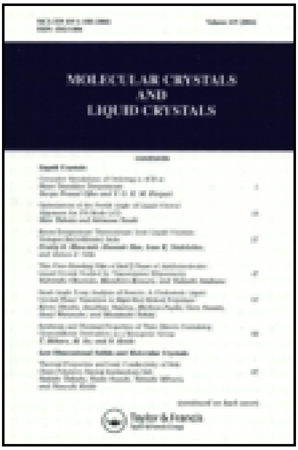

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Manufacture and Physical Properties of Silicon-Organic Films for LC Alignment

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Manufacture and Physical Properties of Silicon-Organic Films for LC Alignment

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Preparation of silicon-organic films for LC alignment is described. Effect of the molecular structure of organic substituents in siloxane chains on type of LC the alignment (homeotropic, tilted, planar) is considered. Contribution of polar and dispersion parts of the surface energy of siloxane films is discussed.

Keywords: silicon-organic compounds; hydrophoby; LC alignment

INTRODUCTION

Interest in silicon-organic compounds (SOC) as liquid crystal orientants is explained by their unique nature and physico-chemical properties. SOC based polymeric films are high hydrophobic, i.e., stable to humidity and other atmospheric factors. They are also thermostable up to 200 °C and stable to frost up to -60 °C [1,2]. Besides of that, SOC with different functional groups at a silicon atom (chloro-, alkoxy-, hydroxy-, acetoxy etc.) are amphiphilic substances which combine hydrophylic and hydrophobic groups in a molecule and able to interact with active centers of a substrate to create a siloxane bond with a surface.

The SOC properties mentioned as well as soft conditions of the SOC films manufacture offer to use these materials as LC orientants. The LC alignment on some siliconorganic films was considered in [3,4]. However, the data from different sources are contradictory. Effects of steric, polar and dispersive interaction were not discussed. Besides of that, new recent developments in display technology challenged wider range of LC alignment angles at surfaces. Manufacture of reproducible homeotropic orientation is of special importance since the switch time of electrooptic effect is lower in this case [5]. Development of new methods to obtain this alignment type could offer increased use of LC materials with the negative dielectric anisotropy for guest-host and controllable birefringence effects [6,7] Its application in in-plane addressed displays [8] could open new possibilities to improve their electrooptic response.

The goal of our paper is to study the mechanism of LC orientation on the surface of silicon-organic films.

Films preparation

The compounds with functional groups at a silicon atom like ethoxy, hydroxy, hydryd groups and other different organic substituents were selected from a lot of SOC for experimental studies. These groups are able to create bonds with the surface of a glass substrate and between neighbouring siloxane moieties. Some monomers (organotri- and diorganodiethoxysilanes), organosilanols, industrially manufactured hydrophobizators GKZh-94, GKZh-136-323, GKZh-119-215 and water emulsions on the base of the hydrophobizators are related to this type of compounds.

All the orienting films were manufactured at equal conditions. The SOC film was coated onto the substrate surface by deepening the substrate into a SOC toluene solution at following conditions:

- concentration of SOC in the toluene solution 1%,
- room temperature,
- 2 hours duration of deepening into the solution what is sufficient to prepare homogeneous absorption film,
- drying temperature 120 °C ,
- 1.5 hours drying duration.

