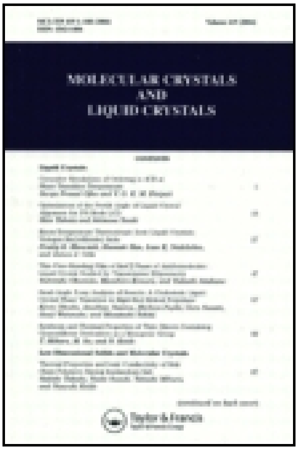

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Liquid Crystalline Alignments on Polar Surfaces Covered with Amino and Hydroxyl Groups

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Molecular alignments of three types of liquid crystalline materials on polar solid surfaces have been investigated by the use of polarized optical microscopy. On an amino-coated glass substrate, p'-alkyl-p-cyanobiphenyls, having one polar cyano group as a terminal moiety, exhibits homeotropic alignment; that is, the molecules align perpendicular to the substrate, whereas p'-pentyloxy-p-cyanobiphenyl and p-(pentylbenzoic acid)-p-cyanophenyl ester, having two polar groups as a terminal and a spacer, appear to align parallel to the substrate surface. These results indicate that the position and the number of polar groups in a liquid crystalline molecule play an important role in the alignment. On a poly(vinyl alcohol)-covered substrate, which has polar hydroxyl groups, different alignments are observed. It has also been found that the alignments depend on the atmospheric humidity.

Keywords Liquid crystal, alignment, polar group, surface, humidity

INTRODUCTION

Control of liquid crystal alignment on the substrate surface has been considered to be important for the production of high performance liquid crystal displays (LCDs). Much work has been devoted in recent years to the problem of nematic liquid crystal alignment on solid surfaces [1–14]. In practical fabrications of LCDs, the "rubbing" technique has widely been applied to produce uniform alignment of liquid crystal, namely the "homogeneous" alignment. Besides the homogeneous alignment, a variety of alignments can be observed depending on the preparation condition.

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These liquid crystalline alignments are divided roughly into three types with respect to the molecular tilt, including perpendicular, parallel, and tilted alignments. Most researchers prefer the term "homeotropic" to "perpendicular," although some researchers use the terms "normal" and "lateral" for perpendicular and parallel orientations, respectively. For the parallel alignments, further classification can be made; various in-plane orientation patterns should be considered, as well as the exhibition of specific textures such as Schlieren and marble, and the uniform homogenious alignment caused by rubbing. Moreover, combination of different alignments on two substrates gives a hybrid alignment in the bulk. In practical preparations, the homeotropic alignment can be obtained by using silane-coupling agent as a surfactant on the substrate, whereas the parallel alignment can be observed on a polymer-coated substrate.

The alignment depends on the topography of the surface [1–5] as well as on its chemistry [5–11]. The former is essentially a geometric effect whose influence on the Frank elastic energy can be calculated, provided that the surface topography is sufficiently known. On the other hand, the role of the chemical nature of the surface has been much more controversial [5, 8, 11] and is still not fully understood. Even the predominance of weak anchoring on clean glass surfaces still seems to be disputed [12]. From the macroscopic point of view, the anchoring phenomena can be interpreted thermodynamically [13].

For polymer surfaces, the mechanism of orientation has been discussed with respect to the interaction between the liquid crystalline molecules and the main chains and side chains of polymer [14]. This can be confirmed by using molecular dynamics (MD) calculations [16]. Nevertheless, the detailed mechanism can hardly be elucidated. In particular, the roles of functional groups are still unknown.

In the present article, we investigate the variety of liquid crystalline alignments on polar substrates; the dependence of the alignment on the chemical structures is discussed in order to elucidate the orientation mechanism involving the molecular interaction, especially between polar groups.

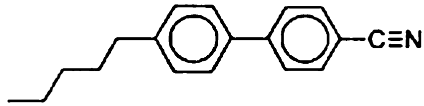
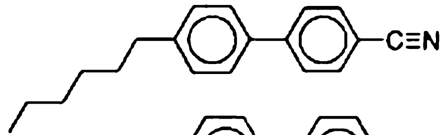
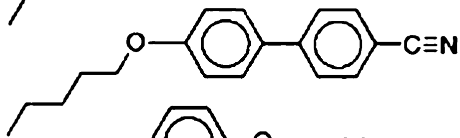
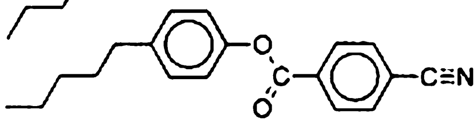
EXPERIMENTAL

