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Surface Anchoring of Liquid Crystal Molecules on Various Substrates

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Ever since Mauguin described the fabrication of liquid crystal cells by rubbing glass plates with paper to obtain uniform homogeneous alignment, scientists have been attempting to study and understand the mechanism of anchoring and the subsequent alignment of these materials on various substrates. More than 35 different methods for creating surface alignment have been reported using both organic and inorganic films as well as various mechanical treatments. In this paper, many of these methods are reviewed and categorized. The mechanism of surface anchoring involves not one but several mechanisms. The nature of the surface material, the liquid crystal structure, and the past history of the surface, all play major roles in determining the mechanism for a specific technique.

INTRODUCTION

Early in this century, Mauguin[1] produced an aligned liquid crystal layer by forming a sandwich structure with p-azoxyanisolecontained between two glass plates, the surfaces of which had been rubbed in one direction with a piece of paper. Since then, scientists have been attempting to study and understand the mechanism of rubbing and the microscopic nature of the liquid crystal-surface anchoring process.

Since these studies were carried out over such a long period of time, it is not surprising that a good deal of confusion has arisen regarding the relationship between the results obtained and the nature of the experiments performed. In this paper, many of the methods used in past studies are reviewed and categorized; some thoughts on the mechanisms believed to be operative are also presented.

DISCUSSION

Many different materials have been used as the alignment substrate or "alignment layer", including both organic and inorganic substances and mixtures of the two. The techniques used to form these materials on the surfaces of such things as glass, ceramics, and organic polymers include: dip coating, spraying, roller coating, offset printing, sputtering, high-vacuum sublimation (evaporation), and even chemical reaction at the surface. In addition, a number of techniques have been used to create preferred molecular directionality and/or tilt of the molecules on these alignment layer surfaces, including: rubbing, high-speed buffing, mechanical abrasion, chemical milling, ion milling, high vacuum sublimation at oblique angles, and laser milling. And finally, the type of materials used to create these latter effects has included such substances as polyesters, cellulose, cellulose acetate, nylon, alumina, diamond, silicon monoxide, magnesium fluoride, and silicon carbide.

In reviewing and organizing these techniques, materials, and effects, it is convenient to separate them into two major categories: (A) organic alignment layer materials and (B) inorganic films and substrates. Within each category we can then identify the following:

1. Specific alignment layer material;
2. Technique for forming alignment layer;
3. Method and specific material used to create directionality and/or molecular tilt;
4. Proposed mechanisms.

To simplify the discussion, we will refer to the use of glass substrates exclusively.

A. Organic films and materials

As mentioned above, the first known report of surface alignment of liquid crystals was provided by Mauguin[1] in 1911 when he rubbed a raw glass plate with a piece of paper and obtained uniform homogeneous alignment of *p*-azoxyanisole. This technique was then used by a number of researchers who fabricated cells for examination by electric and magnetic fields.[2] Chatelain[3] theorized that the orientation resulted from dipole interactions between an ordered layer of adsorbed fatty impurities and the nematic molecules. However, he did not rule out alteration of the substrate surface itself.

As a result of these reports and other papers, it had come to be believed that rubbing always produced homogeneous alignment. Creagh and Kmetz[4] found, however, that lecithin, a surface active agent, produced homeotropic alignment of liquid crystals such as MBBA (*p*-methoxybenzylidene-*p*′-*n*-butylaniline), regardless of whether the surface was rubbed or not. The use of lecithin as a homeotropic aligning agent has also been reported by Hiltrop and Stegemeyer.[5] They proposed a mechanism in which the lecithin is visualized as forming a brush-like film on the surface with the long alkyl chains pointing out of the surface. Holes of molecular dimensions in this film are penetrated by the nematic molecules which become anchored with their long axes protruding out of this monomolecular layer. Elastic interaction between these anchored molecules and adjacent molecules in the bulk cause the homeotropic alignment.