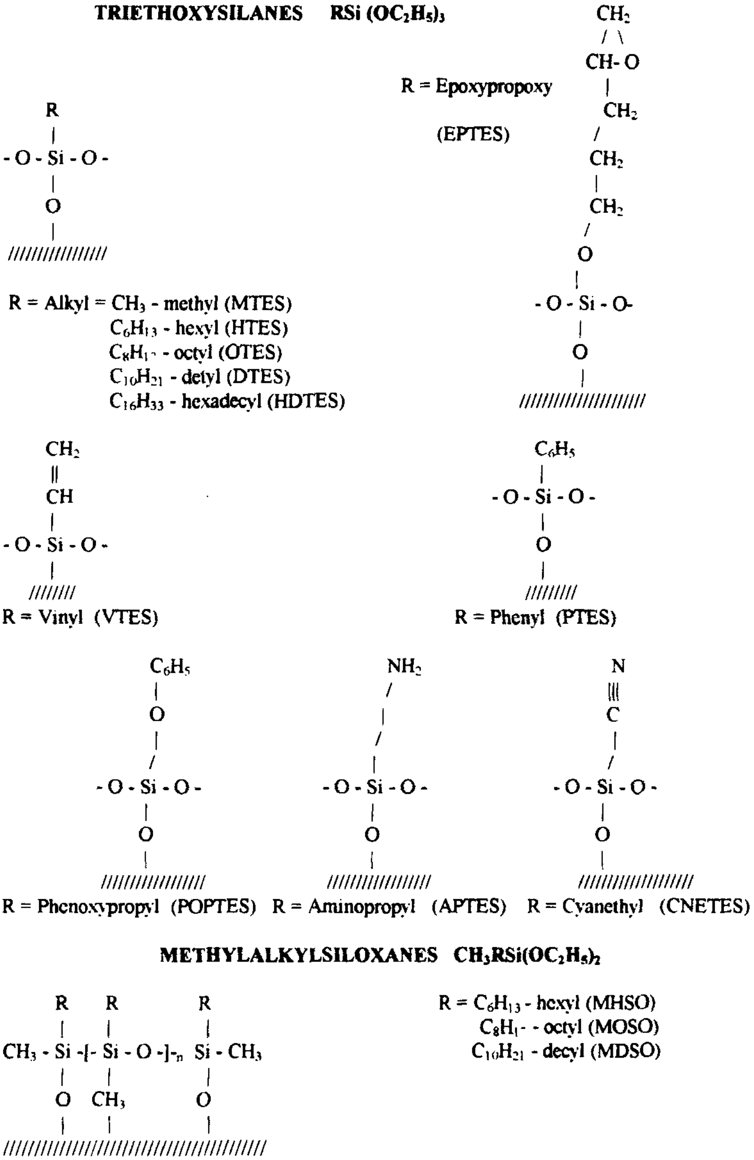


FIGURE 1. Names and abbreviation of SOC studied and structures of different silicon-organic polymeric films on glass or ITO surface (////////).

TABLE 1. LC alignment on SOC films

SOC	Type of LC alignment		
	ZhK-440	ZhK-807	ZhK-1282
Triethoxysilanes			
MTES	∠	∠	∠
HTES	∠	∠	∠
OTES	∠	∠	∠
DTES	∠	⊥	∠
HDTES	∠,⊥	⊥	⊥
PTES	∠	∠	∠
VTES	∠	⊥	∠
EPTES	∠	∠	∠
POPTES	∠	∠	∠
APTES	∠	∠	∠
CNETES	∠	∠	∠
Methylalkylsiloxanes			
MHSO	∠	⊥	⊥
MOSO	∠	⊥	⊥
MDSO	∠	⊥	⊥
Hydrophobizators			
119-215			
$[(C_2H_5O)(C_8H_{17}O)SiO]_n$	∠,⊥	⊥	⊥
GKZh-94			
$[(C_2H_5)HSiO]_n$	∠	⊥	⊥
136-323			
$[(C_2H_5)HSiO]_n[(C_2H_5)_2SiO]_m$	∠	⊥	⊥

Drying temperature of 180°C is necessary to finish polycondensation processes when a film is prepared from hydrophobizators solutions.

Chemical structure of compounds studied is displayed in Table 1 and Fig.1.

Liquid crystals used

Liquid crystal materials ZhK-440, ZhK-807, ZhK-1282 developed in NIOPIK (Organic Intermediates and Dyes Institute, Russia) were used. The first material ZhK-440 is a mixture of weak-polar 4-alkyl-4'-alkoxy- and 4-alkyl-4'-alkanoyloxyazoxybenzenes with a low value of the dielectric anisotropy ($\Delta\varepsilon \cong -0.5$) and an average dielectric constant ($<\varepsilon> \cong 5.5$). The material ZhK-807 is a multicomponent mixture of strong polar 4-alkoxy-4'-cyanobiphenyls ($\Delta\varepsilon \cong +10$).