Preparation of Sample Cells

Liquid Crystals

The liquid crystalline materials used in this experiment are, as listed in Table 1, p'-pentyl-p-cyanobiphenyl (5CB), p'-hexyl-p-cyanobiphenyl (6CB), p'-pen-

TABLE 1 Chemical structures of liquid crystals

Abbreviation	*Chemical structure*
5CB	
6CB	
5OCB	
ME5N	

tyloxy-*p*-cyanobiphenyl (5OCB), and *p*-(pentylbenzoic acid)-p-cyanophenyl ester (ME5N). Each compound has a terminal cyano group attached to the end aromatic ring. For 5OCB, in addition, an ether oxygen atom combines a biphenyl and an alkyl chain. The ME5N molecule has an additional ester group by which two aromatic rings are combined. These compounds were purchased from Merck Co., Ltd.

Substrate

The substrates used were glass slides that had been washed sequentially with acetone and pure water, treated with 1 N aqueous solution of sodium hydroxide and 1 N hydrochloride successively to afford polar hydroxyl groups on the surface. Between every two steps the substrates were soaked with pure water to avoid contamination. In order to obtain amino-covered surfaces, the substrates were treated with an amino-silane coupling agent SH6020P (Toray Silicone) that has an amino group at the end of the long alkyl chain. For a hydroxyl-covered surface, a thin layer of poly(vinyl alcohol) (PVA) was dip-coated. As a reference, we used substrates that had surfaces with a silane-coupling agent AY-43 (Toray Silicone), which has a long alkyl chain terminated with a methyl group. In order to clarify the effect of the interaction between polar groups, these substrates were not rubbed, since the cell would have become homogenous if the substrate had rubbed.

Sandwich Cell

Each liquid crystalline compound was confined in sandwich-type cells constructed with two glass substrates treated in advance, with two small pieces of polyester films of thickness 25 μm placed between the two substrates as the spacers.

Capillary action caused a spontaneous flow of the liquid crystal into the small space between two substrates, resulting in a sample cell with an appropriate alignment of liquid crystalline molecules without air bubbles. The substrates and the liquid crystals were kept at a temperature above the nematic-isotropic transition in order to remove flow-induced orientation. The relative humidity in the atmosphere was controlled at about 40% during surface treatment and cell assembling processes, unless otherwise noted.

Measurements

Orthoscopic and conoscopic observation were performed to determine the liquid crystalline alignment in the nematic phase. The microscopic textures were observed in the nematic phase by using a Nikon OPTIPHOTO2-POL polarized optical microscope with a Mettler FP82HT hot stage regulated by a Mettler FP80. The width of each photograph corresponds to 1.0 mm.

RESULTS AND DISCUSSION

Alignment on Glass Slides

In general, the microscopic observations of the liquid crystal cells can reveal the specific textures, depending on the phase and the alignment. In this experiment, we focus on the alignments in the nematic phase. Figure 1 shows the polarized micrographs of the various liquid crystals on glass substrates between crossed polarizers. The micrograph of 5CB on glass exhibits the Schlieren texture, as shown in Figure 1a, suggesting an almost parallel orientation where the molecules are aligned continuously except in the vicinities of the singularities that appear as the nodes connecting the dark brushes. This parallel alignment can be confirmed by the fact that 5CB on glass exhibited the colorless Schlieren texture even if the cell spacing was thinner; i.e., since the apparent birefringence, and thus the phase retardation, for the light incident normal to the cell surface was large enough to give achromatic transmission, the molecular tilt was estimated to be sufficiently small. In other words, while the Schlieren texture can also be

