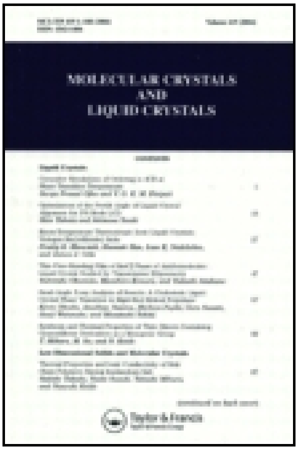

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Alignment Properties of Rubbed Polymer Surfaces

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Alignment Properties of Rubbed Polymer Surfaces†

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The orientation of liquid crystal (LC) molecules on rubbed polymer surfaces, characterized by the tilt bias angle, is found to be determined by the physical and chemical properties of the polymer and liquid crystal material as well as by the coating and rubbing technique used. We compare different rubbing configurations with respect to their rubbing work, the resulting plastic deformation of the surface and the homogeneity of the LC alignment. The coefficient of friction is found to be a function of the rubbing speed and rubbing load. The effect of the rubbing work applied to polymer coated substrates on the tilt bias angle is shown for Polyimide, Polyamide and Polyamide-imide materials. Extremely small tilt bias angles could be realized with bidirectional rubbing or a teflon coated rubbing material, whereas high tilt bias angles (30°) could be achieved by adequate combination of rubbed polymer substrates and surfactants used for homeotropic orientation. On identically treated polymer coated substrates the tilt bias angle increases with the dielectric anisotropy of the liquid crystal material. The experimentally observed increase of the relaxation times with increasing rubbing work is compared to numerical calculations in order to study the effect of tilt bias angle, surface coupling elasticity and surface viscosity on the relaxation.

INTRODUCTION

Although the alignment of liquid crystal (LC) molecules on rubbed polymer surfaces is of vital interest for the industrial realization of display devices, little has been published about the effect of rubbing and material parameters on the resulting LC orientation.[1,2]

The mechanisms effecting the alignment of the molecules are still

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subject to some speculation, but recent experimental results[3,4] stress the difference between the alignment on surfaces with microtopography (e.g. oblique evaporated SiO_x) and molecularly anisotropic, but smooth polymer surfaces.

We have found the orientation of the LC molecules, characterized by the tilt bias angle (TBA), to be determined by (i) the polymer material and coating technique, (ii) the rubbing process, (iii) the rubbing material, (iv) the rubbing configuration and resulting deformation of the polymer and (v) the physical and chemical properties of the LC material.

EXPERIMENTAL

Standard float glass substrates with an SiO_2 diffusion barrier and indium-tin-oxide transparent electrodes are cleaned in an ultrasonic bath with detergents, followed by rinsing in acetone vapour and then dip-coated with three different thermally and chemically stable organic polymer materials as listed in Table I. The concentration of the polymer solutions was 1% by weight.

The polymer solvents were evaporated during curing of the substrates at 120°C and one material (PIQ-13) required three stage curing in order to form a polyimide film from the polyimide precursor. Whereas unrubbed PI and PAI layers did not show any preferred in plane orientation of the LC molecules, the polyamide was anisotropic in the direction of withdrawal from the polymer solution and aligned the LC molecules in that direction even without rubbing. The mechanical aspects of the rubbing process have been studied in the case of the three configurations shown in Figure 1.

Configuration 1 consists of a metal wedge fixed to a balanced bar; the edge is covered with the rubbing material (velour cloth) and drawn over the polymer coated substrate with adjustable constant speed and variable load. The small contact area between rubbing cloth and

TABLE I

Polymer materials used in the experiments

Class	Type	Manufacturer	Solvent
Polyimide (PI)	PIQ-13	Hitachi	NMP
Polyamide-imide (PAI)	AI 1130-L	Amoco	NMP
Polyamide (PA)	Nylon 6/6	Polymer Institute Univ. Karlsruhe	formic acid

