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The effect of rubbed polymer films on the liquid crystal alignment

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The observation of surface profiles on rubbed polymer films demonstrated that micro-grooves had been formed on the polymer surface. On the other hand, the infrared (I.R.) and U.V.-visible dichroic measurements of the rubbed polymer films have revealed that the polymer backbone chains are oriented parallel with the rubbing direction. We determined whether micro-grooves or polymer chain orientation causes the alignment of liquid crystal (LC) molecules. It was found in polystyrene (PS) films that LC molecules aligned perpendicular to the rubbing direction, although there were micro-grooves whose direction was the same as a rubbing direction. It was also found that the rubbed polyimide (PI) films lost LC alignment ability when they had been covered with Pt–Pd films about 30 Å thick, even though micro-grooves were still present. The experimental results imply that LC molecules are aligned by the effect of the orientation of the polymer chains on a rubbed polymer surface.

1. Introduction

Homogeneous aligning techniques of liquid crystal (LC) molecules are very important in the field of LC applications. Such homogeneous alignment can be achieved by using directionally-controlled substrates which are obtained by oblique evaporation [1] or by utilizing LB (Langmuir–Blodgett) films [2], unidirectionally stretched polymers [3], and rubbed polymers. Of these, the polymer rubbing method is particularly attractive because of feasibility for mass productivity and large area treatment. The question of why the rubbed polymer causes LC alignment along the rubbing direction, however, has not yet been adequately addressed up to the present.

Berreman [4] has examined the aligning effect of the glass surface rubbed with diamond paste on leather, and observed micro-grooves on its surface along the rubbing direction for the first time. Calculating an elastic strain energy based on physical shapes of the grooves, he attributed the origin of the LC alignment to the elastic interaction between the LC molecules and the micro-grooves.

On the other hand, in polymer aligning films, there was an idea that LC molecules are aligned by molecular interactions between LC and polymer molecules, as micro-grooved substrates of some kinds of polymers had no ability to align LC molecules. Patel, Leslie and Goodby testified that some straight-chain polymers bring about the good alignment of smectic LC materials on the concept that LC alignment might be originated from an orientation of polymer chains [5].

With these circumstances for the background, we studied the alignment of LC molecules on rubbed polymer films of several kinds. As a result, we have found that the direction of the LC alignment is not necessarily identical with the rubbing direction. Furthermore, we examined the physical shape of the film surface and the degree of the polymer chain orientation in aligning films. In the latter part

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of this paper, we made discussions on the origin of the aligning ability of rubbed polymer films.

2. Experimental

2.1. *Materials*

Polyimide (PI) (PIX-5400, Hitachi Chemical Inc.), polyvinyl alcohol (PVA) (PVA-117, Kuraray Co., Ltd.), polystyrene (PS) (HRM-2-311, DENKI KAGAKU KOGYOU), and gelatin (RX-10, Nitta Gelatin) were used as aligning polymers. The guest host LC mixture E63D102 (BDH) was used to measure aligning directions of LC molecule and to confirm the degree of LC alignments.

2.2. *Preparation of thin polymer films*

Polymer films were deposited on a substrate from polymer solutions by spinning method and baked at an appropriate temperature. Detailed conditions are summarized in table 1. The thickness of the polymer films was measured by the alpha-step^R(TENCOR INSTRUMENTS) and found to be about 1700 Å for gelatin films, about 1000 Å for PI and PS films, and about 400 Å for PVA films. Each polymer film was rubbed with a nylon cloth (NB-1L, Hiroki Company) by pressing it down onto the cloth under a 24·3 g/cm^2 load and subsequently moving it unidirectionally over the cloth 27 cm for ten times at a velocity of 6·8 cm/s (a standard condition).

Table 1. Preparative conditions of thin polymer films.

	Polymer materials			
	PI	PS	PVA	Gelatin
Concentration/wt%	4·5	1·5	1·5	6·7
Solvent	NMP	toluene	water	water
Substrate	ITO, glass, CaF$_2$	ITO, CaF$_2$	glass	ITO
Baking temperature/°C	250	150	120	120
Baking time/h	2	0·5	1	2

PI, polyimide: PS, polystyrene; PVA, polyvinyl alcohol; NMP, *N*-methyl 2-piloridone.

