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Characterization and Alignment Properties of Rough Substrates

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We have determined by atomic force microscopy the average roughness of substrates covered with a different indium tin oxide (ITO) thickness. We have found that the higher the ITO thickness is the higher the roughness. Then, the preferential alignment of liquid crystalline mixtures, formed by a low molecular weight liquid crystal and a liquid crystalline monomer, on such substrates has been investigated. Samples have turned out to be homeotropically aligned by surface interactions. These cells have been UV irradiated in order to achieve the photo-polymerization of the liquid crystalline monomer. We have found that rougher surfaces are able to store the homeotropic alignment in the anisotropic polymer matrix. The order degree of polymerized films has been estimated as a function of liquid crystal content.

Keywords: Liquid crystals; Liquid crystalline blends; Homeotropic alignment

Pacs Number: 78.20 Jq; 64.70.-p; 61.30.-v

I. INTRODUCTION

In liquid crystal display technology it is important to achieve a uniform and predefined orientation of the liquid crystal molecules in the easiest way. Nematics can be oriented by means of either surface treatments[1] or external fields.[2] Both methods can be used in order to induce a well defined liquid crystal orientation, i.e. a well defined "easy direction" for the nematic director, **n**. Surfaces are usually treated in order to give either homeotropic orientations of liquid crystal, i.e. **n** perpendicular to the surfaces, or planar alignments, i.e. **n** lies in the surface plane. It has been demonstrated that oblique orientations of SiO_x can give tilted

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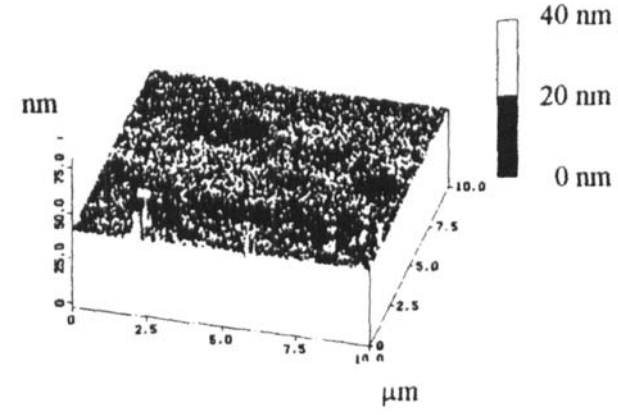
states depending on the evaporation parameters.[3] Generally a clean "flat" surface[1] can lead to degenerate (all directions in the plane of the surface are easy direction), homeotropic, and tilted orientations of liquid crystal, depending on the nature of the substrates and mesogenic molecules. Recently, mixtures containing low molar mass liquid crystalline acrylates and liquid crystal molecules have been successfully used in the production of anisotropic networks.[4–8] These molecules can be oriented by rubbed polyimide layers and the aligned state can be frozen by UV photo-polymerization of the low molar mass liquid crystalline acrylate.

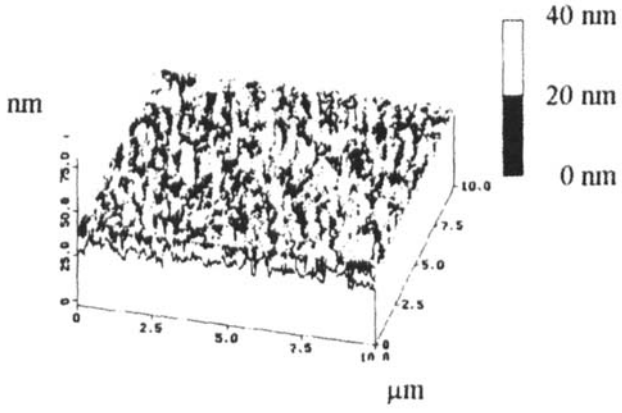
In this paper we have characterized by atomic force microscope (AFM) surfaces with different ITO coverage and investigated the preferential alignment induced by such "clean" rough surfaces on mixtures containing a liquid crystalline acrylate and a nematic liquid crystal. We have observed that the nematic mixtures homeotropically align on the surfaces. Such aligned samples have been exposed to UV radiation and it has been found that the final alignment was almost perpendicular to the rougher substrates. The order degree of polymerized films has been determined as a function of non-reactive liquid crystal content.