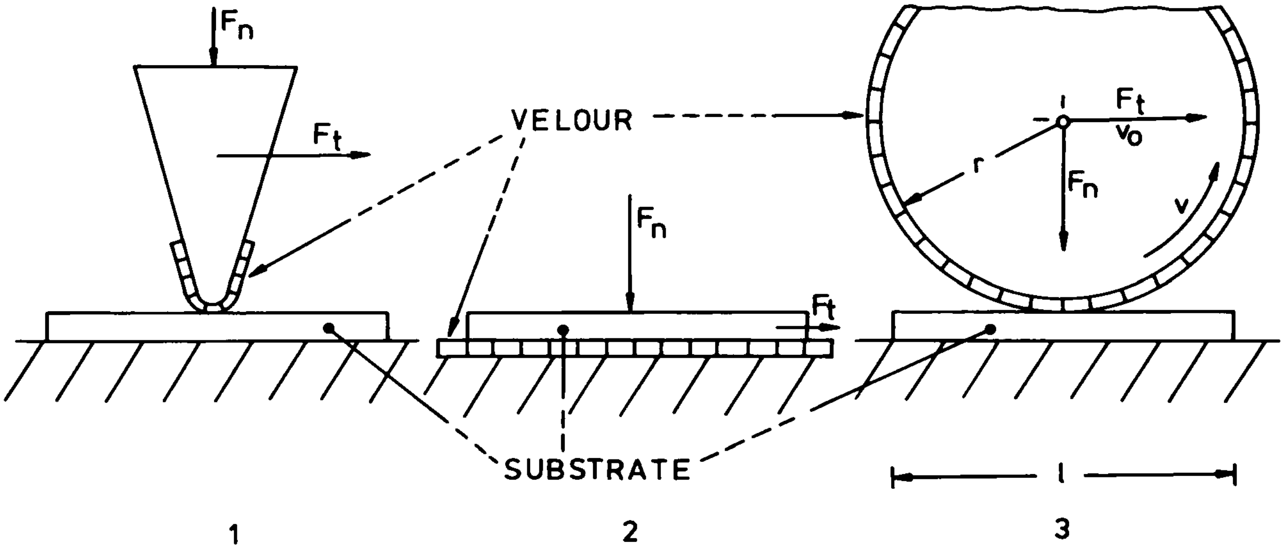

FIGURE 1: Three configurations of rubbing used in the experiments.

1) Wedge covered with the rubbing material (usually velour cloth) and drawn across the substrate. The results given in Table II have been obtained with wedges of different materials without velour cloth. 2) The entire substrate is in contact with the rubbing cloth as it is moved across the velour. 3) Rotating cylinder covered with rubbing cloth and moved across the substrate with adjustable speed of translation v_o and rotation v.

substate results in a high rubbing pressure and effects strong plastic deformations of the polymer layer as observed with a scanning electron microscope (SEM).

Configuration 2 provides a reduced rubbing pressure compared to 1 with the same load applied, since the entire substrate is in contact with the rubbing cloth as the substrate is moved over the velour. The homogeneity of the resulting LC alignment is considerably improved compared to configuration 1.

Configuration 3 consists of a rotating cylinder covered with the rubbing cloth (velour) and is drawn over the coated substrate with adjustable speed of rotation and translation. This configuration covers a wide range of rubbing work and provides excellent homogeneity of alignment as well as reproducibility.

In the rubbing *configuration 3* the rotating cylinder is covered with a mohair velour, whereas in configurations 1 or 2 we use cotton or nylon velour.

The work performed during the translation of the rubbing material relative to the substrate is transformed into plastic deformation and heating of both media in contact. The rubbing work w per unit area of the substrate surface A ($A = l \cdot b$) for the three configurations of Figure 1 is given by:

$$1)\ w = \frac{W}{A} = F_t \cdot \frac{l}{l \cdot b} = F_n \cdot \frac{\mu}{b},$$

$$2)\ w = \frac{W}{A} = F_t \cdot \frac{s}{l \cdot b} = F_n \cdot \frac{\mu \cdot s}{l \cdot b},$$

$$3)\ w = \frac{W}{A} = \frac{M}{r} \cdot \left(\frac{v}{v_o} + 1\right) \cdot \frac{1}{b} \simeq F_t \cdot \frac{v}{b \cdot v_o},$$

with the following parameters

F_t : force tangential to the substrate,

F_n : force applied normal to the substrate,

M : torque of the DC-motor,

l : length of the rubbed substrate,

b : width of the rubbed substrate,

s : translation of the substrate,

μ : coefficient of kinetic friction,

v_o : translational velocity of rubbing cylinder,

v : peripheral velocity of rubbing cylinder.