2.3. *Observations of surface profiles of polymer films*

The polymer surface was examined by a scanning electron micrography (SEM) (S-800, Hitachi Works) with a magnification of 50000 and by a three-dimensional non-contact surface profiler (TOPO-3D, WYKO Co.) with thickness resolution of 3 Å.

2.4. *Observations of the orientation of polymer chains*

Orientation of the polymer chains was estimated by the infrared (I.R.) and U.V.-visible dichroic measurements. I.R. dichroic spectra were recorded with an FT-I.R. spectrophotometer (60SX, Nicolet) using the rubbed polymer films cast on calcium fluoride (CaF$_2$) plates. U.V.-visible dichroic measurements were carried out with a U.V. spectrophotometer (UV-260 Shimazu Corporation) using a rubbed PVA film doped with a dye (RED-14C, an azo dye manufactured by Nippon Kayaku Co., Ltd.) deposited on a glass plate. The dye concentration was 20 per cent by weight; the dye was used to visualize the PVA chain orientation by the dichroic measurement. Both the I.R. and U.V.-visible dichroic spectra were obtained using probe rays which were incident perpendicularly onto the film plane with their polarization plane either parallel or perpendicular to the rubbing direction.

3. Results and discussion

3.1. *Physical profile of the polymer film surface*

Figure 1 displays an electron micrograph of the surface of the rubbed PI film measured by a SEM. This picture shows that micro-grooves have been formed along the rubbing direction with separation of some 100 Å to 1000 Å on the surface of the polymer film. The depth of the micro-grooves was found to be some 10 Å to 300 Å by a surface profiler.

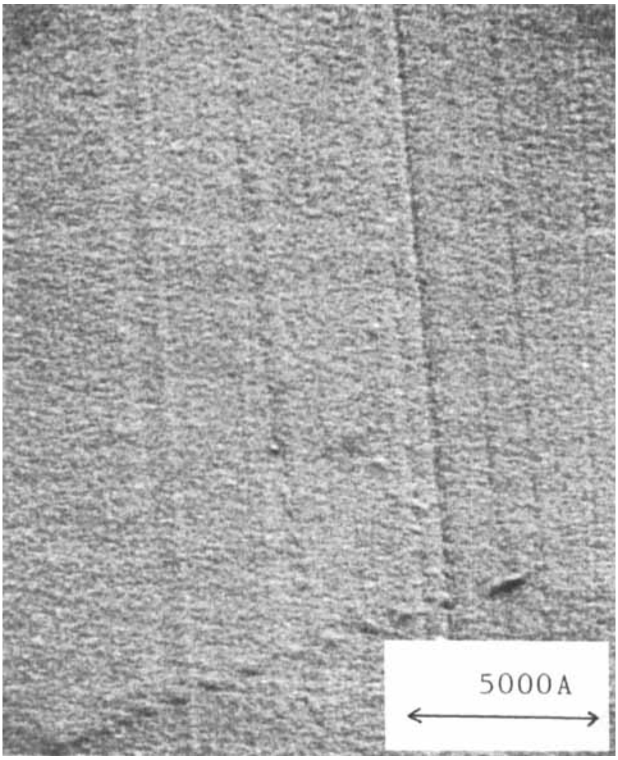

Figure 1. SEM observation of the surface on the rubbed polyimide (PI) film (magnification × 50 000). The film thickness is about 1000 Å.

3.2. *Orientation of the polymer chains in polymer films*

Figure 2 shows the FT-I.R. spectrum of the rubbed PI film. The orientation degree of the polymer chains was estimated from the dichroic ratio of the absorbance $A(1724)$, denoting the absorbance at 1724 cm^{-1}, for the stretching vibration of the carbonyl ($>$C=O) group in an imido ring. The absorbance was normalized to minimize experimental errors by dividing the absorbance $A(1724)$ by the absorbance $A(1499)$ of the CH inplane vibration of benzene ring as a reference vibration. That is, the dichroic ratio is given by $R_\perp/R_\parallel$, where $R_\perp$ and $R_\parallel$ denote the absorbance ratios $A_\perp(1724)/A_\perp(1499)$ and $A_\parallel(1724)/A_\parallel(1499)$, respectively; and $A_\perp$ and $A_\parallel$ denote the