II. EXPERIMENT

The liquid crystalline acrylate monomer used in this study is the well-known 1,4-phenylene bis[4-(6-(acryloyloxy)hexyloxy)-benzoate] (C6H) of Hikmet and coworkers[5] which is characterized by a negative dielectric anisotropy, $\Delta\varepsilon$. It was synthesized according to the procedure outlined in ref. 5. ZLI 4788–000, a commercially available nematic liquid crystal having $\Delta\varepsilon = -5.7$, was supplied by Merck. Mixtures were prepared by weighing the appropriate amounts of C6H and ZLI 4788–000 in vials and subsequently stirring them at 120°C. About 1.5 wt. % of photoinitiator (Irgacure 651, Ciba-Geigy) was added. Then a small quantity of mixtures was introduced by capillarity in homemade cells, whose thickness was set to be 15 μm by glass spheres (Nippon Shokubay). The cell walls had different ITO conductive substrates (0, 20, 45, and 120 nm, Balzers). A quantitative indication of cell surface morphology was obtained by using an atomic force microscope (Nanoscope III, Digital Instruments) in contact mode at constant vertical force. A key element of the AFM analysis is its microscopic force sensor, or cantilever. The used cantilever (model Pointprobe, LOT Oriel) is formed by a single crystal silicon with integrated single crystal silicon tip. The tips have the shape of a pyramid with a square base. This shape is improved at the apex of the tip. In the last 200 nm, the vertex angle of the tips tapers from its macroscopic value (~ 40°) to virtually zero at the very end, thus enabling a "true"



(a)



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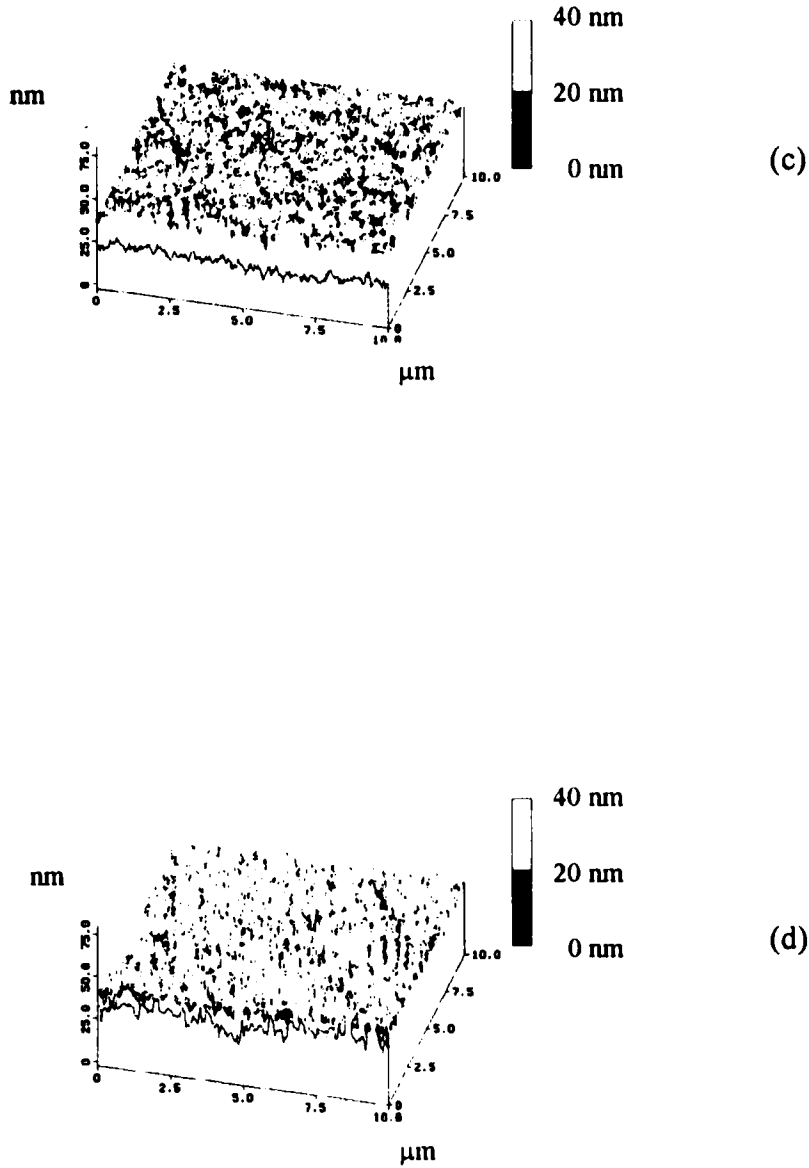