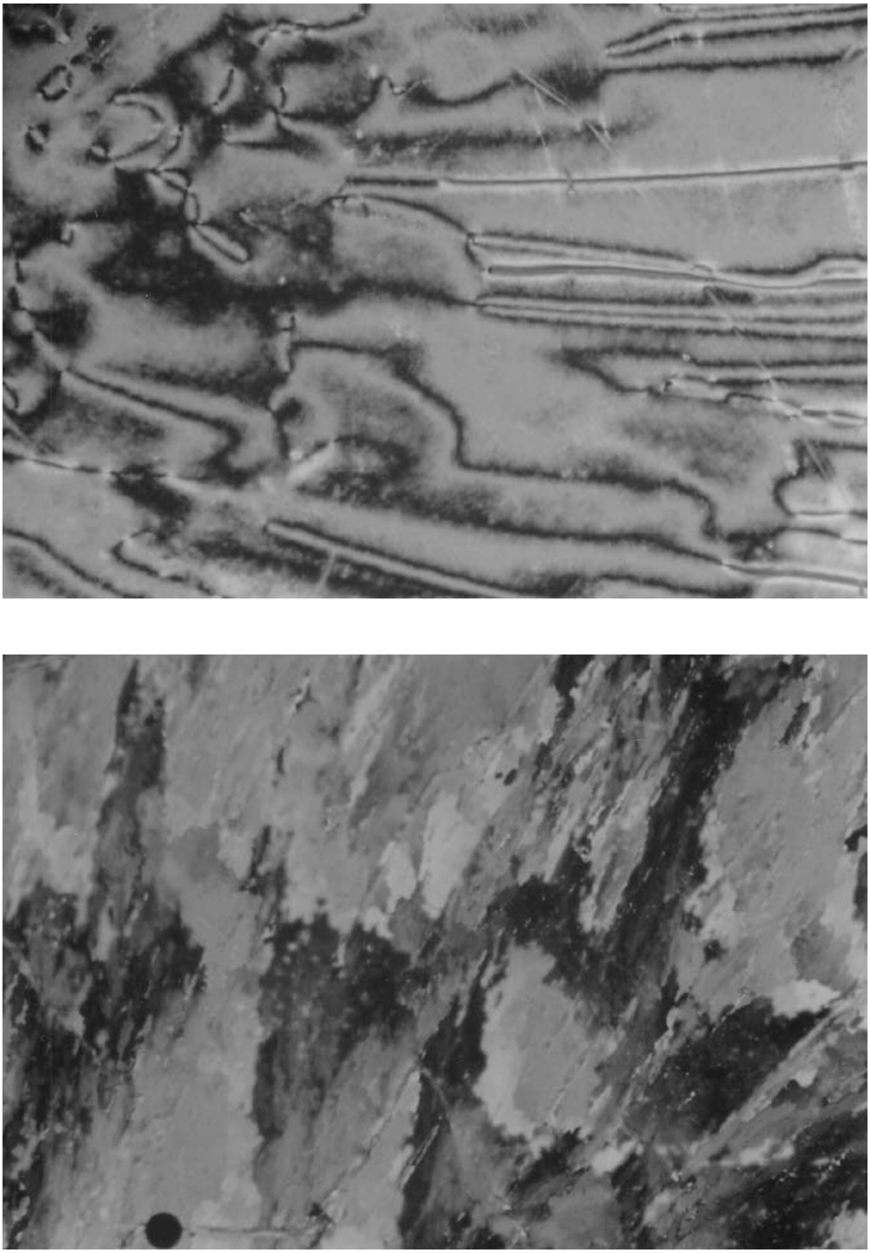


FIGURE 1 Polarized optical micrographs of three types of liquid crystals on the glass substrates: (a) 5CB, (b) 5OCB, and (c) ME5N.

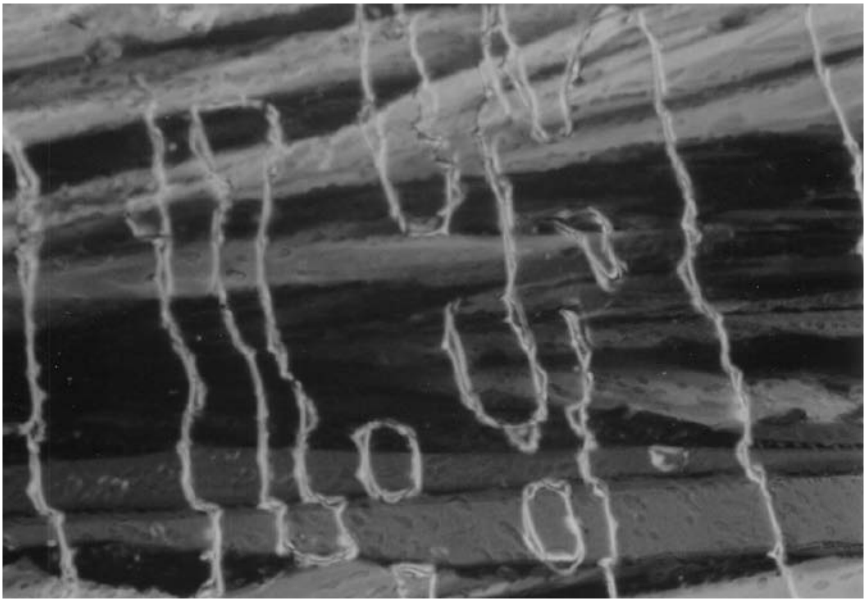


FIGURE 1 (*continued*)

