their deformation responses to the shear forces produced by contact with fibers during the rubbing process.

3.2. Molecular orientation

Fig. 2(a) displays a polar diagram of the transmitted light intensity with respect to the angle of rotation of a P4VP film rubbed at a rubbing density of 50, as obtained from the optical retardation measurements; the transmitted light intensity (=[in-plane birefringence]×[phase]). The polar diagram indicates that there is a maximum in the transmitted light intensity along the 270°↔90° direction, which is perpendicular to the rubbing direction, but that there is a minimum in the transmitted light intensity along the 180°↔0° direction, which is parallel to the rubbing direction. A similar diagram was obtained for a P2VP film rubbed at a rubbing density of 50 (Fig. 2(b)). In the present study, P4VP and P2VP were found by spectroscopic ellipsometry measurements of their films to be negatively birefringent polymers; these negative birefringences originate from their pyridine rings, which are linked orthogonally to the vinyl backbones as side groups and have larger polarizabilities than the vinyl chain backbone, which lies along the chain axis. Taking these facts into account, the observed anisotropic polar diagrams (Fig. 2(a) and (b)) indicate that on the rubbed film surfaces of P4VP and P2VP the pyridine side groups are preferentially oriented in a direction perpendicular to the rubbing direction but the vinyl backbones are oriented parallel to the rubbing direction. In contrast, unrubbed P4VP and P2VP films produce isotropic polar diagrams of the transmitted light intensity in retardation measurements, indicating that both the polymer films are isotropic in the film plane.

Fig. 2(c) shows the variations of the optical retardation (=[in-plane birefringence]×[film thickness]) with rubbing density for the P4VP and P2VP films. The retardation

