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A

Report on

Surface coupling agent (DMOAP) for colloidal liquid crystal studies.

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Abstract:- Alignment of liquid crystal molecules on the surface treated substrates or on the solid silica particles was achieved by using octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (DMOAP). Liquid crystal molecules, most commonly rod like nematics, align on the surface of the treated silica by physicochemical processes and anisotropic forces generated from functionalized surface coupling agent. DMOAP coupling agent can be used for planar and as well as homeotropic anchoring in nematic liquid crystal environment as a result, we observed from point defects to the wrapping of the unoriented liquid crystal in the form of entangled defect lines to compensate the distortion in molecular orientations caused by particle surfaces. This polymer treatment helps to study the physical properties of liquid crystals and numerous potential applications of colloidal studies in LC environment.

1. Introduction;

Uniformly oriented thin liquid-crystal (LC) layers are required for most liquid-crystal device (LCD) applications and physical investigations. Permanence of the orientation is necessary for long device lifetime. The usual method for producing uniformly oriented thin film LC samples is to generate substrate interfaces which have an orienting action on the LC molecules. These interfaces have been generated by the below mentioned means

        1 .Chemical cleaning or etching,

        2. Rubbing,

        3. Mechanical surface scribing or deformation,

        4. Physical adsorption, and

        5. Deposition of organic and inorganic thin films.

The surface-generated orienting forces acting on the LC may result from hydrogen bonding, physicochemical processes (i.e. Vander Waal's, mechanical interactions and / or dipolar interactions) as a result of the LC's anisotropic elasticity. The balance of these forces, and therefore the resulting LC orientation, will be determined by the chemical composition of both the surface and the LC and by the surface topology. If either the chemical composition of the surface or its topology changes in time, the balance may be changed and a corresponding change in the LC orientation will result. Previously described orienting interfaces change chemically with time, thereby resulting in a corresponding degradation of the LC orientation. This degradation is one of the major causes of LCD failure.

2. Surface coupling Agents (Chemisorbed Surfactants):

In recent days silane surface coupling agents have been used to generate chemically stable interfaces on a wide variety of conducting and insulating substrates. These interfaces can be simply and reproducibly deposited. They have a strong LC orienting interaction and due to

their chemical stability are expected to have the permanence required for long device lifetimes.

Coupling agent molecules (CAM's) for orienting LC's should possess two or more different kinds of molecular groups. At least one of these must be a bonding group which reacts chemically with the substrate to form a chemically stable bond, and at least one must be an orienting group which interacts with the LC molecules in such a way as to produce the desired orientation. Typically, a thin layer (often approximating a monolayer) of the coupling agent molecules is bonded to each of the two substrates supporting the LC film. In addition to direct chemical bonding of the CAM's to the substrates, the CAM layers may be further stabilized by polymerization of the CAM's among themselves. Mostly, alkoxysilane monomers of the general formula $RSiX_3$, are a particularly useful class of CAM's for orienting LC's. In the general formula, R is an organofunctional orienting group attached to the silicon atom in a thermally and hydrolytically stable manner, and X designates hydrolyzable groups upon silicon. For alkoxysilane, X denotes alkoxy groups. The strength of the silane-substrate interaction depends both on the chemical nature of the silane and of the substrate as well as on the silane deposition conditions.

Alkoxysilanes will not react directly with siliceous or metal oxide surfaces, but must be hydrolyzed first. The hydrolysis reaction is rapid and is usually best conducted in a dilute aqueous solution. Adsorbed water on the surface may also be sufficient to hydrolyze the CAM's.
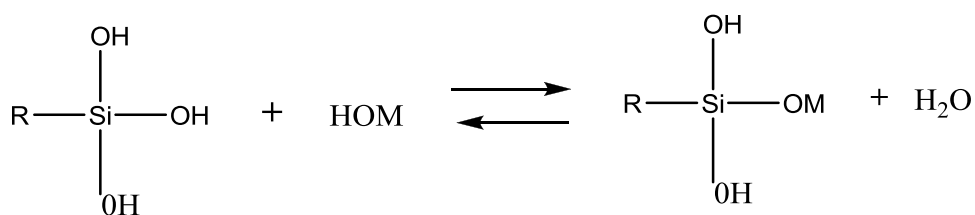
$$RSiX_3 + 3H_2O \xrightarrow{\text{pH} <7} RSi(OH)_3 + 3HX$$
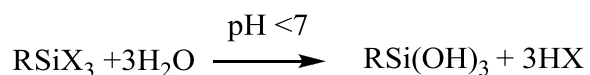
The hydrolyzed silane molecules will then chemisorbs on a hydrophilic surface forming a hydrogen bonded silane layer or an oxane bonded layer,