The material ZhK-1282 is a mixture of cyanobiphenyls with Demus ethers (4-alkoxyphenyl ether of 4′-alkylcyclohexancarbonic acid) and a small amount of other substances. It contains both polar and weak polar substances. Its $\Delta\varepsilon$ is +6.5.

Experimental methodics and results

The following SOC parameters were determined from measurements:

- type of orientation,
- surface energy,
- electrostatic charge.

The type of orientation (homeotropic and tilted or planar) was determined when a LC cell with SOC orienting films was positioned onto a rotating table of a polarizing microscope. The textures observed differed by the brightness of the view field. Exact measurement of the tilt angle values is a topic of further investigations. A modification of the Owens-Wendt method [9] of calculation of the surface tension of a solid polymer and its polar and dispersive components was used. Edge angle values θ_1 and θ_2 of liquid drops positioned onto a film surface was measured by a horizontal microscope. Two liquids of different polarities (water and iodine methyl CH_3J) were selected for the measurements. Then both polar σ^p and dispersion σ^d contributions to the surface energy σ were calculated by using the following relations [9,11]:

$$(\sigma_i^d + \sigma_i^p - a_i)\sigma^d\sigma^p + \sigma_1^p\sigma^d(\sigma_i^d - a_i) + \sigma_i^d\sigma^p(\sigma_i^p - a_i) - a_i\sigma_i^d\sigma_i^p = 0 \quad (i=1,2) \qquad (1,2)$$

(where $a_i=0.25\sigma_i(1+\cos\theta_i)$, σ_i^d, σ_i^p - dispersive and polar parts of surface energy of liquids used in the experiment.)

Surface charge values were measured in accordance with the method described in [18]. The substrates area with a SOC was as large as 12 cm^2. A digital electrometer V7-30 and a special chamber to exclude ambient conditions influence were used. All the measurements were taken at room temperature.

TABLE 2. Influence of SOC concentration and molecular structure on film properties and LC alignment

SOC chemical formula	Solution concentration, %	Substrate's surface	Surface energy, mJ/m^2			Film's charge, C	LC material alignment		
			σ	σ^p	σ^d		440	807	1282
$CH_3Si(OC_2H_5)_3$	1	Glass	42	10	32	$4\ 10^{-12}$	∠	∠	∠
	1	ITO	43	15	28	$1\ 10^{-10}$	∠	∠	∠
	3	Glass	43	14	29	$8\ 10^{-12}$	∠	∠	∠
	5	Glass	41	12	29	$3\ 10^{-12}$	∠	∠	∠
	5	Rubbed gl.				$6\ 10^{-11}$			
$C_6H_{13}Si(OC_2H_5)_3$	1	Glass	57	30	26	$2.2\ 10^{-12}$	∠	∠	∠
	1	ITO	41	3	38	$1.5\ 10^{-10}$	∠	∠	∠
	3	Glass	48	19	29	$3.5\ 10^{-12}$	∠	⊥	⊥
	5	Glass	48	18	30	$2.9\ 10^{-12}$	∠	⊥	⊥
	5	Rubbed gl.				$6\ 10^{-9}$			
$C_{10}H_{21}Si(OC_2H_5)_3$	1	Glass	50	20	30	$2.8\ 10^{-12}$	∠	⊥	∠
	1	ITO	53	19	23	$2\ 10^{-9}$	∠	∠	∠
	3	Glass	47	17	31	$4.1\ 10^{-12}$	∠	⊥	⊥
	5	Glass	46	15	31	$1.3\ 10^{-12}$	⊥	⊥	⊥
	5	Rubbed gl.				$6\ 10^{-10}$			
$[(CH_3)_2SiO]_3$	1	Glass	57	35	22	$5.5\ 10^{-10}$	∠	⊥	⊥
	3	Glass	57	34	23	$8\ 10^{-10}$	∠	⊥	⊥
	3	ITO	50	17	36	3 10-10	∠	∠	⊥
	5	Glass	50	26	24	$1.2\ 10^{-10}$	∠	⊥	⊥
$[(C_2H_5)_2SiO]_3$	3	Glass	59	35	24		∠	⊥	∠
	3	ITO	50	10	40		∠	∠	∠
	5	Glass	56	31	25		∠	⊥	∠
Surface without treatment	-	Glass	47	16	32		∠	⊥	⊥
	-	ITO	40	4	36		∠	⊥	∠