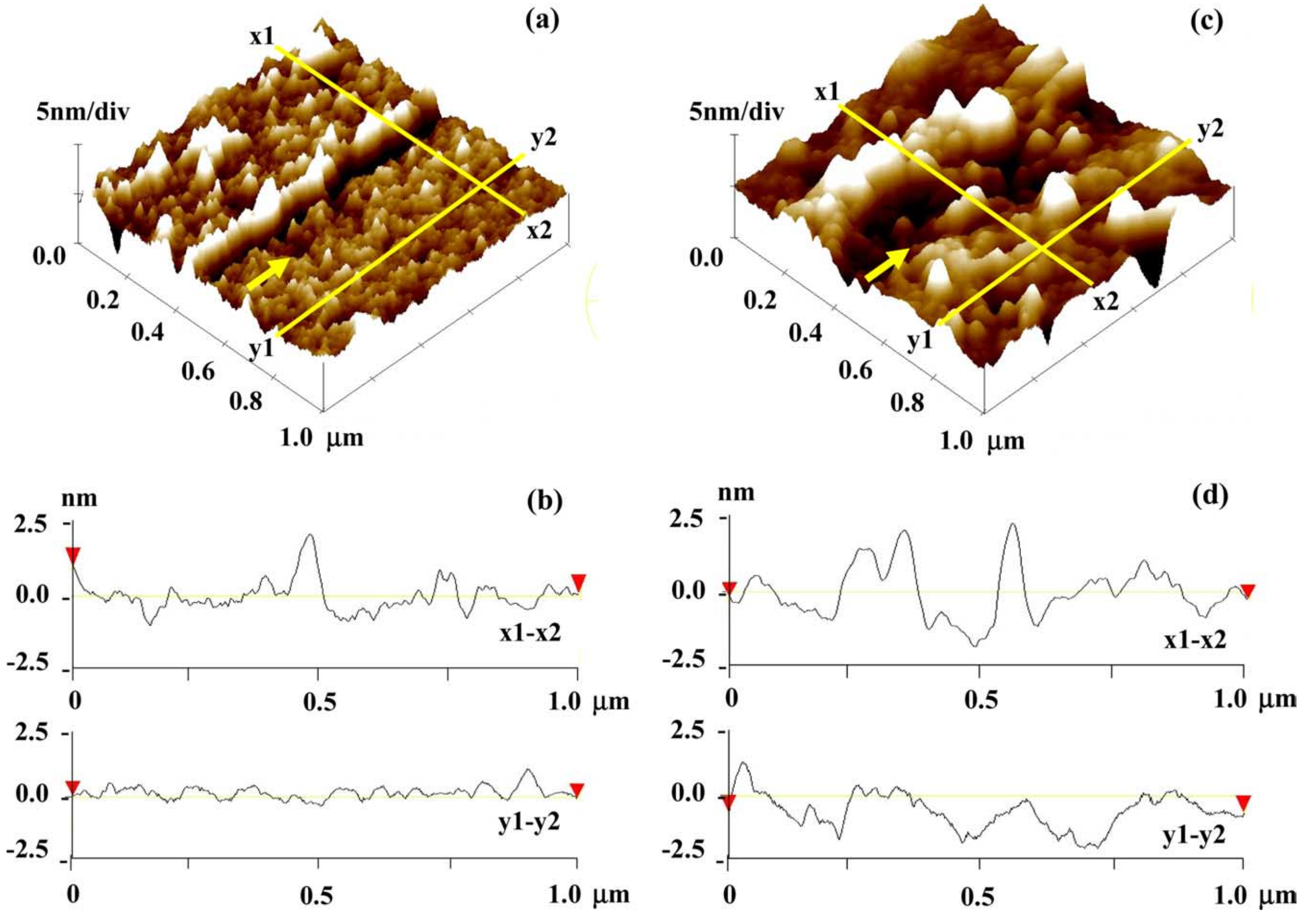

Fig. 1. AFM images and surface profiles of films rubbed with a rubbing density of 50: (a) image of a rubbed P4VP film; (b) surface profiles along the *x*1–*x*2 line (perpendicular to the rubbing direction) and the *y*1–*y*2 line (parallel to the rubbing direction) in image (a); (c) image of a rubbed P2VP film; (d) surface profiles along the *x*1–*x*2 line (perpendicular to the rubbing direction) and the *y*1–*y*2 line (parallel to the rubbing direction) in image (c). The arrows indicate the rubbing direction.

(i.e. degree of orientation of the polymer chains) of the rubbed film of each polymer rapidly decreases with rubbing density up to a rubbing density of 80 and then more slowly decreases with further increases in the rubbing density. This variation in the retardation with rubbing density resembles that obtained for rubbed films of PS, which also have negative optical retardation.

Dichroic IR spectral analyses were conducted for the P4VP and P2VP films before and after rubbing by polarized transmission FTIR spectroscopy that can only detect vibrational modes with in-plane components. In these measurements the unrubbed P4VP and P2VP films exhibited isotropic spectra (data not shown), indicating that the unrubbed films are both isotropic in the film plane. In contrast, the two spectra of the rubbed films of each polymer in Fig. 3—one measured with IR light polarized parallel to the rubbing direction, the other with IR light polarized perpendicular to the rubbing direction—do exhibit anisotropy; both polymer films were rubbed at a rubbing density of 50.

The bands at (1596 and 1556 cm^{-1}) and at (1589 and 1568 cm^{-1}) are due to quadrant stretching of the pyridine rings of P4VP and P2VP, respectively, while those at (1492 and 1413 cm^{-1}) and at (1471 and 1433 cm^{-1}) are associated with semicircle stretching of the pyridine rings of P4VP and P2VP, respectively, [36–38]. The asymmetric stretching vibrational modes of CH_2 groups in the vinyl main chains appear at 2925 cm^{-1} for P4VP and at 2924 cm^{-1} for P2VP, while the symmetric stretching vibrational modes of CH_2 in the vinyl main chain appear at 2856 cm^{-1} for P4VP and at 2852 cm^{-1} for P2VP.

The dipole transition moments for the quadrant stretching (1596 cm^{-1}) and semicircle stretching (1492 cm^{-1}) vibrations of the pyridine side group of P4VP are oriented in the *para*-direction of the pyridine ring, which is attached orthogonally to the polymer backbone. On the other hand, the dipole transition moments for the pyridine ring stretching vibrations at 1556 and 1413 cm^{-1} are oriented perpendicular to the dipole transition moments for the 1596 and 1492 cm^{-1} bands, and lie in the plane of the pyridine ring. As shown in Fig. 3(a), all these bands are more intense when the polarization of the incident IR beam is perpendicular to the rubbing direction. The directions of the dipole transition moments of the bands at (1596 and