Where M indicates matal or silicon ion

or an oxane bonded layer
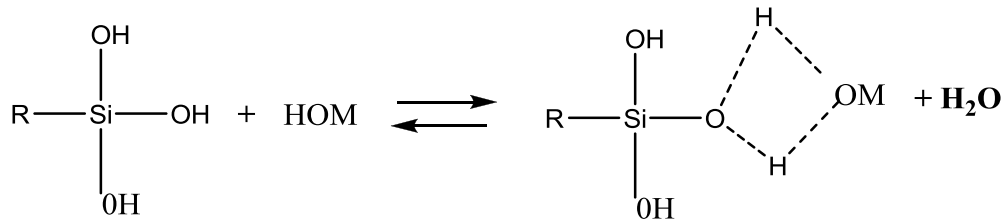
where, M indicates metal or silicon ions

Although these reactions are reversible in the presence of water, once the silane coating is cured by drying at room or elevated temperatures, the coating is permanently bonded to the substrate. Temperatures up to 250° C may be used in curing or subsequently.

The curing process, in addition to drying the silane layer, may also serves to polymerize the silane monomers to form polysiloxanes. In the absence of polymerization, the silane coating might be subject of moisture or other reactive agents attack. However, after curing, even if a Si -O-M bond is destroyed (e g., by hydrolysis), Si-O-Si-O-Si polymer chains hold the R-Si group in a fixed position thereby enabling the Si -O-M bond to eventually reform via above mentioned reaction . Thus, the polymerization results in a dynamic bond equilibrium which preserves the integrity of the interface.

Particular alkoxysilane materials, which are used advantageously in fabricating LC display devices, include N, N-dimethyl-N -octadecyl-3 -aminopropyl-trimethoxysilyl chloride
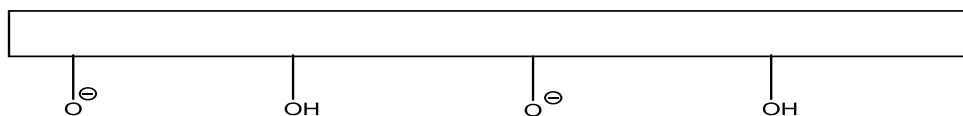
(DMOAP) and N -methyl-3-aminopropyltrimethoxysilane (MAP). These materials are produced experimentally by Dow Corning as XZ2-2300 and XZ -2024 respectively. The chemical formulas for these materials are given in the below mentioned figure together with schematic representations showing the orientations of their component propyl $(CH_2)_3$ and octadecyl $(C_{18}H_{37})$ hydrocarbon chains after silane bonding to a substrate. Note that both the amino and silane sites of these CAM's are believed to adsorb or bond to the substrate.
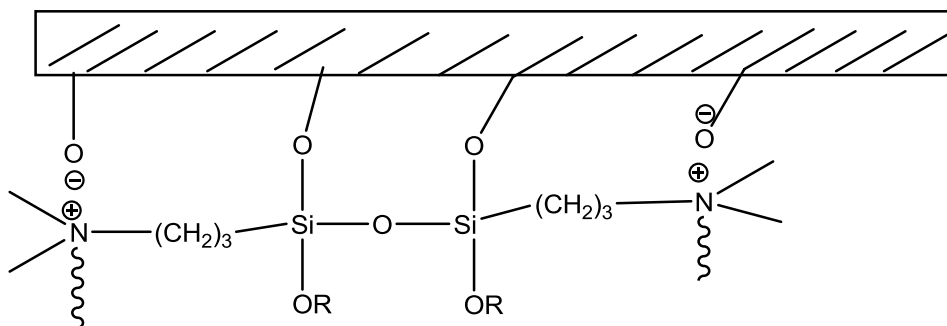
3. Structure of DMOAP:-