The siloxane films were prepared from toluene solutions at SOC concentrations 1 w.%, 3 w.% and 5 w.%. Two types of substrates' surfaces were used: a pure glass and a ITO transparent electrode evaporated onto the glass. Some films were rubbed to compare results obtained for various technologies.

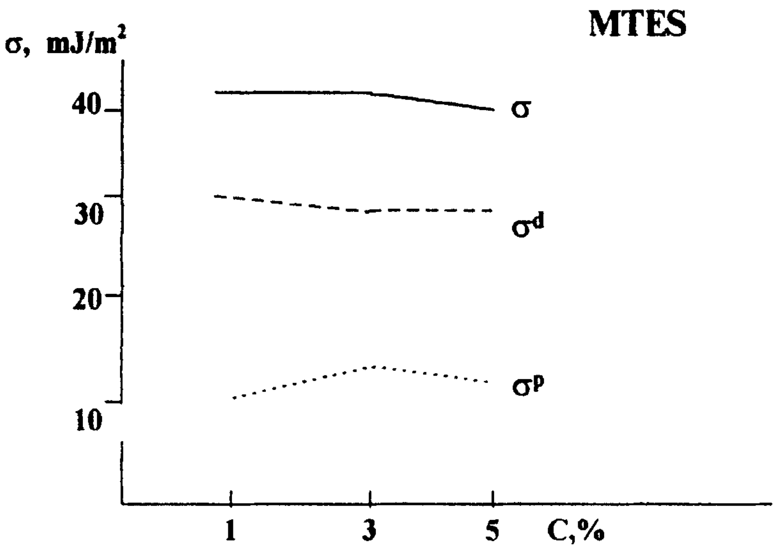
Results and discussion

The results obtained are listed in Table 1 and Table 2. It follows from these data that the LC material ZhK-440 have the tilted/planar alignment on all the surfaces. Some SOC (HDTES and 119-215) give domains with homeotropic and tilted LC orientation. Both ZhK-807 and ZhK-1282 have planar alignment on films of siloxanes with shorter substituents. For substances with long substituents with ten or sixteen carbon atom in a chain the homeotropic orientation takes place. All the hydrophobizators give the homeotropic orientation for both polar LC materials. Oligomeric dimethyl and diethyl silanes result in homeotropic alignment for both ZhK-807 and ZhK-1282 at any SOC concentration. Tilted alignment of ZhK-807 takes place when olygomeric derivatives mentioned are coated onto *ITO* surface.

The surface energy varies from 40 mJ/m^2 to 60 mJ/m^2 for different coatings. It depends weakly on the SOC concentration or its molecular structure (Figs.2, 3). Except of 1% HTES, the polar component is 1.5-2.0 times less in comparison with the dispersive component for all the compounds and solutions. The difference of surface energy values for films coated onto the pure glass or the ITO layer is remarkable only for hexylsiloxane.

The surface charge values is of the order of units of picocoulombs. That means the films are very good dielectrics. As a rule, the surface charge values for coating on the ITO surface are 25-700 times higher in comparison with the surface charge value on the pure glass surface. The siloxane film surface rubbing results in a 20-2000 time increase of the surface charge value. The longer is an alkyl chain in a siloxane molecule the higher is this increase.

Let us consider possible intermolecular interactions of LC and film materials.