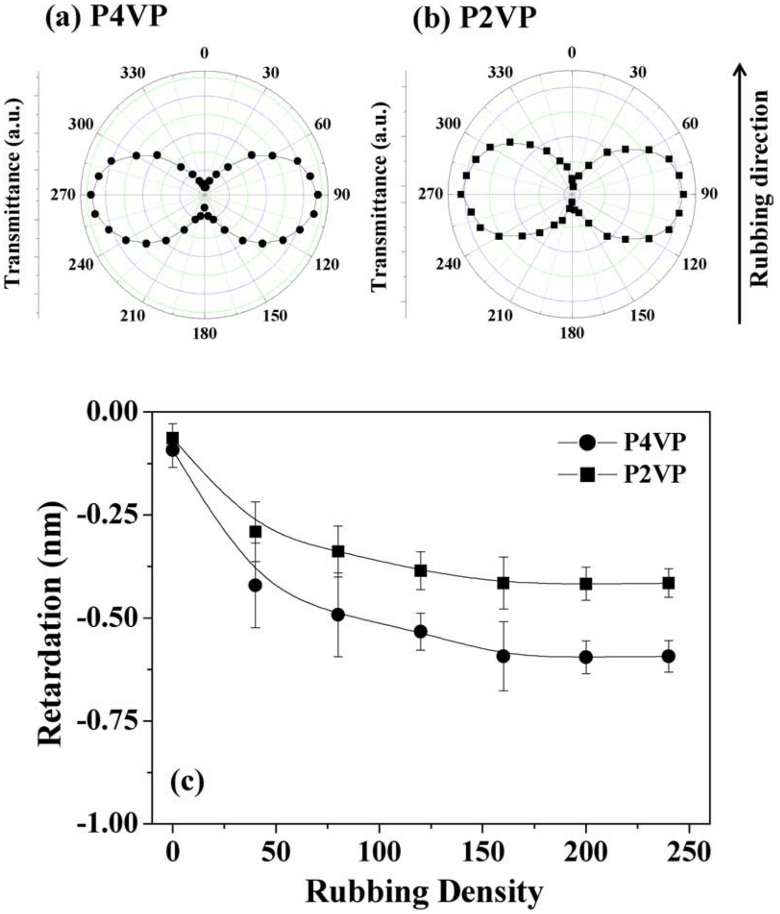

Fig. 2. Polar diagrams of the light transmittances (=[in-plane birefringence]×[phase]) taken from the optical phase retardation measurements of films rubbed at a rubbing density of 50, as a function of the angle of rotation of the films: (a) P4VP and (b) P2VP. (c) Variations of the optical retardations (=[in-plane birefringence]×[film thickness]) of P4VP and P2VP films rubbed with varying rubbing density.

1492) and (1556 and 1413) cm^{-1} indicate that the pyridine side groups of P4VP lie in planes perpendicular to the rubbing direction.

Fig. 3(a) also shows that the bands for the asymmetric CH_2 stretching vibration at 2925 cm^{-1} and the symmetric CH_2 stretching vibration at 2856 cm^{-1} are slightly more intense when the polarization of the incident IR beam is perpendicular to the rubbing direction. The dipole transition moments for the asymmetric and symmetric CH_2 stretching vibrations are perpendicular to the polymer backbone, and moreover these dipole transition moments are orthogonal to each other. Thus the dichroic IR results lead to the conclusion that the vinyl backbones of the P4VP polymer chains are aligned parallel to the rubbing direction on the rubbed film surface.

As can be seen in Fig. 3(b), the quadrant stretching and semicircle stretching bands of the pyridine rings in the rubbed P2VP film, as well as the asymmetric and symmetric CH_2 stretching bands of the vinyl main chain, are more intense when the polarization of the incident IR beam is perpendicular to the rubbing direction, as was observed for the rubbed P4VP film. These results indicate that on the rubbed P2VP film surface the pyridine side groups lie in planes perpendicular to the rubbing direction and that the vinyl backbones are aligned parallel to the rubbing direction. These dichroic IR results are consistent with the results derived from the optical retardation measurements.

We also conducted reflection IR spectral measurements with *p*-polarized radiation at an incidence angle of 82°. Fig. 4 shows the external reflection IR spectra measured with IR light polarized parallel to the rubbing direction and propagated toward the rubbing direction, as well as the transmission IR spectra measured with the IR light polarized parallel to the rubbing direction. As can be seen in Fig. 4(a), in the reflection spectrum **B** the intensities of the bands at 1596 and 1492 cm^{-1} with dipole transition moments that are aligned in the *para*-direction of the pyridine ring of P4VP are comparable to those in the transmission spectrum **A**. In **B** the intensities of the bands at 1556 and 1413 cm^{-1}, with dipole transition moments that are aligned in the pyridine ring plane but perpendicular to those of the vibrations at 1596 and 1492 cm^{-1}, are also comparable to those in **A**. These IR spectral results suggest that the *para*-directions of the pyridine side groups on the rubbed P4VP film surface are, on average, positioned with a tilt angle of about 45° in a plane perpendicular to the rubbing direction.