At a constant value of the rubbing work an increasing contact area between the rubbing cloth and the substrate improves the homogeneity of the LC alignment (see *configurations 1 and 2*).

Whilst in the idealized case, the coefficient of kinetic friction μ is assumed to be independent of the contact area and the rubbing velocity, we found a continous increase of μ with the relative velocity of the substrate and the rubbing cloth in the range of $1.3 \cdot 10^{-3}$ m/s to 7 m/s and a decrease of μ with increasing rubbing load as shown in Figure 2. This dependence of the coefficient of friction on rubbing

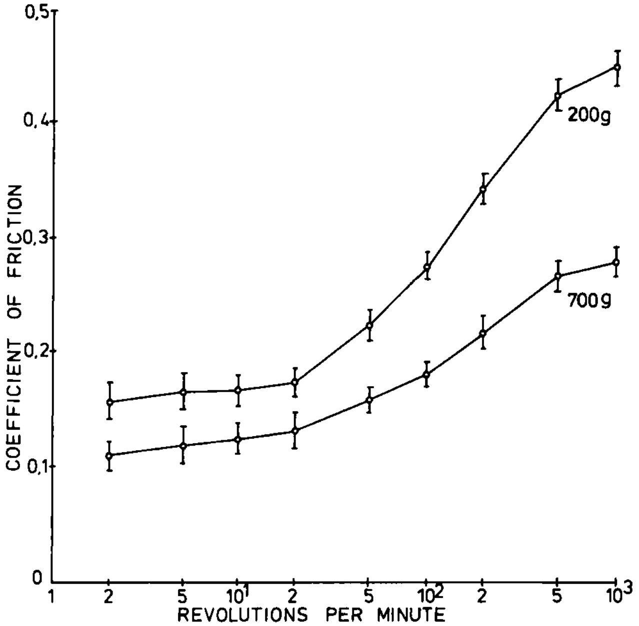

FIGURE 2: Coefficient of kinetic friction as a function of the number of revolutions (*configuration* 3, with the diameter of the rotating cylinder being 12 cm) for two different rubbing loads. Polymer material: PAI, rubbing material: mohair velour.

pressure and velocity indicates the formation of a "liquid" interfacial layer upon rubbing. In order to include these dependencies, we measure the resulting force tangential to the substrate for the evaluation of the rubbing work. This may easily be achieved by monitoring the power consumption of a DC-motor at constant speed of rotation. In *configuration 3*, a relation between the force tangential to the substrate and the electrical parameters of the motor is given by,

$$F_t = \frac{1}{v}\left[(U_1 I_1 - U_o I_o) - R(I_1^2 - I_o^2)\right],$$

where U_o, I_o are the idling voltage and current, U_1, I_1 are the voltage and current during rubbing and R is the resistance of the motor.

A wide range of rubbing work may be covered with this configuration by adjustment of the electrical parameters U_1, I_1 and the ratio of rotational and translational velocity v and v_o. The plastic deformation of the rubbed polymer layer depends on the elastic and thermal properties of both the polymer layer and the rubbing material (cloth) and will not be equal in the general case.