N,N-Dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP)

$$Cl^- \quad {}^+\!N - (CH_2)_3 \; Si(OCH_3)_3$$

with substituents $C_{18}H_{37}$ above N and CH_3, CH_3 below N.
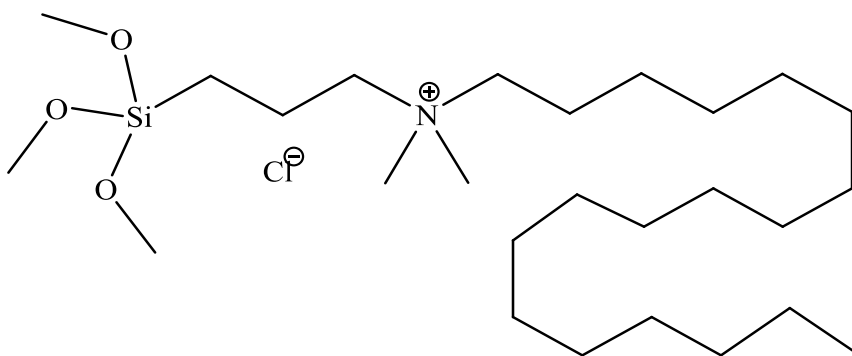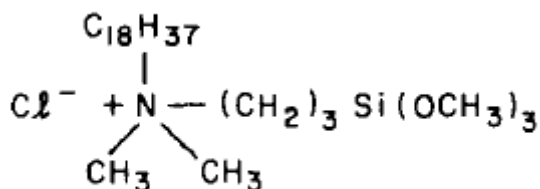
Oxidized silica surface:

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4. Formation of DMOAP film on treated Silica :
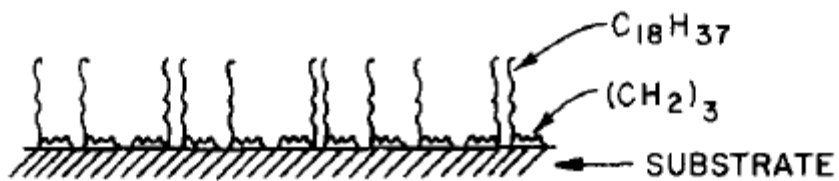
4-cyano-4'-n-pentylbiphenyl (5CB) :

N-methyl-3-aminopropyltrimethoxysilane (MAP):

$$H_3C - N - (CH_2)_3 \ Si \ (OCH_3)_3$$
$$|$$
$$H$$

$(CH_2)_3$

SUBSTRATE

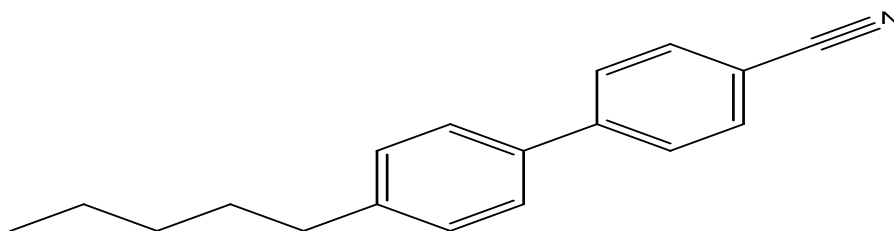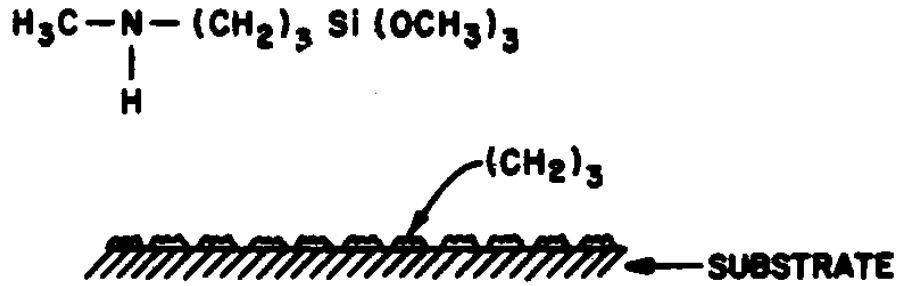Typical deposition procedure is to clean the substrate thoroughly to remove all organic and inorganic residues, dip the substrate in a dilute solution of the alkoxysilane (typically 0.1% by volume in water), and agitate at room temperature for about 5 min. The substrate is then rinsed in deionized water to remove excess silane, excess water is then blown free with clean N_2 and finally the silane coating is further cured in dry N_2 typically at 120°C for 1 h

Although considerably more than a monolayer of silane may be initially deposited on the substrate, the above rinse procedure is believed in many cases to leave essentially a monolayer of silane coating on the substrate. The layer thickness depends not only on the deposition method, but also on the composition of both the CAM's and the substrate. A layer of silane applied to a substrate is essentially permanently bonded to the substrate in such a manner that the orienting groups of the silane CAM's are free to interact with and align neighboring LC molecules.