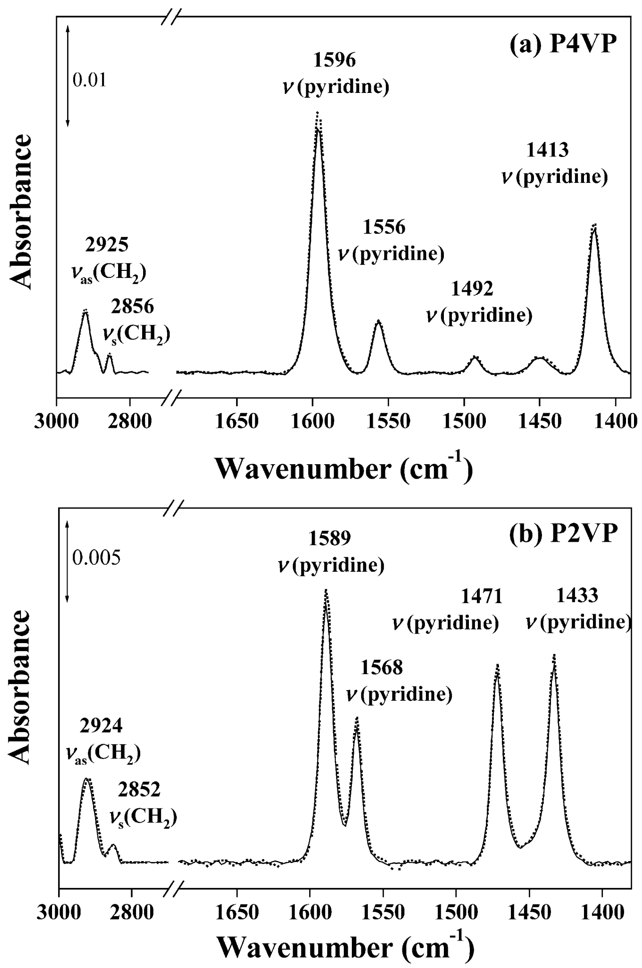

Fig. 3. Dichroic FTIR spectra of films rubbed with a rubbing density of 50: (a) P4VP and (b) P2VP. Solid and dashed lines represent the FTIR spectra with IR light polarized parallel and perpendicular to the rubbing direction, respectively.

Different from the rubbed P4VP film above, the rubbed P2VP film reveals that the bands at 1589 and 1471 cm^{-1} having dipole transition moments along the *para*-direction of the pyridine ring are less intense in the reflection IR spectrum than in the transmission spectrum, as shown in Fig. 4(b). The bands at 1568 and 1433 cm^{-1} having dipole transition moments that lie in the phenyl ring plane but perpendicular to those of the vibrations at 1589 and 1471 cm^{-1} are in contrary stronger in intensity in the reflection spectrum than in the transmission spectrum. Collectively these IR spectral results indicate that the *para*-directions of the pyridine side groups in the rubbed P2VP are, on average, aligned favorably in the rubbed film surface but perpendicular to the rubbing direction.

In addition, both the rubbed P4VP and P2VP films show that the asymmetric and symmetric CH_2 stretching vibration bands whose dipole transition moments are perpendicular to that of the polymer backbone are more intense in the reflection IR spectrum than in the transmission spectrum (Fig. 4). These results indicate that the C–H bonds are preferentially oriented normal to the rubbed film surface.