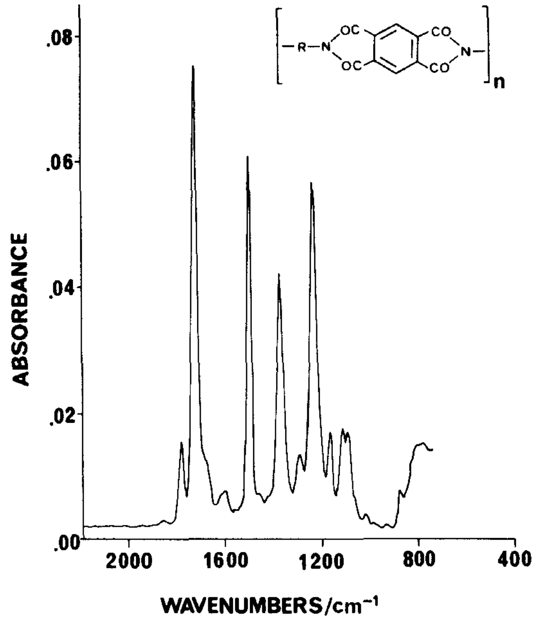

Figure 2. FT-I.R. spectrum of the rubbed polyimide (PI) film. The film thickness on a CaF_2 substrate is about 1000 Å. The structure of PI is shown in a figure, where $R = -C_6H_4-O-C_6H_4-$.

Table 2. Influence of the cumulative number of rubbings on the anisotropy of the absorbance of polyimide (PI) films. $R_\perp$ and $R_\parallel$ are given by $A_\perp(1724)/A_\perp(1499)$ and $A_\parallel(1724)/A_\parallel(1499)$, respectively.

Cumulative number of rubbing	Absorbance ratio $R_\perp$	Absorbance ratio $R_\parallel$	$\frac{R_\perp}{R_\parallel}$
0	1·25	1·26	0·99
10	1·29	1·22	1·06
100	1·29	1·22	1·06

absorbances obtained with a probe ray polarized perpendicular and parallel to the rubbing direction, respectively.

Table 2 shows the influence of the cumulative number of rubbings on $R_\perp$, $R_\parallel$, and $R_\perp/R_\parallel$. Without a rubbing treatment, the anisotropy of the absorbance $A(1724)$ was not observed at all. With increase of the cumulative number of rubbings, the ratio $R_\perp/R_\parallel$ increased. This observation implies that the degree of the polymer chain orientation increases by a rubbing treatment and that the carbonyl groups make an angle of more than 45 degrees with the rubbing direction. That is, it might be inferred that polymer backbone chains are highly aligned along the rubbing direction by the rubbing treatment, as the angle between the carbonyl group and the polymer backbone chain has been regarded to be considerably large. (M. Murakami obtained the angle of about 77 degrees from X-ray diffraction studies [6].)

The orientation of PS chains was evaluated by measuring the anisotropy of the absorbance $A(2924)$ occurring from the angular vibration of methine ($-CH_2-$) groups in PS backbone chains. Also in this case, the absorbance was normalized by dividing

Table 3. FT-I.R. measurements of the polystyrene film, $R_{\perp}$ and $R_{\parallel}$ are given by $A_{\perp}(2924)/A_{\perp}(1494)$ and $A_{\parallel}(2924)/A_{\parallel}(1494)$, respectively.

	Absorbance ratio $R_{\perp}$	Absorbance ratio $R_{\parallel}$	$\frac{R_{\perp}}{R_{\parallel}}$
Unrubbed film	0·98	0·98	1·00
Rubbed film	1·02	0·97	1·05

the absorbance $A(2924)$ by the absorbance $A(1494)$ of the inplane vibration of benzene rings as a reference vibration. The results are summarized in table 3. Table 3 again implies that polymer backbone chains are oriented along the rubbing direction in a PS film.

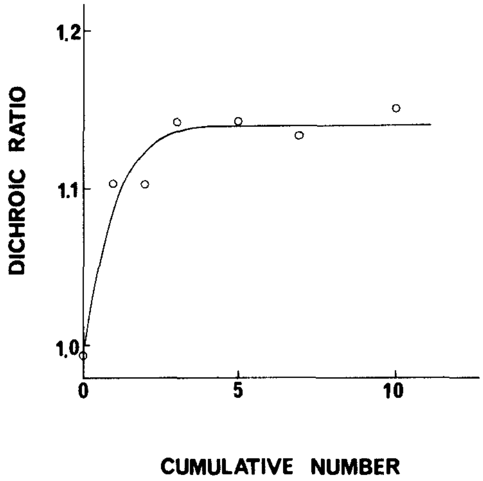

Figure 3. Influence of the cumulative number of rubbings on the dichroic ratio of the azo dye which is doped in a PVA film. The film thickness is about 400 Å. The dye concentration is 20 per cent by weight.