FIGURE 1 **A.** AFM images of the investigated substrates. The horizontal scan area is 10 μm x 10 μm. The vertical range is 75 nm. ITO thickness: a) 0 nm, b) 20 nm. **B.** AFM images of the investigated substrates. The horizontal scan area is 10 μm x 10 μm. The vertical range is 75 nm. ITO thickness: c) 45 nm, d) 120 nm

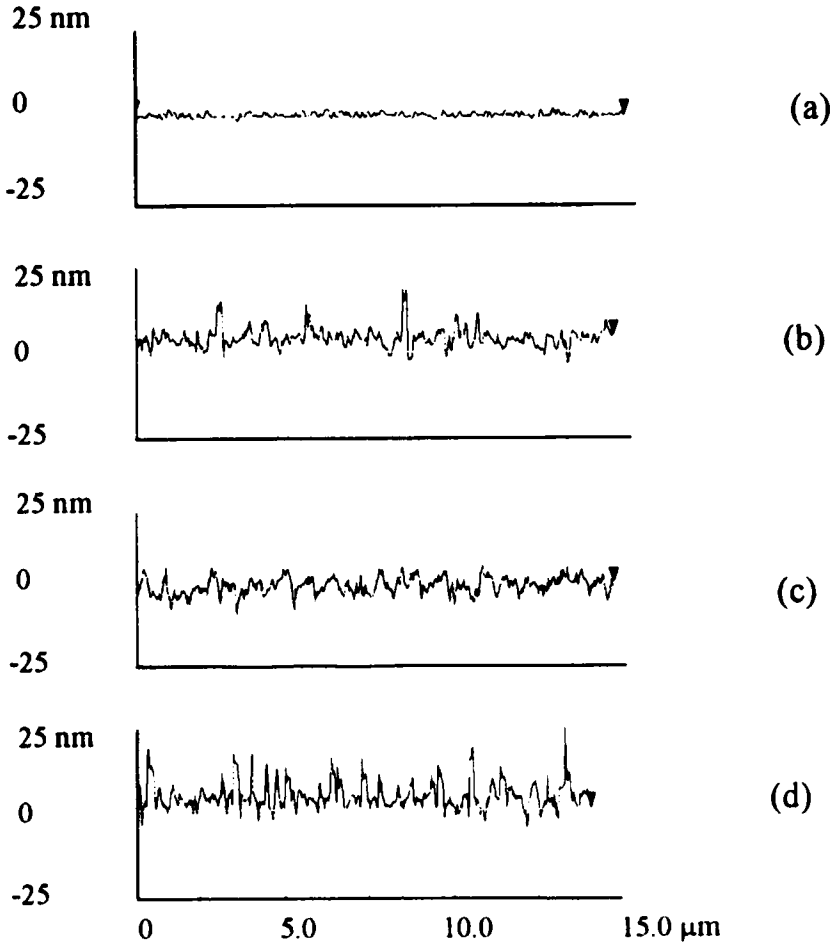

FIGURE 2 Section analysis of the investigated substrates along the diagonals of the AFM images. ITO thickness: a) 0 nm, b) 20 nm, c) 45 nm, d) 120 nm

imaging. The tip curvature radius is guaranteed to be at least 15 nm. AFM calibration was performed on a freshly cleaved mica surface according to the prescribed procedure.[9] The nematic-isotropic, T_{NI}, and crystal-nematic, T_{KN}, temperatures of mixtures were determined with a polarizing optical microscope (Laborlux 12 Pol, Leitz). The sample temperature was varied with a programmable hot stage (PR 600, Linkam) at a rate of 1 °C/min. The refractive index determination was carried out by an Abbe refractometer and a rotary compensator. Films were separated from substrates by a lancet after freezing in liquid nitrogen.

Several samples were discarded before having good quality films. The polymerization of homeotropically aligned samples at controlled temperatures was achieved by means of UV radiation from a 125 W high-pressure mercury lamp (HPK 125, Philips) for 15 minutes. Sample cross sections were cut after immersion in liquid nitrogen, left under vacuum for several hours, and gold coated (thickness ~ 10nm) by a sputter coater. Morphology analysis was performed on cross sections by means of a Leica LEO 420 scanning electron microscope (SEM). The electron beam was accelerated by 5 keV.