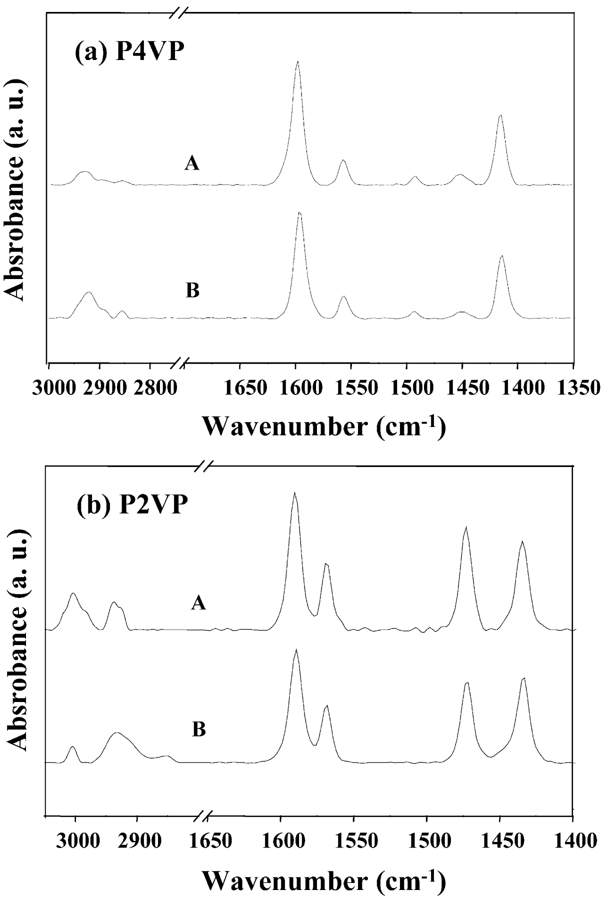

Fig. 4. (a) Linearly polarized FTIR spectra of a P4VP film rubbed with a rubbing density of 50: **A**, transmission spectrum; **B**, external reflection spectrum. (b) Linearly polarized FTIR spectra of a P2VP film rubbed with a rubbing density of 50: **A**, transmission spectrum; **B**, external reflection spectrum. The polarization direction of the incident IR beam was parallel to the rubbing direction in the films. The external reflection spectra were measured with *p*-polarized radiation at an incidence angle of 82°; the polarization direction was parallel to the rubbing direction and propagated toward the rubbing direction.

This is the first time IR spectroscopic techniques have been used to determine the three-dimensional orientation geometry of the pyridine rings at on the surface of rubbed P4VP and P2VP films.

3.3. Alignment and anchoring energy of LCs

Fig. 5(a) shows a representative polar diagram of the transmitted light intensity (=[in-plane birefringence]× [phase]) with respect to the angle of rotation of a rubbed P4VP film coated with 5CB; the film was rubbed at a rubbing density of 50. A similar polar diagram was observed for a rubbed P2VP film coated with 5CB, as shown in Fig. 5(b); this film was also rubbed at a rubbing density of 50. Similar polar diagrams were obtained for LC-coated P4VP and

P2VP films that had been rubbed at rubbing densities in the range 60–360.

As can be seen in Fig. 5, the rubbed films coated with 5CB exhibit a minimum light intensity along the direction 270° ↔ 90°, which lies perpendicular to the rubbing direction. These results indicate that the LC molecules in contact with the rubbed film surface of both polymers are induced homogeneously to align parallel to the rubbing direction.

Taking into account the results for surface morphology and orientations of the polymer chain segments described in earlier sections, the LC alignment data show that the LC molecules are induced to align parallel to the grooves and the oriented polymer main chains, i.e. parallel to the rubbing direction, indicating that the alignment of LCs is directly induced by the cooperation of the grooves and the oriented vinyl main chains, not by the oriented pyridine side groups. These LC alignment results are similar to those observed for rubbed PS films [30,31], for which the director of the LC alignment always coincides with the orientation direction of the generated microgrooves. However, the observed LC alignment of our study is a significant departure to that reported previously for rubbed P4VP films [32], when the LC alignment was found to be perpendicular to the rubbing direction.

TN cells filled with 5CB were prepared from P4VP and P2VP films rubbed at a rubbing density of 50–360, and then used for measuring the twist angle of the LC molecules in the cells. For TN LC cells prepared from rubbed P4VP films, the twist angles were measured to be 84–86°, depending on the rubbing density employed in the rubbing process. From these twist angles, the azimuthal anchoring energy of the LC molecule on the rubbed P4VP surface is estimated to be 3.0×10^{-5} to 5.2×10^{-5} J/cm^2. The TN LC cells retain the same level of azimuthal anchoring energy for 5 weeks. These anchoring energy values are much larger than those (0–3×10^{-7} J/cm^2) measured for rubbed PS films [31], but are still much lower than those (greater than 1×10^{-3} J/cm^2) observed for the rubbed films of conventional PIs currently used in the LC display industry [8–18,21,22].