In a related study, Kahn[6] found that a quaternary ammonium salt containing silicon and having a long alkyl chain such as *N*,*N*-dimethyl-*N*-octadecyl-3-aminopropyltimethoxysilyl chloride produced homeotropic alignment of MBBA. In these cases the surface active agent has an ionic "head" and long, non-polar "tail." A mechanism which supports the observed facts would say that the "head" becomes anchored to the substrate with the non-polar "tail" protruding from it. The alkyl chain of the MBBA molecule would then be attracted to the tail and the long axes of the MBBA molecules would then be perpendicular to the substrate surface (eg, homeotropic alignment). The attractive force between the head of the aligning layer material and the glass surface may be so great that even rubbing may not be sufficient to disrupt it.

Another concept that has been evoked is that uniform homogeneous alignment is caused by grooves in the organic alignment layer material as a result of the rubbing action. Although this is certainly a plausible mechanism, it is by no means the only mechanism.

It is widely known, although little has been published, that rubbed polymer films of such polymers as polyvinyl alcohol, polyimides, polyesters, polysiloxanes, etc. will produce uniform homogeneous alignment and very small tilt angles of most liquid crystals which come into contact with them. One of the major problems with much of this work has been the lack of consistency. In some cases, the rubbing is done with diamond paste, while in others a "soft" organic material is used. In the diamond rub case, microgrooving of the surface coating is easier to visualize; it might be classified as grinding by the definition of Adamson.[7] The mechanism in this case would then involve the molecules lying in the grooves with their long axes parallel to the groove direction.

In most cases, however, the polymer film is rubbed or buffed with another organic polymer material, often described as the "cloth". Because of the proliferation of the synthetic fibers industry during the past 40 yrs, which has apparently been ignored by workers in this field, cloth can have a variety of chemical structures. It is the nature of the rub material as well as the surface coating that determines the microscopic structure of the treated surface layer. According to Adamson,[7] the action of rubbing or buffing, sometimes called polishing, produces very high localized heating which results in melting of one of the polymer materials. The higher melting material causes melting of the lower melting material.

The orientation of polymer molecules in films by external forces is well-known[8] and well studied by X-ray diffraction and other techniques. The alignment and tilt of liquid crystal molecules on such treated surfaces then becomes a complex combination of geometrical (steric) factors and Van der Waal's interactions between the oriented polymer and liquid crystal molecules.

The mechanism proposed above is an alternative to the grooving theory. It can also be used to explain the Mauguin case (rubbing glass with paper) as follows: The high local temperatures created during the rubbing of glass, a high melting material, with paper (cellulose) results in a transfer of the melted cellulose material to the glass with the long polymer chains oriented in the rub direction. The cellulose molecules become anchored to the surface via hydrogen bonds. The liquid crystal molecules then become aligned to these oriented chains. It is an experimental fact that you cannot destroy the alignment layer with ordinary solvents, but you can destroy it by heating above 250°C (above the melting point of cellulose).

B. Inorganic films and substrates

1. Evaporation techniques One of the most widely used techniques for the alignment of liquid crystal materials on surfaces was the oblique evaporation of various silicon oxides. The first report of the use of this technique was made by Janning.[9] It involved depositing thin silicon monoxide films, 100 Å units or less, onto substrates at an angle of approximately 85° to normal.

The angular deposit causes the film to grow in a preferred direction. Liquid crystals applied to such a surface, become aligned in the direction of film growth. That is, the molecular director points toward the direction of evaporation.

In Janning's experiment both the front and rear plates were treated in the same way, and the plates were then assembled into a twisted-nematic field effect device using MBBA as the liquid crystal material.

Guyon and his coworkers[10] studied the technique further, being particularly concerned with the angle of incidence, Ψ, of the beam of evaporating material. Films of gold or silicon monoxide evaporated at normal incidence ($\Psi = 0$) gave non-uniform, homogeneous alignment. When the incidence angle was greater than 45°, the alignment was uniform and homogeneous. In this case the director is perpendicular to the plane of incidence of the beam. Then, remarkably, when the incidence angle was greater than 72–75°, the alignment was uniform and homogeneous, but the director was oriented parallel to the direction of the beam.