MTES
σ, mJ/m²
40
30
20
10
σ
σ^d
σ^p
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3
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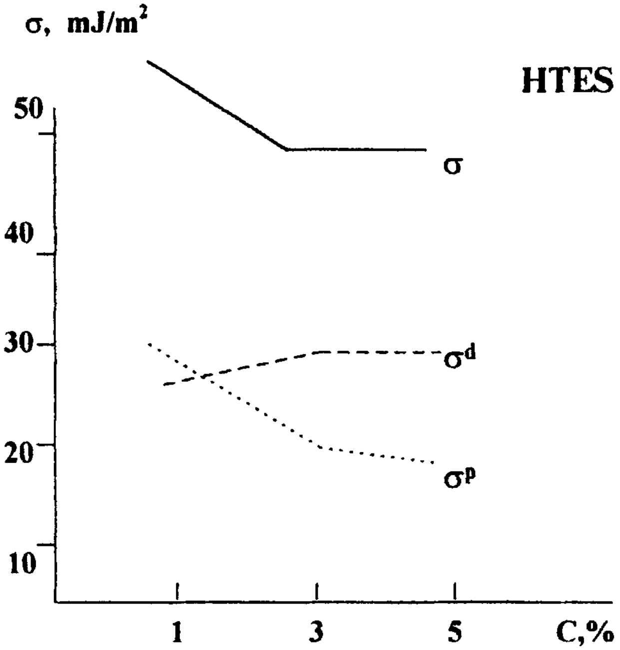
C,%


σ, mJ/m²
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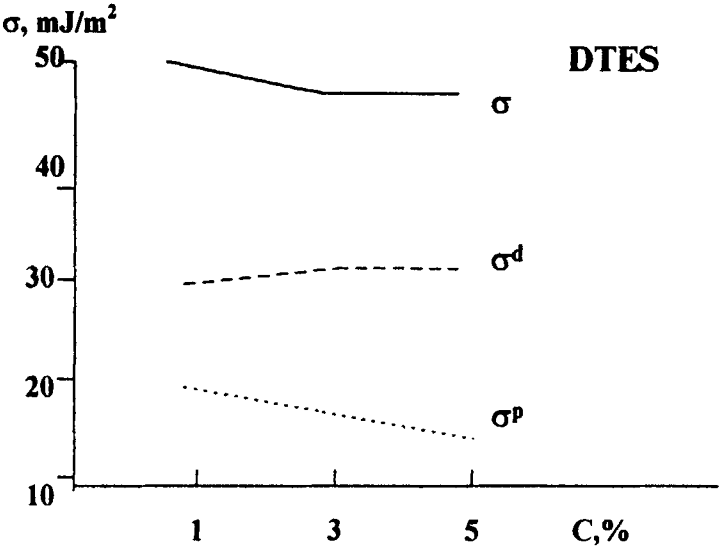

FIGURE 2: Dependence of surface energy σ and its polar and dispersion components on SOC concentration C in initial toluene solution.

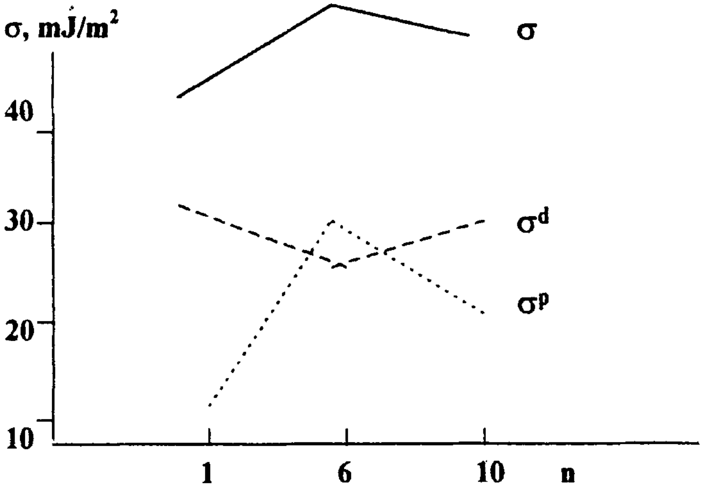

FIGURE 3: Dependence of surface energy σ and its polar and dispersion components on carbon atoms number n in the alkyl chain at C=1%.