In contrast, the TN LC cells prepared with rubbed P2VP films were found to have twist angles in the range 42–47°, depending on the rubbing density, which correspond to an azimuthal anchoring energy of 2.5×10^{-6} to 3.0×10^{-6} J/cm^2 of the LC molecules on the rubbed P2VP films. However, after 10 days the twist angles of the P2VP TN LC cells were significantly reduced to near 0°, implying an azimuthal anchoring energy of nearly zero; after this period the homogeneous LC alignments were completely disrupted. This result indicates that the anchoring of LC molecules on rubbed P2VP film surface has limited stability. These anchoring energies are lower than those measured for rubbed P4VP films, but are larger than those ($<3\times10^{-7}$ J/cm^2) determined for rubbed PS films.

We also attempted to measure the polar anchoring energies of the LC molecules in anti-parallel LC cells fabricated with rubbed P4VP and P2VP films. However, the uniform, homogeneous LC alignments of the LC cells of both polymers were easily disturbed even at the very low electric voltages applied in the polar anchoring energy measurements, regardless of the rubbing density used on the films. These results suggest that the LC molecules have very low polar anchoring energies on the rubbed P4VP and P2VP film surfaces that are too small to be measured.

In order to understand the observed LC alignments and their low anchoring energies, we need to consider all the factors possibly involved in the interactions of the LC molecules with the rubbed P4VP and P2VP film surfaces.

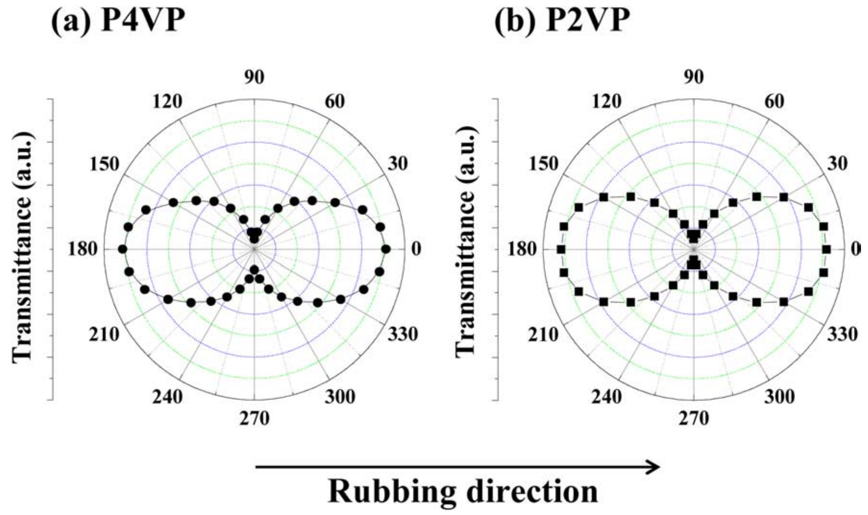

Fig. 5. Polar diagrams of the light transmittances (=[in-plane birefringence]×[phase]) taken from the optical phase retardation measurements of rubbed films coated with 5CB: (a) P4VP and (b) P2VP. The films were rubbed at a rubbing density of 50 and the thickness of the coated LC layer was 300 nm in each case.

First, the LC molecules are composed of an aromatic biphenyl mesogen and an aliphatic *n*-pentyl tail. The aliphatic tail might interact anisotropically with the parallel oriented vinyl main chains via a van der Waals type interaction, positively contributing to the observed LC alignments, but the aromatic mesogen might interact anisotropically via a π–π interaction with the perpendicularly oriented pyridine rings, negatively contributing to the observed LC alignments.

Second, as described above the rubbed film surface has microgrooves present along the rubbing direction, which seem too large to interact effectively with the LC molecules (approximately 2 nm in length and 0.3 nm in diameter). However, the LC molecules exhibit high short range and long range order, so the microgrooves might interact anisotropically with the LC molecules, positively contributing to the observed LC alignment.

