Optical Retardation and FT-IR Characteristics of Rubbed Polyimide Langmuir-Blodgett Alignment Layers of Liquid Crystals

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Abstract−Optical retardation and FT-IR characteristics of polyimide alignment layer of liquid crystals were investigated with Langmuir-Blodgett (LB) films rubbed perpendicularly to the dipping direction. While the retardations of LB films remained unchanged as the number of transfers increased, those of rubbed films increased up to 7 layers, but after a maximum retardation, they decreased steadily as the number of transfers increased. The retardations of films thicker than about 7-9 layers shifted negatively, indicating that the optical axis completely switched to the direction of rubbing. Further, difference of retardation between unrubbed and rubbed films indicates that there existed a limit in the number of layers, i.e., about 30 layers, to be influenced by the surface forces. It is an interesting observation that the substrate surface freezes the polymer chains up to 7-9 layers, persistent to the rubbing strength, while the surface rubbing force penetrates into about 30 layers. The IR dichroic ratio ($A_\parallel / A_\perp$) of 1,500 cm^{-1} and of 1,240 cm^{-1} decreases by rubbing, while little change at 1,720 cm^{-1}, indicating that benzene groups are reoriented to the direction of rubbing, while imide groups are not reoriented.

Key words: Polyimide, Langmuir-Blodgett Film, Alignment Layers, Depth Profile of Rubbing

INTRODUCTION

The uniform alignment of liquid crystals has now become a conventional issue, yet practical problems have not been resolved in the LCD industries [Uchida, 1985]. Various treatment methods such as an oblique evaporation of SiO$_x$, a rubbing of polymer film, a Langmuir-Blodgett (LB) film and a photoaligned film of photosensitive polymers have been proposed to align liquid crystals in an LCD cell. The rubbing process, among these methods, has been industrially accepted for an alignment of liquid crystals simply by rubbing a polymer film coated on a substrate in a panel fabrication.

Liquid crystal molecules, it is well known, are aligned on a rubbed polymer surface along a rubbing direction, while the alignment mechanism of liquid crystals by rubbing is still not clearly understood. Generally, it is accepted that two phenomena are considered to play a key role in the alignment mechanisms. One is attributed to a microgroove formed by rubbing fabrics on the surface of a film [Berreman, 1972; Flanders et al., 1978], and the other is to the molecular interaction of liquid crystals with surface polymer segments rearranged by a shear stress during rubbing [Castellano, 1983; Geary et al., 1987; Ishihara et al., 1989; Ichinose et al., 1991]. However, it is not clear whether two mechanisms compete or cooperate, and if it is complementary, what degree of their relative contributions is originated from.

Recently, we studied contact angles and pretilts of liquid crystals on rubbed polyimide films [Kim and Kim, 1996] or mixed LB films [Koo et al., 1997]. The relative contributions of two mechanisms to pretilt angles of liquid crystals are quantitatively separated [Koo et al., 1999; Kim et al., 2001], when alignment layers are prepared by the deposition of LB films on top of rubbed polyimide films.

The LB method showed some difficulties in forming a uniform domain [Ogawa et al., 1990], but it was generally accepted for a molecular scale process, capable of controlling a molecular scale of fabrication to reveal the mechanism of alignment [Sorita et al., 1991]. The rubbing usually creates grooves and new molecular interactions, while the LB transfer does not introduce grooves and pretilts of liquid crystals. The step-by-step deposition on the top of a rubbed surface was found to reduce the pretilts of liquid crystals and finally to zero as in a normal LB surface.

Although two mechanisms and their relative contribution have become clear, the influence of corresponding surface forces into the depth of films needs to be identified. The small angle X-ray diffraction measurement showed a significant interfacial region of molecular reorientation of polymer chains up to 100 Å [Nejoh, 1991], but no observation has been reported for the influence of rubbing on a layered LB film. In this study, after the LB films were prepared on the surface of an indium-tin-oxide (ITO) glass or a silicon wafer and then rubbed, the optical retardation and FT-IR dichroism were measured to monitor the reorientation of polymer chains in LB films created by dipping and rubbing.