Molecules of azoxycompounds in ZhK-440 have undevided electron pairs and conjungated bonds. Therefore they can generate two types of chemical bonds with the SOC moieties: hydrogen bond with carbohydrate substituents or coordination linkages with free *d*-orbitales of the Si atom. Such interaction results in the homogeneous planar or tilted LC alignments. Mixed alignment of ZhK-440 with homeotropic and tilted domains on HDTES and olygoethoxy-(2-ethylhexoxy)siloxane (hydrophobizator 119-215) films is observed. In the first case, the probability of cohesion of long substituents $C_{16}H_{33}$ is increased and a packing of polymer moieties can result in occurence of siloxane groups on the film surface when most of them are connected with the glass surface. Then the dispersive interaction of oxygen atoms in SiO group and aromatic moieties in the mesogenic molecule has to result in planar or tilted alignments. The generation of homeotropic domains is due to the hydrophobic interaction of alkyl substituent in both HDTES and LC molecules. In the material 119-215 an additive inhomogeneity can take place due to rotation of branched 2-ethylhexoxy groups around Si-O-C bonds. Alignment of the polar materials ZhK-807 and ZhK-1282 on alkyl substituted triethoxysiloxane films depends strongly on the alkyl chain length and the concentration of the SOC in the initial toluene solution.

Short carbohydrate substituents do not screen the interaction of siloxane bonds with aromatic cores of mesogenic molecules and the probability of planar orientation is higher. For the case of longer substituents, the repulsion of carbohydrate chains and terminal groups of mesogens is of greater importance.

Vinyliethoxysilane has an additive conjugation on Si-C bond due to interaction of π-electrons of carbon atom and free *d*-orbitale of silicon atom. It can reduce intermolecular interaction of siloxane and LC and result in homeotropic alignment of ZhK-807.

In methylorganodiethoxysilanes and other olygomeric substances including hydrophobizators studied mutual position of methyl and alkyl radicals screens siloxane bond and homeotropic alignment of ZhK-807 on these films is observed. The specific feature of olygomeric compounds is higher share of polar surface energy in total σ value in comparison with dispersive one. It provides repulsion of polar group in SOC and LC material and results in homeotropic alignment of mesogens with positive dielectric anisotropy and planar alignment of materials with negative $\Delta\varepsilon$ value.

When a SOC film is coated onto ITO electrode surface the LC alignment is planar or tilted in most cases. It is illustrated by the data displayed in Table 2 for 1% or 3% solutions and in Table 3 for strongly diluted solutions (0.01%) of various SOC. These films have only units of SOC monolayers and therefore they screen weak the action of a substrate on LC. Homeotropic alinment on both types of surfaces is observed only in case of HDTES with long substituent.

TABLE 3. Alignment of ZhK-1282 on surfaces of thin SOC films coated onto pure glass and ITO electrode.

SOC formula	Glass	ITO
$C_2H_5Si(OC_2H_5)_3$	⊥	∠
$C_{10}H_{21}Si(OC_2H_5)_3$	⊥	∠
$C_{16}H_{33}Si(OC_2H_5)_3$	⊥	∠
$((C_2H_5)_2Si)_3$	⊥	∠

CONCLUSION

The type of the LC alignment on the surface of a siloxane film depends strongly on the polarity of LC molecules, steric factors, relation of polar and dispersive parts of the film surface energy. A reliable homeotropic LC orientation can be obtained for cyanoderivative LC and a long substituent in the polymeric chain of alkyltriethoxysiloxane. Dimethyl and diethylsilanes films with higher share of the polar energy in comparison with the dispersion one align polar molecules homeotropically. The more diluted is the initial solution of a SOC the higher is probability of tilted or planar alignment. The order of a value of the film surface charge is 10^{-12} C for coatings on the pure glass surface, 10^{-10} C on ITO electrode surface, 10^{-10}-10^{-9} C for rubbed siloxane coatings. Typical value of the SOC surface energy is as high as 40-60 mJ/m^2. The contribution of its polar parts is about 30-40% for alkyltriethylsiloxanes, 55-60% for dialkylsilanes. The results obtained can be used for LC displays manufacture with given tilt value in a wide range.

Acknowledgments

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