Electron micrographs of the films prepared by evaporation at $\Psi = 80°$ showed a definite columnar growth structure. No such defined structure is apparent to this or other observers in the electron micrographs of the films evaporated at $\Psi = 70°$, although Guyon claims to see "channels roughly perpendicular to the direction of the beam."

In a similar, but somewhat more sophisticated study, Goodman and co-workers evaporated silicon monoxide at angles of $\Psi = 60$ and 83° and examined the surfaces with transmission electron microscopy at various glancing angles of the electron beam. At 83°, the columnar growth, which is again observed, appears as needle-like crystals which protrude from the surface at an angle of 35–40° with the glass substrate. On the basis of elastic energy factors, they explained the observed results and proposed that the molecular director orients itself parallel to the long direction of the columns. Unfortunately, this explanation is not consistent with the results obtained by Crossland, *et al.*,[12] who found that the tilt angles of cyanobiphenyl liquid crystals varied between 28 and 40° depending upon the molecular chain length.

It is widely known that films deposited at glancing and oblique angles of incidence often adopt a morphology which has been described as consisting of tilting columns of the evaporant material pointing towards the evaporation source. The angle between these columns and the substrate is difficult to measure accurately, and no systematic comparison between the tilt angle of the nematic director and the column angle in the aligning film has yet been reported. The hypothesis that the nematic director is aligned along the column direction appears too simplified for at least two reasons. Firstly, the tilt angle does not change significantly as the angle of incidence of the aligning film of silicon monoxide increases from 5 to 14° from the substrate and it is most unlikely that the column angle remains constant as the angle of incidence of the beam varies over this range; secondly, the tilt angle was found[12] to depend on the liquid crystal material used.

A 90° rotation of the molecular alignment with respect to the film incidence occurs when the angle between the incidence direction and the substrate exceeds approximately 18° (i.e. $\Psi < 72°$). This change is accompanied by a decrease in the tilt to zero.

This fact has led some to theorize that these evaporation angles produce a topographical structure with very narrow, parallel channels into which the liquid crystal molecules lie. The question is where is the evidence for the existence of such channels? In many attempts to observe these channels, we and others (13, for example) have been unsuccessful.

It has been found[14] that the physical and chemical properties of evaporated films of silicon monoxide change as function of deposition rate, incidence angle, chamber pressure and post evaporation temperature. This suggests that the stoichiometry of the film also changes as a function of these parameters. Hollinger *et al.*[23] have found this to be the case.

Thus, the mechanism of uniform alignment of the liquid crystal molecules on these evaporated films is still a matter of speculation. We submit that the alignment is likely to be more a function of the *molecular interaction* between the silicon monoxide and liquid crystalline compounds than any topographical features. We theorize that the $\Psi < 75°$ films of silicon monoxide produce highly ordered hexagonal structures which associate with the aromatic rings of the liquid crystal compounds (*eg*., *via* Van der Waal's forces) to produce the uniform, non-tilted alignment.

II. Rubbed films Since films evaporated with $\Psi < 75°$ exhibit no tilt, twisted nematic field effect cells made using this technique exhibit a high degree of reverse tilt.[15] This occurs because the molecules can turn either to the right or to the left when an electric field is applied and the molecules begin to turn in the direction of the field. This results in the activated segments taking on a "patchy" appearance.

Raynes[15] discovered two solutions to this problem. One uses a higher percentage of chiral additive in the nematic liquid crystal mixture; however, this results in a higher threshold voltage. The other uses unidirectional rubbing of one or both surfaces with paper. The rubbing is performed in a direction perpendicular to the direction of evaporation. Using cyanobiphenyl type compounds, tilt angles of 1 to 3° can be obtained with this technique. No specific mechanism is suggested by Raynes other than to say that a reorientation of the surface occurs.