produced by a conical alignment with a small cone angle like the homeotropically aligned smectic C phase, the present Schlieren texture should be associated with relatively small tilt angle that gives rise to a larger birefringence. Since almost the same texture was observed for 6CB, the chemical feature of having a single polar group as a terminal could be associated with a parallel alignment.

For 5OCB a discontinuous multidomain (marble) texture (Figure 1b) is found, whereas for ME5N stripes of relatively large domains, including disclination loops (Figure 1c), can be observed. The longitudinal direction of the stripes may be associated with the flow, while the liquid crystalline material was filled into the cell in the isotropic phase. This result indicates that the flow-induced orientation cannot be neglected even in the isotropic phase. Consequently, the three types of liquid crystals align parallel to a glass surface, although the domain sizes and the defects are different.

Alignment on PVA-coated Glass Slide

Figure 2 shows the polarized micrographs of the various liquid crystals on PVA thin films coated on glass. In comparison with the case of a glass substrate, the micrograph of 5CB on glass exhibits a discontinuous marble

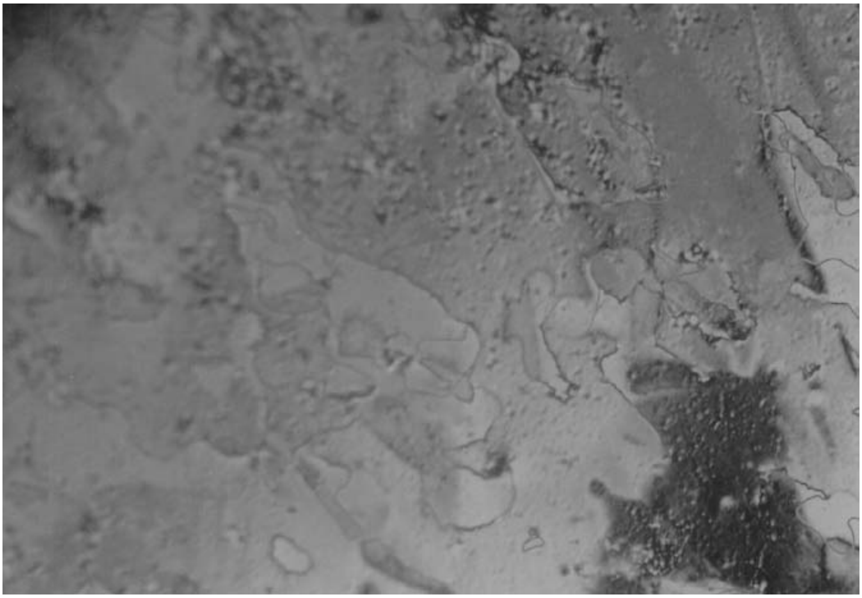


FIGURE 2 Polarized optical micrographs of three types of liquid crystals on the PVA-covered glass substrates: (a) 5CB, (b) 5OCB, and (c) ME5N.