EXPERIMENTAL

Polyamic acid used as a precursor of polyimide was PMDA-3,3'-ODA. A polyamic acid salt (PAAS) was synthesized by attaching two molecules of N,N'-dimethylhexadecylamine (DMC16, Tokyo Kasei Kogyo Co.) to each unit of polyamic acid. N,N'-dimethylformamide (DMF, Aldrich) was used as a solvent for PAAS to be spread on purified water. PAAS molecules of 1 mmol/*l* concentration, were spread on a water surface and compressed to determine a π-A isotherm with a LB trough (KSV-5000, KSV Instrument Ltd., Finland). The compressed monolayers were transferred onto the surface of ITO glasses, employing a vertical dipping against the sur-

Table 1. The rubbing strength used in this experiment

Rubbing parameters (L)*	Rotational speeds of cylinder (rpm)	Moving speed of substrate (cm/sec)
No	0	0
50	280	0.7
100	560	0.7
150	870	0.7
200	1,110	0.7
250	1,250	0.7

*Nominal rubbing parameter in this experiment.
**Polyimide coated substrate was strongly rubbed with deeply pressing to a rubbing cloth.

face of water at various deposition pressures. In the previous work, we reported π-A isotherms, transfer ratios and thermal imidization conditions of PAAS, and the existence of an optimal condition [Tae et al., 1995]. The optimal speed of deposition was 5 mm/min. After being deposited, the PAAS films were thermally cured at 300 °C for 1 hr [Kim and Kim, 1996], and then the cured LB films were rubbed by a rubbing machine with a roller of velvet (Yoshikawa Co.) at several rotational speeds. The rubbing direction was perpendicular to a dipping direction. A rubbing strength (L/l) applied to a film surface is defined as [Sato, 1992].

$$L/l=N(1+2\pi rm/60v) \qquad (1)$$

where N is the cumulative number of rubbings, l is the contact length of the circumference of a rubbing roller, n is the number of revolutions per minute (rpm) of the roller, r is the radius, and v is the velocity of the substrate stage. The rubbing strengths and conditions used in this work are listed in Table 1.

Two methods were used to estimate the degree of orientation of polyimide. The optical retardation method [Han et al., 1993; Sun et al., 1995; Seo et al., 1995], a very sensitive method of measuring the optical retardation, reported by Frattini and Fuller [Frattini and Fuller, 1984], was employed. The IR absorption spectra were measured by an FTS-60 spectrometer with a detector of deuterated triglycine sulfate (DTGS). For all absorption measurements, 100 spectral scans were averaged with a 4 cm⁻¹ resolution. The samples were vacuum-dried at 80 °C for 12 hours. The substrate used was a silicon wafer, and 100 layers of LB films were cumulatively deposited for FT-IR experiments.

The optical retardation (δ) is proportional to the thickness and the anisotropy of refractive index of a film and is defined as

$$\delta =\frac{2\pi\Delta n\cdot d}{\lambda} \qquad (2)$$

where Δn is the difference of refractive indices between x and y directions in a layer plane, d is the thickness of a film, and λ is the wavelength of a laser. In this experiment, d was determined by a surface profiler system (α-step).