Figure 3 shows the increase of the dichroic ratio of the dye-doped PVA film with increase of the cumulative number of rubbings. The dichroic ratio was defined by the ratio of the absorbance $A_{\parallel}$ to the absorbance $A_{\perp}$ at the absorbance peak at 515 nm. The increase of the dichroic ratio corresponds to the increase of the degree of the polymer chain orientation induced by the rubbing treatment.

These experiments clearly demonstrate that the polymer backbone chains are oriented along the same direction as the micro-grooves shaped in parallel to the rubbing direction. Therefore, it is quite difficult to determine whether micro-grooves or the orientation of polymer chains causes the LC alignment.

3.3. *Which is effective for LC alignment, the effect of micro-grooves or that of the orientation of polymer chains?*

We found that some polymer films aligned LC molecules in different directions from a rubbing direction. The observation results of the alignment are summarized in table 4. It is confirmed by SEM observations that micro-grooves have been formed parallel to the rubbing direction in all polymer films. LC molecules are aligned along the rubbing direction when PI and PVA are used as aligning polymers, whereas LC

Table 4. Changes of the liquid crystal (LC) aligning direction with aligning polymers.

	Aligning polymers		
	Polyimide	Polystyrene	Gelatin
Rubbing direction	↑↓	↑↓	↑↓
LC aligning direction	↕	↔	⤡⤢†
Micro-groove direction	↕	↕	↕
Direction of Polymer backbone chain	↕	↕	unknown

† LC alignment is twisted from one substrate toward another.

molecules are aligned at angles of 90 degrees and 45 degrees with a rubbing direction in the case of PS and gelatin films, respectively.

Such difference of the LC alignment results from the variety in the chemical structure of the polymer. In the case of PI, for instance, the polymer backbone involving aromatic groups is supposed to play an important role in the LC alignment. For PS, on the other hand, side phenyl groups in PS chains are probably responsible for the LC alignment. The finding that the LC molecules align with an angle of 45 degrees from the rubbing direction in gelatin films, however, is somewhat problematic and requires further investigation for interpretation of its origin.

Anyway, these observations imply strongly that LC molecules are aligned by the chemical interaction with the polymer chains in aligning layers.

The following experiment has been conducted to confirm that the orientation of polymer chains is responsible for the alignment of LC molecules. In order to mask the interaction between LC molecules and the polymer chains, the surface of the rubbed PI films was covered with a Pt–Pd evaporated film about 30 Å thick. We confirmed by the SEM and the surface profiler that a roughness of the surface of the PI film had not been changed before and after the evaporation of Pt–Pd, and then prepared an LCD cell filled with GH LC materials. The cell spacing was set at 6 microns by glass fibre spacers. Figure 4 shows the microscopic photograph of the LCD cell. The degree

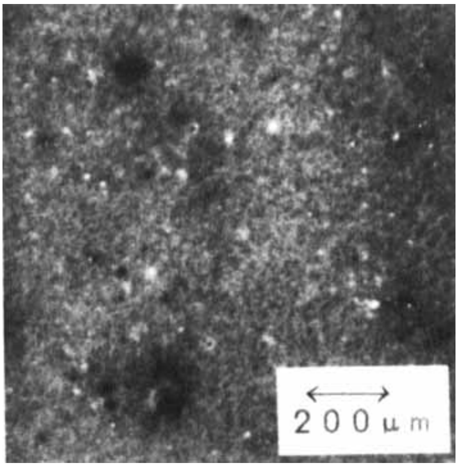

Figure 4. Microscopic observation of the liquid crystal (LC) alignment in a homogeneously aligned cell. The aligning layer is the rubbed polyimide (PI) film and its surface is covered with a Pt–Pd evaporated film about 30 Å thick.

of the LC alignment was not so good and the dichroic ratio of the peak absorbance of 638 nm was reduced to 5·9 from 9·7 by the Pt–Pd evaporation on a PI film. This indicates that the presence of the micro-grooves does not contribute to the LC alignment so much in polymer aligning films.

It is concluded that LC molecules are aligned by the orientation of polymer chains on the film surface that is induced by a rubbing process.

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