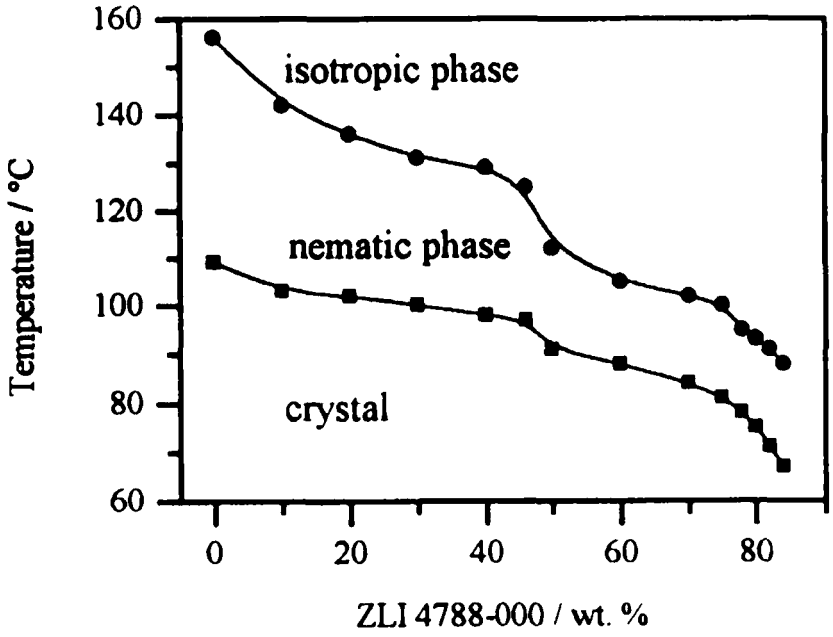

FIGURE 3 Phase diagram of ZLI 4788–000 and C6H mixtures as a function of ZLI 4788–000 wt. % loading

III. RESULTS AND DISCUSSION

Figures 1.a and 1.b show the AFM images of the investigated substrates. It is possible to observe an increase of surface jags as the ITO thickness increases. Such behavior is more evident in figure 2, where the section along the diagonal of the previous images is reported. A quantitative analysis can be obtained by a software treatment of AFM images, which allows the evaluation of the average roughness, R_a, the standard deviation of heights, Z_{rms}, and the average difference

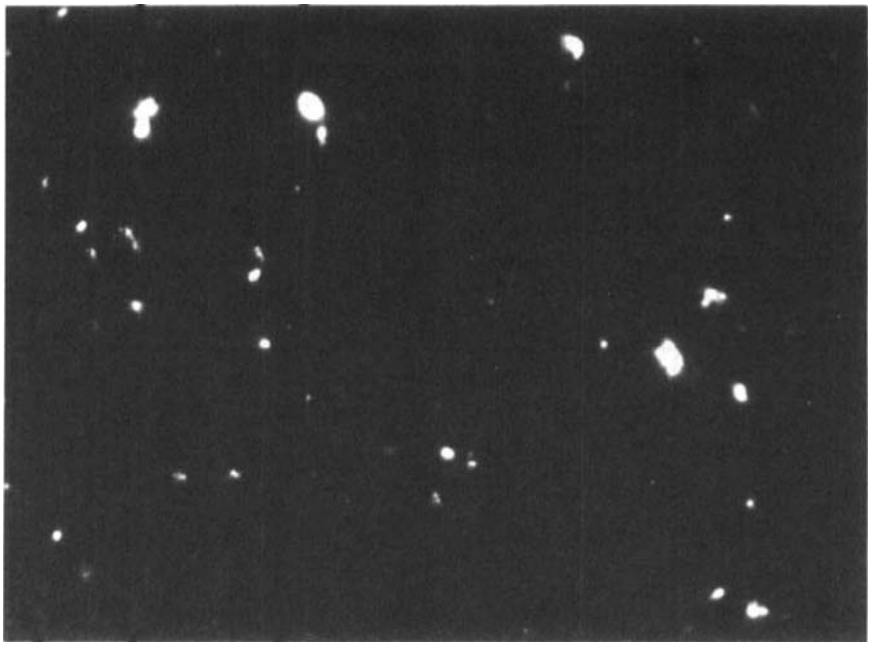

FIGURE 4 Birefringent domains in the uniaxial aligned samples. The ITO thickness of substrates was 45 nm. The photograph area is 600 × 450 μm^2

between the five highest and the five lowest values of heights along the section, R_z.[9] Values are reported in Table I. From such values it is possible to state that the higher the ITO substrates is, the higher the roughness, due probably to the ITO covering technique.