RESULTS AND DISCUSSION

The optical retardation and FT-IR measurements of polyimide films were performed after PAAS LB films were cured. The FT-IR
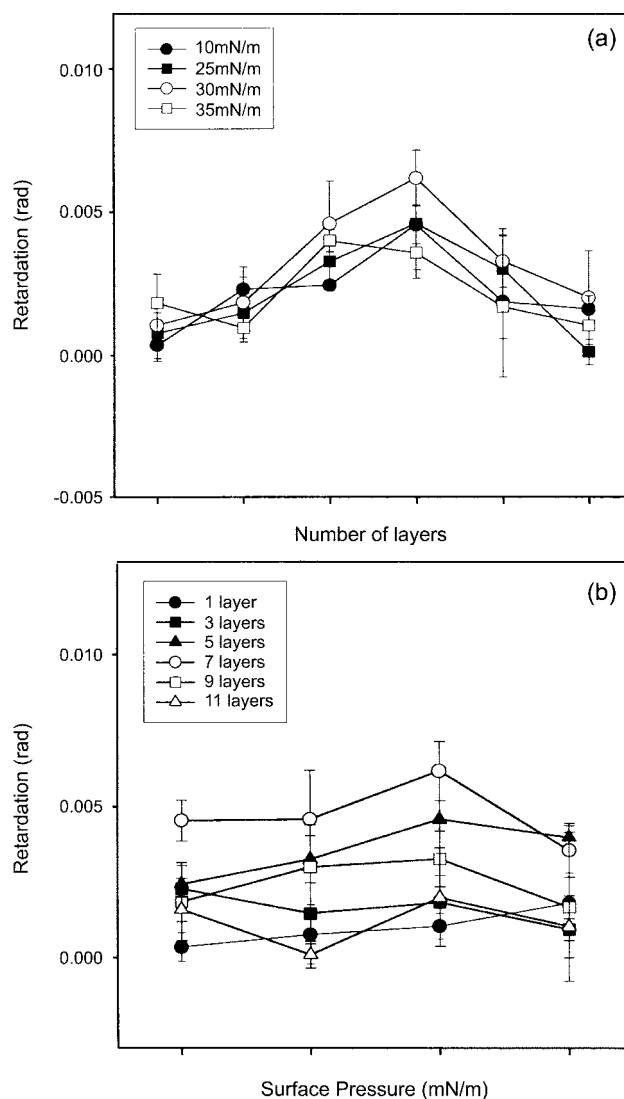

Fig. 1. Relationship between (a) the number of layers, (b) surface pressure and retardation for polyimide LB films.

dichroic ratios of functional group are often used to determine the orientation of a polymer film, but several hundreds of LB layers are required to have a reliable ratio of the characteristic peak-to-noise intensity. In our current interests, however, the polymer orientation may have an anisotropy only within several layers and therefore, the optical retardation method was discussed in detail.

1. Optical Retardation of LB Films

Fig. 1 shows the optical retardation of the LB films of polyimide as a function of the number of layer and surface pressures. Fig. 1(a) shows that the optical retardation increases up to the 7th layer, but that it decreases beyond it. The optical retardation is proportional to the thickness of a film and the average refractive index of a film is as given by Eq. (2). Therefore, the linear increase may indicate that the refractive index of each layer is constant since the thickness of each layer is equal, and as a result that the layer structure and molecular state of each layer are safely assumed to be identical. Such a stable formation of layers may be attributed to the strong surface force and the intermolecular interaction during a dipping process. However, we also observe the decrease of retardation
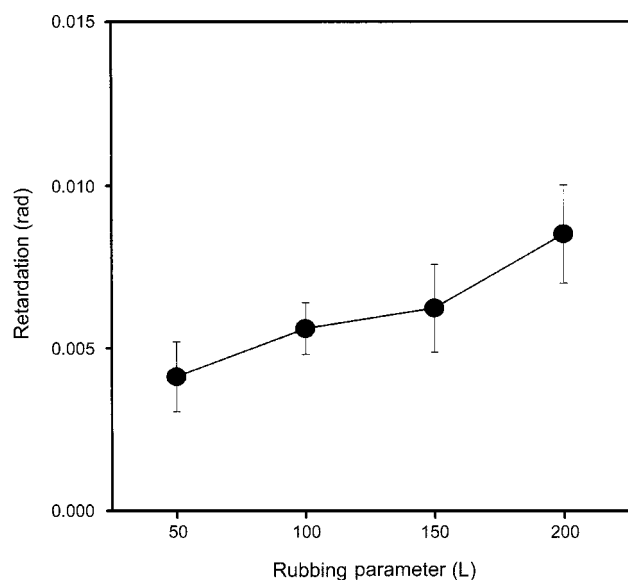
Fig. 2. Relationship between the rubbing parameter and retardation for rubbed polyimide films.

after the 7th layer, of which the distance from an ITO surface can be estimated to be about 35 Å. Since the observed refractive index is averaged, the added layer next to the 7th layer should be significantly random and effectively the overall refractive index would drop. This observation may indicate that the strong surface force is applied up to the 7th layer enough to sustain the molecular orientation formed during the dipping process and that the interlayer interaction may not be strong enough to maintain it.