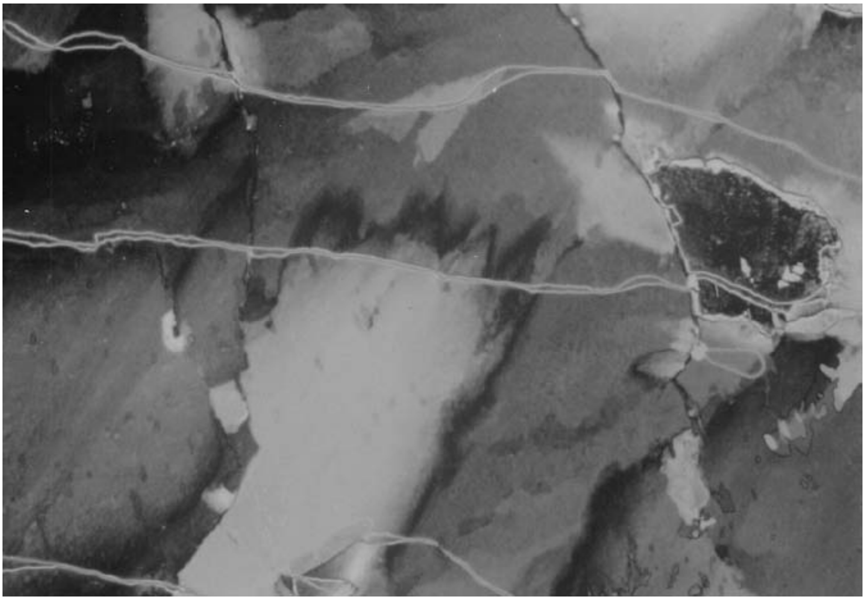


FIGURE 2 (*continued*)

texture, as shown in Figure 2a. For 5OCB, stripes of domains are found, as shown in Figure 2b, where the longitudinal direction of the stripes may be associated with the flow direction. For ME5N, a marble texture including rather large domains can be observed in Figure 2c. These results indicate that all liquid crystals used in this experiment align parallel to the substrate surface to form domains, each of which has a uniform in-plane orientation, although the difference in the domain sizes and the defects are observed.

Alignment on Amino-covered Glass Slides

Figure 3 shows the polarized micrographs of the various liquid crystals on amino-covered glass substrates. The orthoscopic picture (Figure 3a) reveals a uniform dark image and completely differs from those for the glass or PVA substrates. Whenever the stage was rotated, the image remained the same. Moreover, conoscopic observation revealed a dark cross located at the center of the image. In the case of another one-polar liquid crystal, the microscopic studies for 6CB gave the same results. These results indicate that the liquid crystalline molecules on the densely packed amino groups prefer the homeotropic alignment. It should be noted that, in general,