Thus, using DMOAP (MAP), created surfaces which consist mainly, as shown in Figures octadecyl (propyl) hydrocarbon chains lying normal (parallel) to the substrate.

The propyl chains are randomly aligned and do not have any axis of symmetry in the substrate plane thus in the MAP case, the oriented LC will tend to have its long molecular axes parallel to the plane but with random azimuth. This type of surface results in good storage of thermally or electrically induced scattering centers in nematic-cholesteric mixtures and provides an extremely transparent nonscattering erased state as well.

5. Surface treatment procedure for silica beads using DMOAP:-

1. Take the untreated silica beads and mix with 1ml of distilled water.
2. Add 2% of DMOAP solution to the mixture of water and silica beads colloidal solution
3. Mix for 5 minutes to get uniform alignment of octadecyl chains on the surface of silica.
4. Centrifuge the mixture to remove excess solution from surface treated silica beads.
5. Clean with distilled water, repeat step 3 and 4 for removing excess liquid.
6. Dry the silica particles for 20 minutes at $120\,^{0}$c in the oven.
7. Finally, small percentage of well treated silica beads uniformly dispersed into 5CB Nematic liquid crystal.

In DMOAP the moleculer octadecyl chain can be arranged to be either parallel or perpendicular to the silica surface or substrate. This gives permenant bond with silica surface or substrate. These surface coupling agents will act differently than surfctants, where the both sides bonding occures. In DMOAP coupling, only one side it makes bond with silica and otherside do not.

6. Characterization of Polymer deposition:-

Surface tension of the desired combination of polymers and liquid crystals can give the partial information about free energy of the desired orietation (Neglecting the microscopic and anisotropic LC-substrate interactions). Whether the polymer chains gives homeotropic or planar alignment on different substrates like silica beads, tin oxide glasses or substrate glasses defined by surface tension phenomenon [1]. In addition to this one can probe AFM force measurement technique to find the thickness of the aligned layer and smectic layers on the substrate [4].

General condition for wetting the desired substrate surface was achieved by the condition that the surface tension of liquid less than the surface tension of substrate. Solid substrate may be characterized by critical surface tension γ_C,

$$\gamma_C > \gamma_L$$

If this condition matches, the liquid spreads uniformly on the substrate. The contact angle at liquid –solid interface becomes zero. In case of liquid crystals this condition gives parallel or planar alignment of molecules.

If the surface tension of liquid $\gamma_C < \gamma_L$, this is the condition for homeotropic alignment of liquid crystals. Here, the contact angle can be calculated using

$$\cos\theta = r\left[1 + b\left(\gamma_C - \gamma_L\right)\right]$$

Here, r is the roughness parameter equal to unity for a smooth surface and b is empirically derived parameter. Liquid surface tension can be measured directly, but critical surface tension must be determined indirectly, e.g., by observing the contact angles of a variety of liquids on a given surface and applying the cosθ equation.

Although the critical and liquid surface tensions have their origins in microscopic intermolecular interactions; they are macroscopic quantities. However, without having any particular knowledge of the intermolecular forces involved, prediction of the alignment of a particular LC of known surface tension γ_L on a particular surface of known surface tension γ_c is possible merely by knowing the relative magnitudes of γ_c and γ_L.

The difference,

$\mathbf{\Delta\gamma} = \gamma_L - \gamma_c$, is a measure of the free energy favoring LC molecular orientation normal to a surface over orientation parallel to a surface. It was observed that 'when the substrate surface tension is relatively low, the intermolecular forces within the liquid crystal are stronger than the forces across the interface. The fluid does not wet the solid and the elongated nematogenic molecules align perpendicular to the surface to maximize their intermolecular interactions. When the critical surface tension of the solid is greater than that of the liquid crystal, the forces across the interface dominate. The surface energy is

minimized if the fluid wets the solid and the elongated liquid crystal molecules pack flat against the substrate." Although this macroscopic model is not universally valid because it does not take into account all possible microscopic and anisotropic LC-substrate interactions. For example, when a liquid is placed in contact with a substrate, a monolayer of liquid molecules may be preferentially adsorbed by the substrate. The molecules of the adsorbed monolayer may often have polar ends in contact with the substrate and nonpolar ends extending away from the substrate. In this manner, the adsorbed monolayer may effectively reduce the γ_c of the substrate. Thus the liquid crystal may fail to wet its own adsorbed monolayer, and normal orientation could result even when γ_c for the original substrate is greater than γ_L.