Fig. 1(b) shows that the optical retardations at different surface

pressures are not very sensitive, but that the degree of retardation at the 30 mN/m is higher than those of other surface pressures. The high retardation at the 30 mN/m is not irrelevant to the packing state of monolayer, which is much densely packed at the pressure [Tae et al., 1995]. The slight decrease at the 35 mN/m was expected, because it was less stable near the collapse pressure. It is also concluded that the mean orientation of LB films is significantly influenced by the stably packed state of a monolayer at an air-water interface, though it is reduced by the evaporation of DMC16 during the curing process.

Fig. 3 shows a cross-polarized image of nematic liquid crystals in a cell made by polyimide LB films. The alignment layer of each cell was deposited at different surface pressures. All liquid crystal cells were antiparallelly constructed, and the number of layers was 7, because it showed the best orientation as shown in Fig. 1. The degree of alignment at 10 mN/m, which is equivalent to a liquid phase in the π-A isotherm, is not good as shown in Fig. 2(a) and many domains exist in the cell. However, the degree of alignment of liquid crystal increases with surface pressures. At 30 mN/m as shown in Fig. 3(c), no domains appear but the defects are still observed. It is significant that the textures of liquid crystals in the cells fabricated with LB films follow the same trends of their optical retardations.

2. Optical Retardation of the Rubbed Layers

Fig. 2 shows the change of optical retardations of rubbed films of spin-coated polyimide as the rubbing strength increases. The observation agrees with others, such that the optical retardation increases with rubbing strength and becomes gradually saturated [Sun et al., 1995; Seo et al., 1995]. When a polyimide film is rubbed, it is expected that polymer chains can be oriented to the direction of rubbing, and that the degree of their ordering will increase with rubbing strength. It is also noted that the retardations of rubbed polymer layers
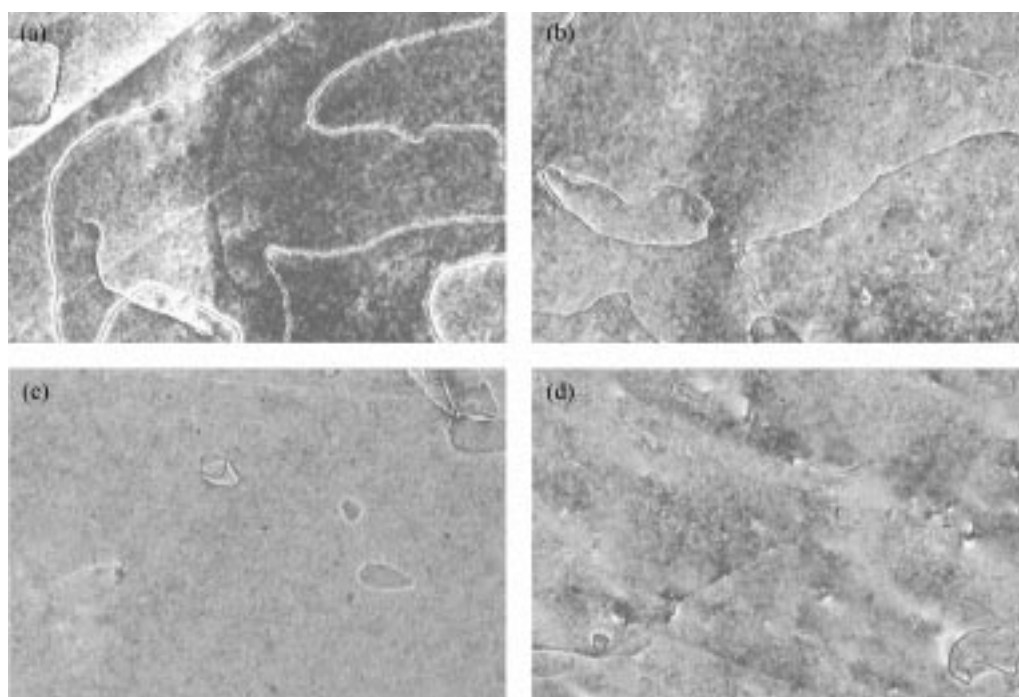