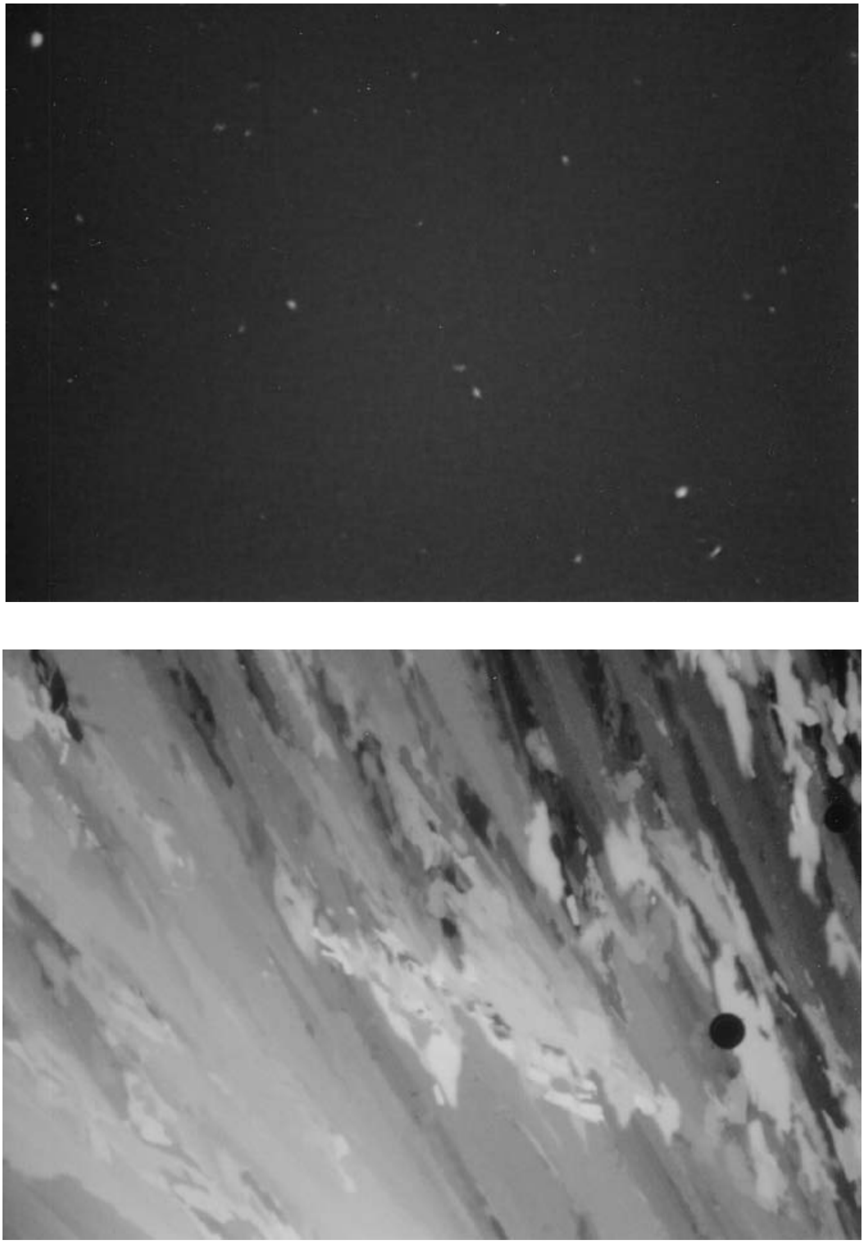


FIGURE 3 Polarized optical micrographs of three types of liquid crystals on the amino-covered glass substrates: (a) 5CB, (b) 5OCB, and (c) ME5N.

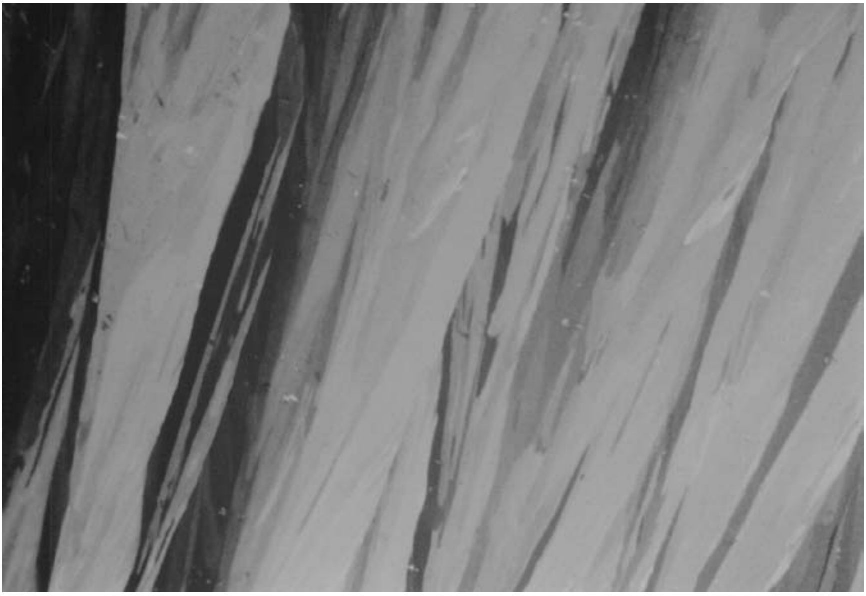


FIGURE 3 (*continued*)

hydrophilic surfaces exhibiting larger surface tension than the liquid crystal generally result in parallel orientation [15]. The present result is inconsistent with the above empirical rule; i.e., even on the hydrophilic amino-covered surfaces, the 5CB and 6CB molecules align homeotropically.

On the other hand, the orthoscopic observations reveal a multidomain texture consisting of midsize stripes for 5OCB (Figure 3b) and oriented stripe domains including disclination loops for ME5N (Figure 3c). The longitudinal direction of the stripes is associated with the flow direction, as well as in the case of PVA-covered substrates. These results indicate that the molecules of 5OCB and ME5N are oriented parallel to the substrate surface with different domain sizes and defect patterns.

From the viewpoint of the chemical structures, it can be concluded that the single polar liquid crystals like 5CB and 6CB exhibit homeotropic alignment, whereas bifunctional 5OCB and ME5N molecule, which have another polar group in addition to the cyano end group, align parallel to the substrate surface. These facts suggest that the number of polar groups play an important role in the alignment. Moreover, the position of the additional polar group can be associated with the alignment. In actuality, the 5OCB and ME5N molecules have an additional polar group in the vicinity of the center of the molecule.

It has also been found that the orientations are strongly affected by the humidity of the atmosphere. As described in the previous section, 5CB exhibits homeotropic alignment on the amino-covered surface when the cell is prepared at the relative humidity of about 40%. On the other hand, when the cell is prepared at 60%, 5CB molecules align parallel to the surface, as shown in Figure 4. The detailed results will be reported elsewhere.