Therefore, the observed LC alignments are due to the anisotropic interactions of the LC molecules with the parallel oriented vinyl main chains and with the grooves developed along the rubbing direction, which override the anisotropic interactions with the pyridine side groups oriented perpendicular to the rubbing direction. However, the relatively low anchoring energies and limited stabilities of the LC alignments suggest that the LC molecules have inherently weak interactions with the oriented polymer segments and the grooves on the rubbed film surfaces of both P4VP and P2VP. Further, the results suggest that although the anisotropic interactions of the LCs with the parallel oriented vinyl main chains are weak, they are only competing against the weak interactions of the LCs with the perpendicularly oriented pyridine side groups. For these LC molecules interacting weakly with both the parallel oriented polymer main chains and with the perpendicularly oriented pyridine side groups, the microgroove topography seems to play a critical role in governing the alignment director of the LC molecules, even though the anisotropic interactions of the grooves with the LC molecules are weak and theoretically ineffective.

For the anti-parallel LC cells fabricated with rubbed P4VP and P2VP films, the pre-tilt angles of the LCs were measured to be zero. This result might be due to the directionally anisotropic interactions of the LC segments with the oriented polymer segments, as discussed in what follows. First, the aliphatic tail of the LC molecule interacts via van der Waals interactions with the parallel oriented vinyl main chains, resulting in the positioning of the LC molecule in the film plane. Second, the aromatic mesogen unit of the LC molecule undergoes polar-to-polar interactions with the lone pair of electrons of the pyridine rings, which may be more favorable than the π–π interactions with the pyridine rings, inducing the LC molecules to position in the film plane along the rubbing direction. Thus, these specific interactions lead the LC molecule to align with zero pre-tilt angle.

4. Conclusions

The surface morphologies of and molecular orientations within P4VP and P2VP films before and after rubbing were investigated in detail by atomic force microscopy, optical retardation analysis, and dichroic IR spectroscopy. The alignments, pre-tilt angles, and anchoring energies of nematic LC molecules on the rubbed films were measured.

The AFM analysis found microgrooves along the rubbing direction in the rubbed film surfaces of both polymers. However, the grooves in the P2VP films were only poorly defined compared to those in the P4VP films. For both polymers, the vinyl backbones are oriented along the rubbing direction, while the pyridine side groups are oriented perpendicular to the rubbing direction; the *para*-directions of pyridine side groups in the P4VP have a tilt angle of about 45° in the plane perpendicular to the rubbing direction but the *para*-directions of pyridine side groups in the P2VP align nearly in the film surface.

Rubbed films of both polymers were found to align LCs along the rubbing direction. This LC alignment is governed for both films by the favorable anisotropic interactions of LCs with the oriented vinyl main chains and the microgrooves, which override interactions with the oriented pyridine side groups. However, for both films this LC alignment was found to have a low anchoring energy and limited stability. These results reveal some important features of the alignment of LCs on rubbed P4VP and P2VP film surfaces. First, the anchoring of LCs on the rubbed films of these polymers is inherently very weak. Second, the anisotropic interactions of LCs with the parallel oriented vinyl polymer backbones seem to be comparable to their interactions with the perpendicularly oriented pyridine side groups. Finally, the effectiveness of the microgrooves in aligning LCs might be limited because their dimensions are larger than those of LC molecules (a few nanometers in length and around 0.3 nm in diameter). Despite the expected limited effectiveness of the microgrooves in aligning LCs, these grooves play a critical role in governing the resulting alignment director of LCs, which also interact with the parallel oriented vinyl main chains in competition with the perpendicularly oriented pyridine side groups.

The pre-tilting angle of LCs on the rubbed P4VP and P2VP films was measured to be 0°, as observed previously. This LC pre-tilting behavior was investigated in detail, taking into account both the geometric structures of the oriented polymer segments and their anisotropic interactions with LCs.

Acknowledgements

This study was supported by the KOSEF via the Center for Integrated Molecular Systems and by the Ministry of Education (BK21 Project).

References

[1] Collings PJ, Patel JS, editors. Handbook of liquid crystal research. Oxford: Oxford University Press; 1997.

[2] Toney MF, Russell TP, Logan JA, Kikuchi H, Sands JM, Kumar SK. Nature 1995;374:709.

[3] Lee ES, Vetter P, Miyahita T, Uchida T. Jpn J Appl Phys 1993;32: L1339.

[4] Mori N, Morimoto M, Nakamura K. Macromolecules 1999;32:1488.

[5] Ge JJ, Li CY, Xue G, Mann IK, Zhang D, Wang S-Y, et al. J Am Chem Soc 2001;123:5768.