Fig. 3. Crossly polarized microscopic textures of nematic LC cells with PMDA/ODA polyimide alignment films; (a) 10 mN/m, (b) 25, (c) 30, and (d) 35 (Number of layers is 7).
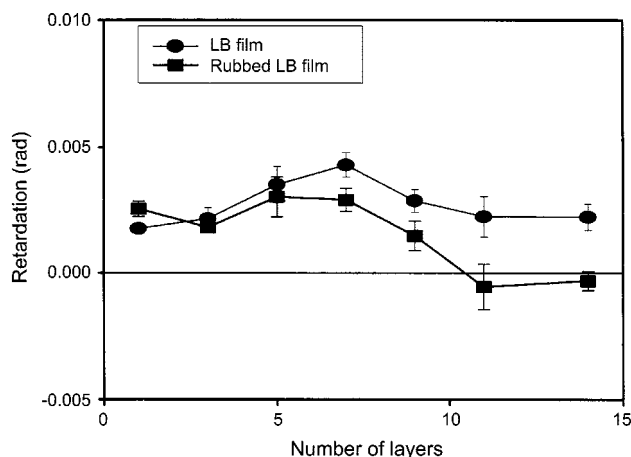
Fig. 4. Relationship between the number of layers and retardation for polyimide LB and rubbed films; rubbing direction is perpendicular to the dipping direction and rubbing strength is 100 cm.

are about 2 times greater than those of LB films, indicating that the rubbing stress may penetrate into a deep layer or that the impact of surface stress may cause the effective ordering at a surface region. This is consistent with the observations of anchoring energies and pretilt angles [Sato, 1992; Seo et al., 1995].

3. Polymer Chain Orientation by Rubbing Process

The LB films were rubbed perpendicularly to the directions of dipping. Fig. 4 shows the significant change of optical retardations of the rubbed LB film (■) from the original LB film (●). The deposition surface pressure for all samples is 30 mN/m and the rubbing parameter is 100 for all layers. The minus retardation means that the orientation direction is perpendicular to the dipping direction, that is, the polymer chains directors may change the orientation from the parallel direction of dipping to rubbing. The large change of optical retardations of thick layers may indicate that the surface stress penetrates into the deep layer. Fig. 4 shows that significant residual retardation remains up to about the 9th layer after rubbing, and that the rubbing treatment does not affect the molecular orientation near a substrate surface. Therefore, the molecular chains of LB films are firmly attached on the surface, i.e., up to the 7-9th layer by the surface force, while the polymer chains beyond the layer may change the orientation parallel to the rubbing direction as the surface stress penetrate deeply into the layer.

Fig. 5 shows the difference of optical retardations of rubbed LB films from original LB films. The difference increases with the number of layers and saturates above the 30 layers. At 30 mN/m, the transfer ratio of each layer is almost constant, and thus the film thickness linearly increases with the number of layers. Therefore, the saturating behavior of retardation at the linearly increasing thickness clearly demonstrates the existence of a certain limit of thickness influenced by a rubbing force. In fact, the retardation difference of layers by rubbing represents a depth profile of the interfacial region influenced by a rubbing process and the interfacial layer thickness can be roughly calculated to be about 30 layers or effectively 150 Å (assumed one thickness of a layer is 5 Å), which is consistent with the X-ray measurement [Nejoh, 1991].
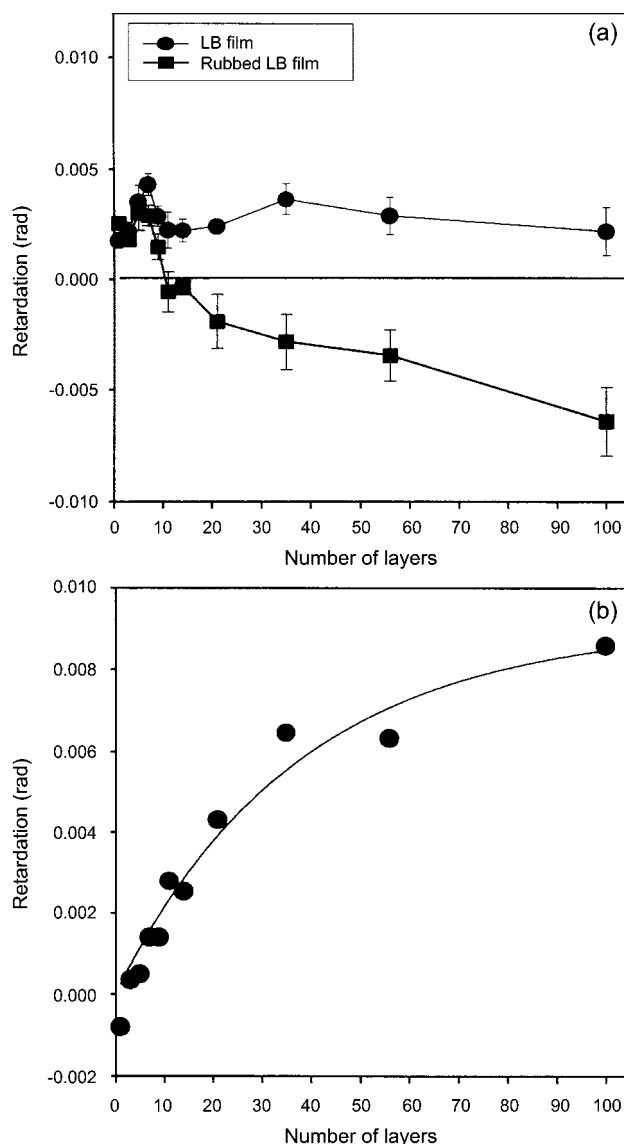
4. FT-IR Dichroic Ratio