Alignment on Alkyl-covered Glass Slides

On the glass slides treated with the silane-coupling agent, AY-47, all of the liquid crystals are aligned perpendicular to the substrate surface. Such behavior has been interpreted as the interaction between alkyl groups of the silane-coupling agent and the liquid crystal [5]. The 5CB, 6CB, 5OCB, and ME5N molecules have nonpolar alkyl groups in addition to the polar cyano, ester, or ether groups. When the substrate surface is covered with nonpolar alkyl groups, the interaction between alkyl chains of the silane-coupling agent and those of liquid crystal must be stronger than that between alkyl chains on the substrate and the polar groups attached to the liquid crystals. Therefore liquid crystalline molecules near the substrate align perpendicular

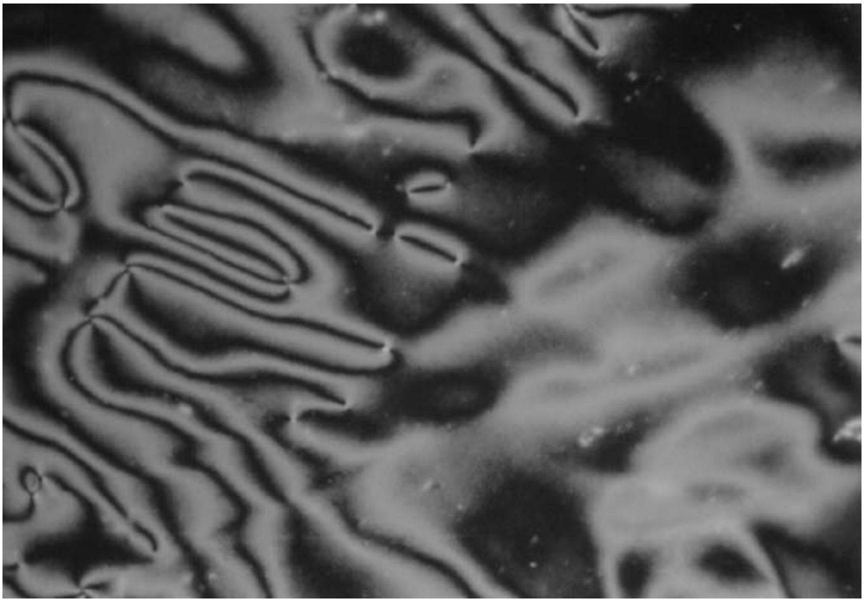


FIGURE 4 Polarized optical micrograph of 5CB on the amino-covered glass substrate prepared at a relative humidity of 60%.

to the substrate, giving rise to homeotropic alignment in the bulk, although the molecules have polar groups in the core moiety.

Mechanism of Alignment

The various orientations depending on the types of the substrates and the chemical structures of the liquid crystals are summarized in Table 2. On an amino-covered surface, the liquid crystals align parallel to the surface, except in the case of single polar materials such as 5CB and 6CB, which exhibit orientation perpendicular to the substrate. It should be noted that these tendencies are independent of the sign of the dielectric anistropy of the liquid crystals. This fact may confirm that the liquid crystalline molecules that have one polar end group tend to align homeotropically on a densely packed polar surface, whereas those having two polar groups show parallel orientation.

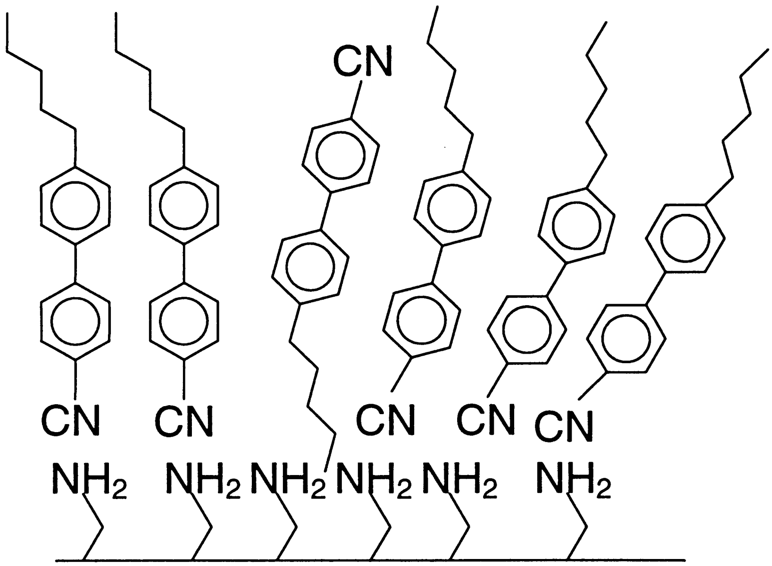
In general, the detailed mechanism of liquid crystalline alignment is too complicated to explain. Here we may demonstrate a simple model, as schematically illustrated in Figure 5. A molecule of 5CB can adsorb with its polar end interacting with the amino groups of the substrate. Thus the molecules tend to align perpendicular to the surface, because the homeotropic alignment gives rise to the highest density of the interacting polar groups. On the other hand, bifunctional molecules, such as 5OCB and ME5N, can no longer align homeotropically, because they can adsorb on the surface both with the cyano end groups and with the additional polar groups like ester or ether. This simple model suggests that the number and the position of polar groups play an important role in the alignment.