TABLE I Quantitative analysis of the investigated substrates. For each substrate R_a, Z_{rms}, and R_z, are, respectively, the average roughness, the standard deviation of the heights, and the average difference between the five highest and the five lowest values of height along the scanned profile

Substrate	*ITO/nm*	R_a/*nm*	Z_{rms}/*nm*	R_z/*nm*
a	**0**	**0.5**	**0.6**	**2.7**
b	**20**	**1.9**	**2.5**	**11.0**
c	**45**	**2.0**	**2.9**	**16.7**
d	**120**	**2.6**	**4.0**	**19.4**

The molecular alignment of nematics generally depends on the physical-chemical and mechanical interactions, which are related to both surface topology and elastic properties of liquid crystal. Therefore, cells characterized by different

substrates are expected to give rise to a different alignment of liquid crystalline mixtures. As a consequence, the alignment of polymerized mixtures will depend on a balance between the initial molecular alignment and the disorder induced by photo-polymerization.

The mesomorphism shown by monomer mixtures is reported in figure 3 as a function of ZLI 4788–000 weight content. The behavior is similar to that of conventional liquid crystal mixtures having the T_{NI} and T_{KN} a decreasing behavior as a function of ZLI 4788–000 content.

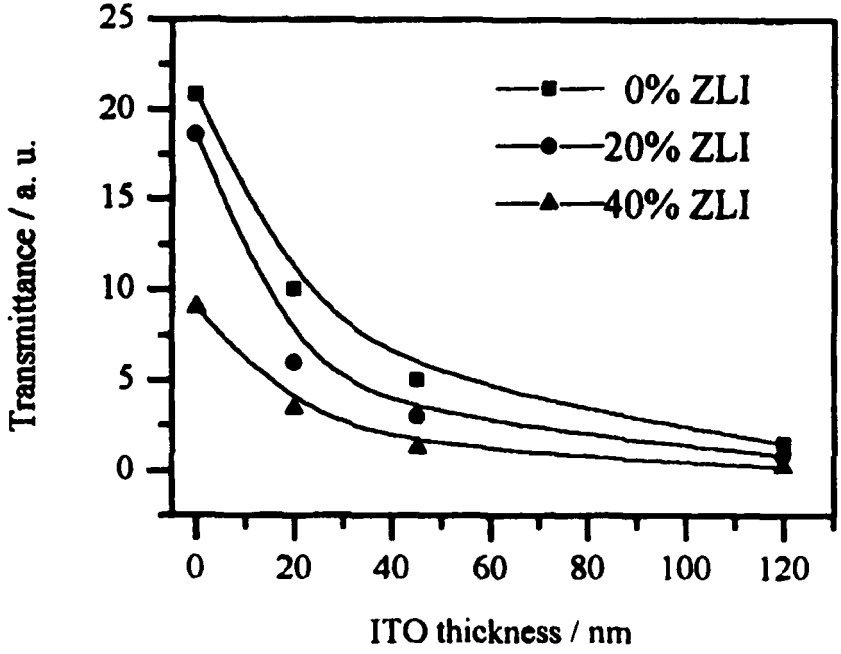

FIGURE 5 Dependence of the film transmittances measured between crossed polarizers on the ITO thickness of the substrates. It is evident that a higher roughness of substrates results in a lower depolarization of the incident light

Once the cells were filled, the alignment of the nematic mixtures was observed between cross polarizers. It was found that rougher surfaces were able to align nematic mixtures almost perpendicular to the substrates. On the contrary, birefringent samples were obtained when glass supports without any ITO layer were used. Such samples were UV irradiated in their liquid crystalline state at 115°C. The discussion of the results will be restricted in this paper to samples with a liq-

uid crystal content lower than 45 wt. % because phase separation appears for larger liquid crystal percentages[10] as confirmed by SEM analysis. After the polymerization, the cells were observed by means of the optical microscope between crossed polarizers and films were found to be still aligned almost perpendicular to the substrates. It was found that some birefringent domains arose in the dark uniaxial areas (figure 4). Their number was larger in cells with a lower ITO thickness.