7. Liquid crystal alignment by textured surfaces :

we have so far considered macroscopically smooth surfaces on which LC alignment results from intermolecular forces of physicochemical origin. Now consider alignment by textured surfaces in which aligning interactions due to the LC's anisotropic orientational elasticity are also present.

Textured Surfaces:

Consider the alignment of a nematic LC on a grooved substrate. Applying the Frank-Oseen continuum theory. They note that the orientational elastic free energy (Frank free energy) of the LC will be minimized when the nematic director *d*, the local alignment direction of the long molecular axes, has neither bend, splay, nor twist, i.e., when all the spatial derivatives of *d* are identically zero. Thus the Frank elastic free energy is a minimum when the nematic molecules are aligned.
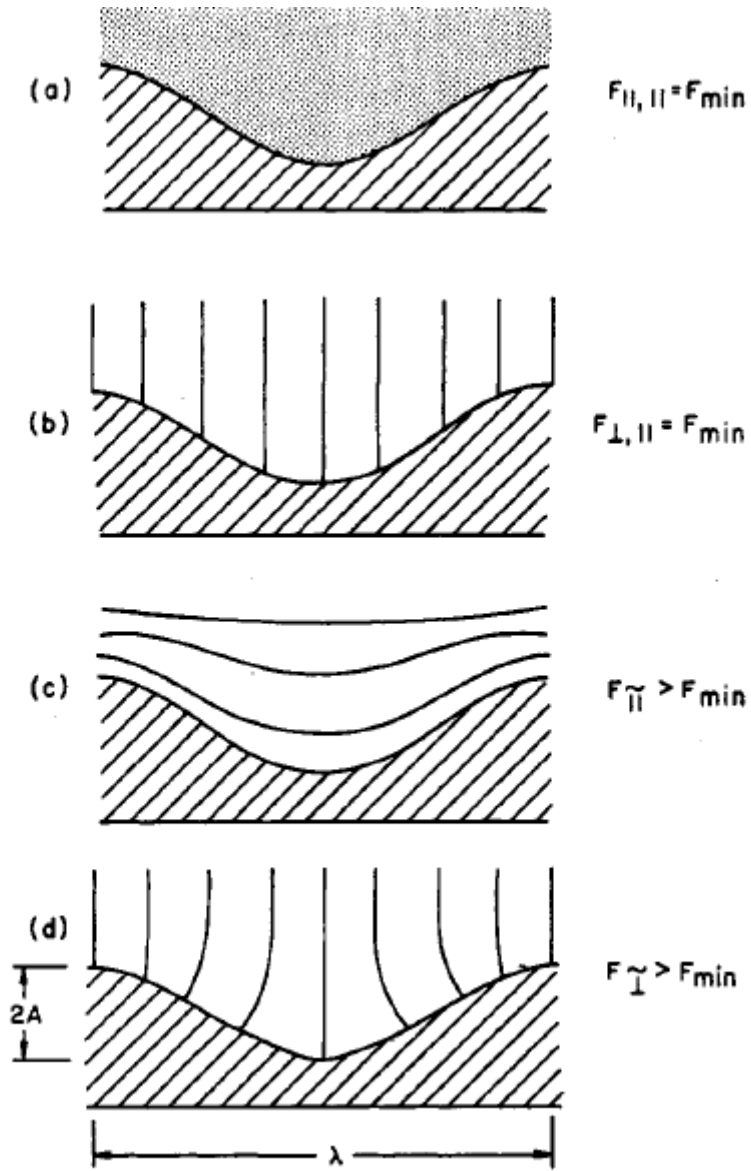
Fig 1 : Elastyic free venergy for nematic materials aligned by grooved substrates. Orientation of nematic directors.

1) Parallel to the grooves and the substrate plane as in Fig. 1(a) or

2) Normal to the grooves and the substrate plane as in Fig. 1(b). The Frank free energy is somewhat higher when the nematic molecules are aligned.

3) Normal to the grooves and parallel to the substrate surface as in Fig. 1(c), or

4) Normal to the grooves and normal to the substrate surface as in Fig. 1(d).