Also on a glass substrate, a 5CB molecule can adsorb with the terminal cyano group interacting to a surface polar group, such as hydroxyl group, of the substrate. Although this one-point adsorption could result in perpendicular orientation, the molecules, in fact, exhibit Schlieren texture, because

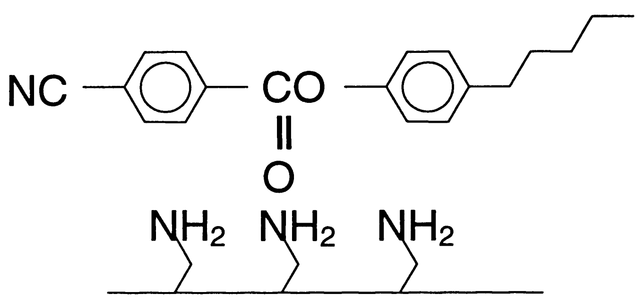
TABLE 2 Liquid crystalline alignments on various substrates

	Substrate		
Liquid crystal	*Glass*	*PVA-covered glass*	*Amino-covered glass*
5CB	Schlieren (***L***)	Marble (***L***)	Homeotropic (***N***)
6CB	Schlieren (***L***)	Marble (***L***)	Homeotropic (***N***)
5OCB	Marble (***L***)	Marble/Stripe (***L***)	Stripe/Marble (***L***)
ME5N	Stripe (***L***)	Marble (***L***)	Stripe (***L***)

L, parallel (lateral) alignment; ***N***, perpendicular (normal) alignment.



(a)



(b)

FIGURE 5. Schematic illustration of adsorption/orientation models for the different types of liquid crystalline molecules on the amino-covered substrates: (a) 5CB and (b) ME5N.

the one-point adsorption and the relatively low density of the surface polar group allow the molecules to tilt and rotate easily around the substrate normal. The molecules can consequently lie down on the substrate to form the Schlieren textures, since a parallel alignment is generally preferential on a solid by the excluded volume effects to increase the packing entropy [17], and the easy rotation of molecules could give rise to continuous in-plane orientations without defects like boundary walls and disclination loops. On the other hand, a molecule having two polar groups, like 5OCB and ME5N, cannot rotate around the substrate normally because of the adsorption at two points on the substrate. In addition, the shear due to the capillary action during the preparation of the cell can give rise to a uniaxial orientation to form relatively large domains with a parallel alignment. Since ME5N, which has an ester group, exhibited larger and more uniform domains than 5OCB, which has an ether group, the alignments revealing these textures may depend on the strength of the polarity.

It should be noted that although PVA glass has polar hydroxyl groups as well as glass, the textures are rather different. This result indicates that the orientations and/or the aggregation structures of the polymer chains play an important role in the liquid crystalline alignment.

As mentioned in the previous section, the atmospheric humidity has an effect on the liquid crystalline alignment. This humidity dependence suggests that water molecules adsorbed on the substrate surface can interfere with the interaction between the polar groups of the liquid crystal and those of the substrate, while these groups could be packed densely with high order at the interface without water molecules.

CONCLUSION

On an amino-covered glass substrate, 5CB and 6CB, which have one polar group as a terminal, exhibit homeotropic alignment; that is, the molecules align perpendicular to the substrate, whereas 5OCB and ME5N, which have two polar groups as a terminal and a spacer, appear to align parallel to the substrate surface. These results indicate that the number and the position of the polar groups play an important role in the alignment. On a poly(vinyl alcohol)-covered substrate, which has polar hydroxyl groups, different alignments were observed. It is also found that the atmospheric humidity gives an effect on the specific alignment.

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