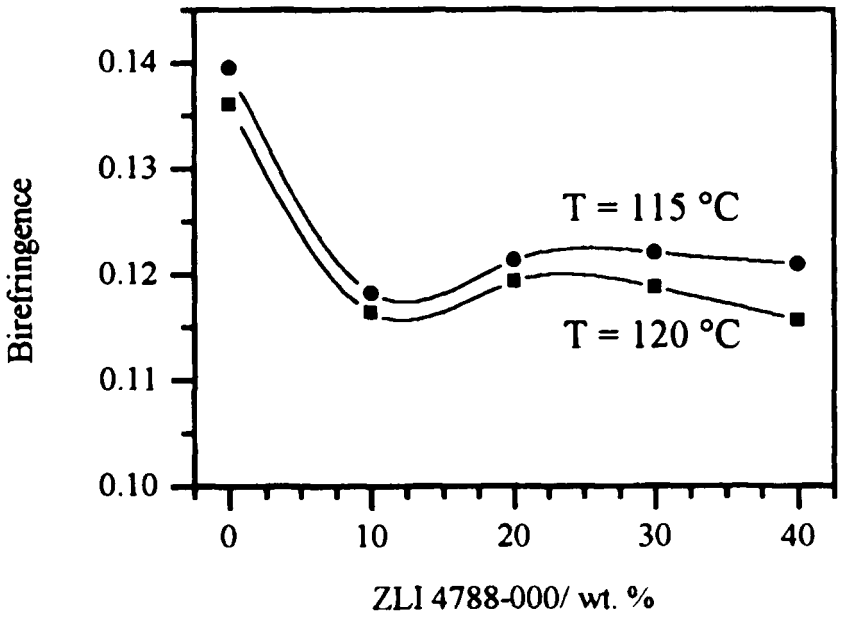

FIGURE 6 Dependence of the sample optical birefringence on ZLI 4788–000 wt. % loading. The polymerization was performed at different temperatures in the nematic range of the mixtures

In order to study the degree of uniaxial orientation of crosslinked mixtures, we measured the optical transmittance between crossed polarizers. It was found that the light intensity is not affected by a rotation of the cells. Figure 5 shows the behavior of such transmittance through samples aligned by different substrates and characterized by increasing ZLI 4788–000 contents. Transmittance between crossed polarizers presents a decreasing behavior as a function of ITO thickness. This means that the homeotropic alignment is kept, after the cross-linkage of liquid crystalline monomer, in a better way by the supports with a higher roughness. In addition, it is evident that the substitution of liquid crystalline monomer with ZLI 4788–000 results in a lower depolarized scattering of light whatever support

is used to prepare sample cells. In our opinion the substitution of C6H with ZLI 4788–000 liquid crystal reduces the molecular disorder induced by the cross-linkage of liquid crystalline monomer. We cannot exclude that a change in the optical anisotropy of mixtures could contribute to the reduction of transmittance when C6H is substituted with ZLI 4788–000. In fact the optical anisotropy of mixtures depends on the ZLI content and the temperature at which the polymerization is performed. Figure 6 shows the behavior of optical birefringence of mixtures polymerized in 5 μm thick cells (Linkam) whose surfaces were treated in order to get a uniform planar alignment.

Our results show that it is possible to obtain homeotropically aligned liquid crystal cells by means of clean (i.e. without any treatment) rough surfaces and to store such alignment if the cross-linkage of the polymerizable component is performed. Such an alignment can be attributed to the typical grooves present in the surfaces and due to the ITO coverage techniques. Such grooves promote an excellent anchoring with an easy axis perpendicular to the glass substrates in order to minimize the excess of elastic free energy. It is evident that a better alignment can be achieved if surfaces with deeper average grooves are used. As a consequence the use of rough surfaces can make easier the production of large area liquid crystal display and light shutters made by liquid crystal-polymer composite.[10]

IV. CONCLUSIONS

We have successfully frozen the homeotropic alignment of nematic mixtures on rough surfaces by means of UV polymerization of the reactive liquid crystalline component. The initial alignment is due to the interactions between the surface jags and the first layer of nematic material. We observed that the degree of order of polymerized films increases for rougher surfaces. The nematic liquid crystal acts as a plasticizer of the cross-linked polymer matrix and determines a reduction of the molecular disorder.

Acknowledgements

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