Fig. 5. The measured results of retardation of polyimide LB and rubbed films; (a) relationship between the number of layers and retardation for polyimide LB and rubbed films, and (b) relationship between the number of layers and difference retardation for polyimide LB and rubbed films.

Fig. 6 shows the polarized FT-IR spectra of an LB film, and a rubbed LB film and IR dichroic ratios are summarized in Table 2. The deposition surface pressure was 30 mN/m, the number of layers was 100, and the rubbing strength was 100. For an LB film, the absorbance of a parallel direction to a dipping is larger than that of a perpendicular direction, but the difference is very small. Therefore, it is difficult to observe the degree of polymer chain orientation in an LB film. For a rubbed LB film, the peak intensity of a functional group, where 1,500 cm^{-1} indicates a tangential ring stretching mode and 1,240 cm^{-1} does a C-O-C stretching mode, increases by rubbing, but the peak intensity of 1,720 cm^{-1}, which is a C=O stretching mode, decreases slightly by rubbing. This result supports that the benzene group is reoriented to the rubbing direction by a rubbing process, whereas the imide group is not reoriented. Since liquid crystals well align to the rubbing direction in the cell, benzene
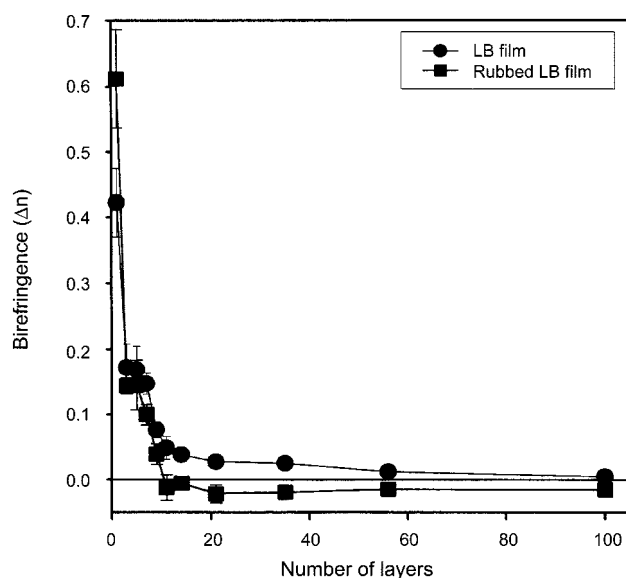
Fig. 6. Relationship between the number of layers and the birefringence (Δn) for polyimide LB and rubbed films (L= 100 cm).

Table 2. IR dichroic ratio ($A_{\parallel}/A_{\perp}$) of polyimide alignment layer

	LB film	Rubbed LB film
$1{,}240\,\mathrm{cm}^{-1}$	1.0248	0.8872
$1{,}500\,\mathrm{cm}^{-1}$	1.0133	0.8834
$1{,}720\,\mathrm{cm}^{-1}$	0.9583	1.03

groups, which are reoriented to rubbing direction by a rubbing process, have a dominant effect on the alignment of liquid crystals.