They took the Frank free energy per unit surface area of the nematic LC to be $F_\parallel$, $F_\perp$, $\tilde{F}_\parallel$ *and $\tilde{F}_\perp$, and for* these four cases, respectively. Thus

$$F_\parallel = F_\perp = \mathbf{F}_{min}$$

$$\tilde{\mathbf{F}}_\parallel > \mathbf{F}_{min}$$

$$\tilde{F}_\perp > \mathbf{F}_{min}$$

8. <u>Expermental Results</u> :-

The colloidal studies have shown clearly the orientation of the LC director around the treated silica sphere. Here, we have experimentally observed the silica colloid with homeotropically treated surface in LC cell shown below. we observe simple point defect (dipole) in thick cell about >3R thickness. In case of thin cells <3R the point defect transformed to line (called as saturn ring) shown below.
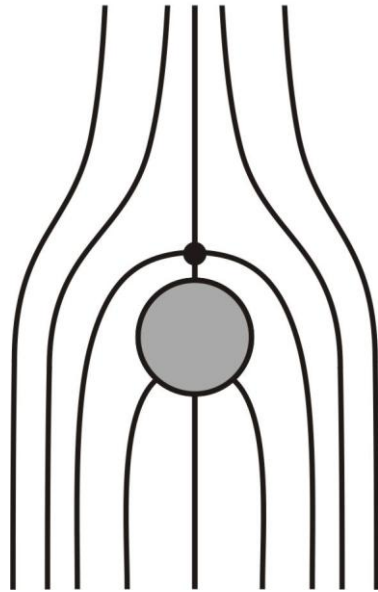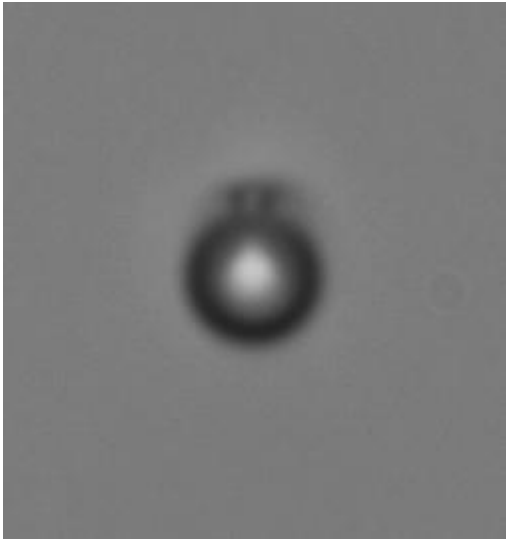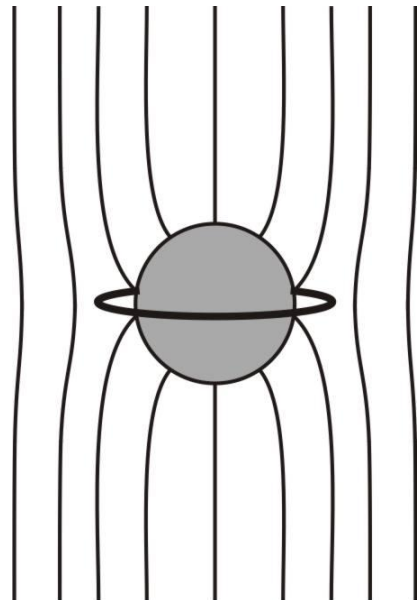
Fig. 2

Fig. 3

It shows the liquid crystal orienation around the silica surface. In case of dipole and quadrupole the director structure shown in schematics. The liquid crystal molecules closest to the surface can align at some angle to the normal. LC molecules those are far from the surface will align parallel to the sample surface.

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AFM studies also confirmed the alignment of LC layer over DMOAP coated substrates. The alignment of LC on the silanted glass substrate has been intesively studied by (Igor Musevic et, al (2001)). Temperature controlled AFM measurement shows that, the prenematic layer in case of 5CB, smoothly decaying pre smectic modulation in 8CB and layer by layer formation in 12CB has been observed on the LC molecular layer strongly adsorbed on the DMOAP coated glass.

The AFM measurement confirms the strongly positionally anchored DMOAP molecules on the substrate and forms a molecular layer of LC molecules on the substrate surface [4].

Conclusion:-

Surface coupling agents, its structure and coating procedure were discussed clearly. Surface coupling agents DMOAP, MAP are exceptionally stable in the presence of moisture and they provide the constant value of critical surface tension desired for liquid crystal device structures, LC colloidal applications and meta material application. Experimentally making the colloidal chains and knots indeed depend on the strong alignment of the coupling agents on substrates.

References:-

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   Liquid Crystals", *Proceedings of the IEEE*, Vol.61, No.7, July 1973.

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4. K. Kocevar and I.Musevic, *Liq. Cryst*, 28, 4, 2001.

5. A. W. Adamson, *Physical chemistry of* surfaces, 2nd *ed. (*John Wiley & Sons, 1967).