A number of other workers have discussed the technique of rubbing or buffing the surface of a dielectric film to obtain a resulting alignment layer which produces low tilt angles. Ristango[16] rubbed a sputter deposited film of silicon dioxide with a piece of cotton cloth (cellulose). The silicon dioxide was deposited normal to the surface and the twisted nematic cells were filled with cyanobiphenyl type liquid crystals. The cells exhibited uniform, homogeneous alignment and a low, but unmeasured tilt angle. Similar results were reported by workers at Sanyo Electric Co.[17] and by Gurtler and Casey,[18] both using silicon oxide films rubbed with various soft and hard materials.

The uniform homogeneous alignment of liquid crystal molecules on surfaces which have been purposely abraded or mechanically grooved has been the subject of several papers. Berreman[19] produced parallel alignment of *p*-azoxyanisole and MBBA on soda lime glass and quartz by lapping the surface with a 1.0 micron diamond paste mixture. Electron micrographs of the surface proved the existence of grooves; however, no grooves were observed when the surface was rubbed with paper or various fabrics. The tilt was always zero in the mechanically grooved cases, as long as the surfaces were clean. Berreman also found that when large grooves were used, the grooves acted as capillaries and the flow of liquid crystal material along the grooves produced a uniform homogeneous alignment.

Flanders and his co-workers[20] obtained uniform homogeneous alignment of MBBA on surfaces of silicon dioxide into which a grating type pattern was plasma etched. In a related study, Little *et al.*[21] produced grooves in the surfaces of indium and tin oxide films by ion-beam milling in an Argon atmosphere.

As a result of this work on mechanically and otherwise abrading the surfaces of vacuum deposited films, the concept developed that "rubbing hard surfaces (i.e. silicon monoxide, glass, quartz) with anything produces grooves which align the liquid crystal material." Apparently, many workers have interpreted the results to apply to all cases.

In a recent report,[14] it was found that uniform homogeneous alignment with tilt angles of 1 to 3° could be obtained by rubbing silicon monoxide films. These films were vacuum deposited on soda lime glass and indium-tin oxide coated substrates at incidence angles of $\Psi < 75°$ (including $\Psi = 0°$) and rubbed with cellulose acetate fabric on a high speed buffing wheel. The same result was obtained whether or not the film was heated at 525°C; the effects of the rubbing survived these high temperatures. Scanning electron micrographs of the surface before and after rubbing and after the high temperature treatment showed no signs of grooves or other abrasions. Auger spectroscopy was used to examine the rubbed and unrubbed films before and after heat treatment, but no evidence of a retained organic film or additional carbon (above the background) was found. On the other hand, an evaporated silicon monoxide film rubbed with 0.5 micron diamond paste showed abrasion grooves when examined by scanning electron microscopy; the film gave zero tilt and uniform homogeneous alignment of a mixture of cyanobiphenyl liquid crystal compounds.

Thus, no evidence for grooves in silicon monoxide films rubbed with soft organic materials has yet been observed. Several mechanisms are possible. One proposes that the rubbing or buffing action causes an actual loosening and spreading of microcrystallites of the deposited film across the surface orienting them in the direction of and tangential to the rub head or buffing wheel. Another suggests that a charging of the surface is produced during the rubbing and that these "trapped charges" produce alignment of the liquid crystal molecules. The difficulty with this mechanism is that it fails to explain the tilt and it assumes that the charges do not dissipate at the high temperatures used during the heat treatment. Whatever the mechanism is, it is certainly not due to grooves. All the work performed, and other experiments reported to date with actual grooved surfaces, yield zero tilt.

CONCLUSIONS

The alignment and tilt of liquid crystal molecules on surfaces treated in various ways is a complex phenomenon; not one, but many mechanisms are involved. The mechanism of alignment and tilt are determined by

1. The technique used to coat the substrate surface;
2. The nature of the surface coating material;
3. The method and nature of material used to orient the surface material. Cloth must be defined;
4. The nature of the liquid crystal material.

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