CONCLUSION

Optical retardation and FT-IR spectra were studied with a rubbed polyimide LB film as alignment layers of liquid crystals. The alignment layers were fabricated by rubbing LB films perpendicularly to their dipping direction after they were transferred at various surface pressures and dipping speeds.

The retardations of LB films increased until seven layers were deposited at 30 mN/m but decreased steadily with the number of transfers. The rubbing also increases the optical retardation of polyimide layers. When the LB films were rubbed, the retardation of rubbed layers shifted negatively after about 7-9 layers, while the simple deposition exhibited no change of retardation with the number of transfers.

Further, a difference of retardation indicates that there existed a limit in the number of layers, i.e., about 30 layers, to be influenced by a surface force. It is significant that the substrate surface freezes the polymer chains up to 7-9 layers, persistent to the rubbing strength, while the rubbing force penetrates into about 30 layers.

The IR dichroic ratio ($A_{\parallel}/A_{\perp}$) of $1{,}500\,\mathrm{cm}^{-1}$, a tangential ring stretching mode, and of $1{,}240\,\mathrm{cm}^{-1}$, a C-O-C stretching mode, decreases by rubbing, while there is little change at $1{,}720\,\mathrm{cm}^{-1}$, a C=O stretching mode. This indicates that benzene groups are reoriented to the rubbing direction by a rubbing process, while imide groups
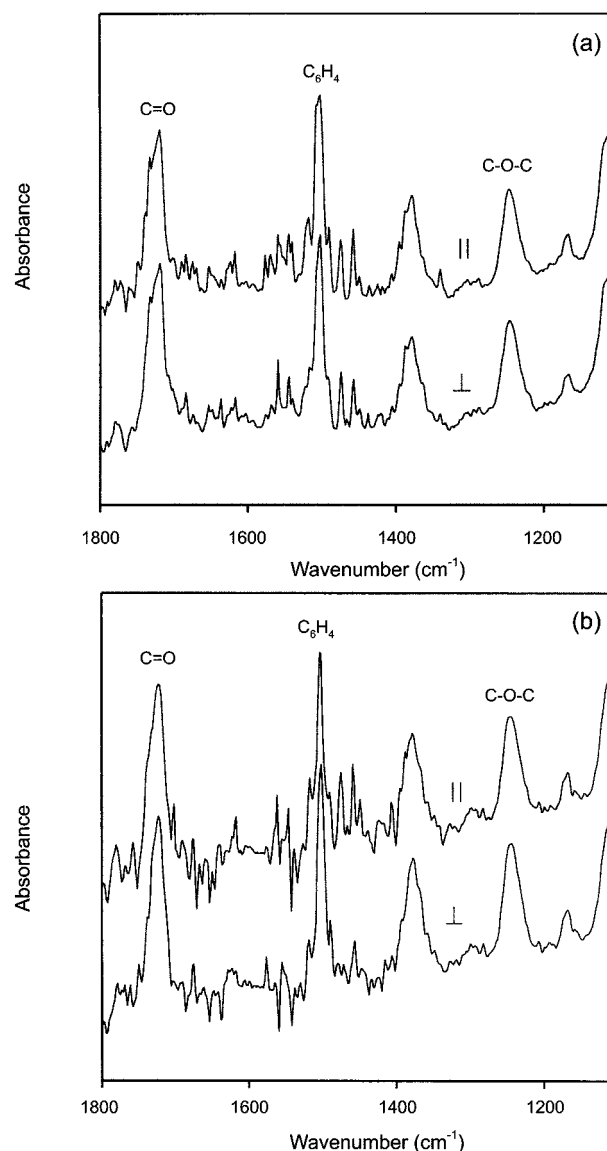
Fig. 7. IR dichroic spectra of the (a) polyimide LB films and (b) rubbed LB film (∥ show the spectra when the polarization vector is parallel to the dipping direction. ⊥ show the spectra when the polarization vector is perpendicular to the dipping direction).

are not reoriented. Liquid crystals well align to the rubbing direction in the cell, indicating that the benzene group had the dominant influence on the alignment of liquid crystals.

In a summary, the rubbing of LB films would realign the polymer chains from a dipping direction to a rubbing direction.

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