[6] Ban BS, Rim YN, Kim YB. Liq Cryst 2000;27:125.

[7] Kim J-H, Shi Y, Kumar Y. Appl Phys Lett 1997;71:3162.

[8] Chae B, Lee SW, Lee B, Choi W, Kim SB, Jung YM, et al. Langmuir 2003;19:9459.

[9] Lee K-W, Paek S-H, Lien A, During C, Fukuro H. Macromolecules 1996;29:8894.

[10] van Aerle NAJ, Tol JW. Macromolecules 1994;27:6520.

[11] Lee SW, Chae B, Lee B, Choi W, Kim SB, Kim SI, et al. Chem Mater 2003;15:3105.

[12] Kim SI, Ree M, Shin TJ, Jung JC. J Polym Sci, Part A: Polym Chem 1999;37:2909.

[13] Kim SI, Pyo SM, Ree M, Park M, Kim Y. Mol Cryst Liq Cryst 1998; 316:209.

[14] Ree M, Kim SI, Pyo SM, Shin TJ, Park HK, Jung JC. Macromol Symp 1999;142:73.

[15] Ree M, Shin TJ, Lee SW. Korean Polym J 2001;9:1.

[16] Park JH, Jung JC, Sohn BH, Lee SW, Ree M. J Polym Sci: Polym Chem 2001;39:3622.

[17] Park JH, Sohn BH, Jung JC, Lee SW, Ree M. J Polym Sci: Polym Chem 2001;39:1800.

[18] Jung JC, Lee KH, Sohn BH, Lee SW, Ree M. Macromol Symp 2001; 164:227.

[19] Nishikawa M, Taheri B, West JL. Appl Phys Lett 1998;72:2403.

[20] Nishikawa M, Taheri B, West JL. Mol Cryst Liq Cryst 1998;325:63.

[21] Chae B, Kim SB, Lee SW, Kim SI, Choi W, Lee B, et al. Macromolecules 2002;35:10119.

[22] Chae B, Lee SW, Lee B, Choi W, Kim SB, Jung YM, et al. J Phys Chem B 2003;107:11911.

[23] Geary JM, Goodby JW, Kmetz AR, Patel JS. J Appl Phys 1987;62: 4100.

[24] Ishihara S, Wakemoto H, Nakazima K, Mastuo Y. Liq Cryst 1989;4: 669.

[25] Seo D-S, Muroi K-I, Isogami T-R, Matsuda H, Kobayashi S. Jpn J Appl Phys 1992;31:2165.

[26] Seo D-S, Oh-Ide T, Matsuda H, Isogami T-R, Muroi K-I, Yabe Y, et al. Mol Cryst Liq Cryst 1993;231:95.

[27] Seo D-S, Yoshida N, Kobayashi S, Nishikawa M, Yabe Y. Jpn J Appl Phys 1995;34:4876.

[28] Stohr J, Samant MG, Cossy-Favre A, Diaz J, Momoi Y, Odahara S, et al. Macromolecules 1998;31:1942.

[29] Stohr J, Samant MG. J Electron Spectrosc Relat Phenom 1999;98–99: 189.

[30] Lee SW, Chae B, Kim HC, Lee B, Choi W, Kim SB, et al. Langmuir 2003;19:8735.

[31] Lee SW, Kim HC, Lee B, Chang T, Ree M. Macromolecules 2003;36: 9905.

[32] Nakajima K, Wakemoto H, Sato S, Yoktani F, Ishihara S, Matsuo Y. Mol Cryst Liq Cryst 1990;180B:223.

[33] Nastishin YA, Polak RD, Shiyanovskii SV, Lavrentovich OD. Appl Phys Lett 1999;75:202.

[34] Yokoyama H, van Sprang HA. J Appl Phys 1985;57:4520.

[35] Nastishin YA, Polak RD, Shiyanovskii SV, Bodnar VH, Lavrentovich OD. J Appl Phys 1999;86:4199.

[36] Ren Y, Murakami T, Nishioka T, Nakashima K, Noda I, Ozaki Y. Macromolecules 1999;32:6307.

[37] Velada JL, Cesteros LC, Katime I. Appl Spectrosc 1996;40:893.

[38] Colthup NB, Daly LH, Wiberly SE. Introduction to infrared and Raman spectroscopy. 3rd ed. San Diego, CA: Academic Press; 1990.