The tilt bias angle (TBA), characterizing the orientation of the LC molecules on the substrate surfaces, is defined as the acute angle between the rubbing direction (translation of the rubbing material with respect to the substrate) and the director at the boundaries. Its measurement is performed with a magneto-optical null method (resolution of 0.1°) in nontwisted cells with a thickness of about 12 μm as described in an earlier paper.[5]

In twisted nematic cells the tilt angle varies throughout the LC layer and exhibits an extreme value in the middle of the cell.[6] Depending on the ratio of the elastic constants K_3/K_2 this extremum will be a maximum (minimum) in the case $K_3/K_2 < 2$ ($K_3/K_2 > 2$) for small values of the TBA. As a consequence, the average tilt angle of TN cells will be different from the TBA measured here.[7]

The nematic phase used in the experiments is ZLI 1132 (Merck) unless otherwise noted and the respective elastic and viscous constants used in the calculations are, according to the results of M. Schadt[8] and P. Gerber,[9] as follows:

$$K_1 = 8.7 \times 10^{-12}\ \mathrm{N},\ K_2 = 9.0 \times 10^{-12}\ \mathrm{N},$$

$$K_3 = 21.0 \times 10^{-12}\ \mathrm{N},\ \gamma_1$$

$$\gamma_1 = 0.188\ \mathrm{Pa \cdot s}, \qquad \text{all values measured at } 22^\circ\mathrm{C}.$$

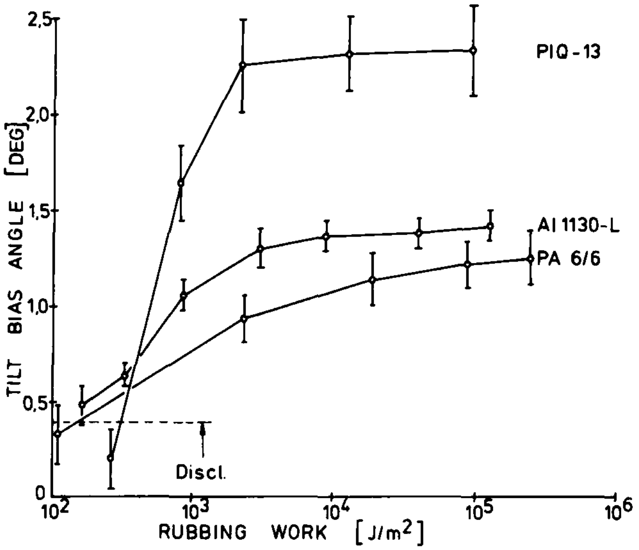

FIGURE 3: Tilt bias angle as a function of the rubbing work (*configuration* 3) for the polymer materials listed in Table I. Rubbing material: mohair velour, liquid crystal material: ZLI 1132 (Merck).

RESULTS

Since we found no significant changes of the TBA for different values of the rotational velocity of the rubbing cylinder in the range of 10 to 500 RPM, all further experiments have been carried out at 100 RPM.

Figure 3 shows the TBA as a function of the rubbing work (*configuration 3*) for the three polymer materials listed in Table I. At low rubbing work, the alignment on all polymers is accompanied by disclinations which disappear with increasing rubbing work. The TBA increases with the rubbing work, until different values of saturation are reached for each material. The effect of different rubbing materials was tested with *configuration 1* using aluminium, PMMA, PAI and teflon as wedge and rubbing materials (without velour) as shown in Table II. We found considerable differences of the TBA and homogeneity of orientation under the condition of constant rubbing load for these materials.

Good uniformity of orientation at a TBA of 0.3° has been achieved with the teflon wedge. In order to combine such a low TBA, which is desirable for a steep electro-optical response in TN cells, with a good homogeneity of alignment, the velour fabric on the rubbing

TABLE II

Tilt bias angles on PAI for various rubbing materials (= wedge materials) as determined using rubbing *configuration 1*

Wedge material	Aluminium	PMMA	PAI	Teflon
TBA	1.3°	0.8°	0.7°	0.3°

cylinder was spray-coated with teflon. The resulting TBA as a function of the rubbing work is shown in Figure 4. In contrast to the curves in Figure 3 the TBA now decreases with increasing rubbing work, but even at small values (0.2°) the orientation of the molecules is free of disclinations and homogeneous over the cell surface. The alignment in this case is influenced by teflon material transferred from the fibers to the polymer layer and visible as stringlike deposits on the polymer surface in SEM observations.

A further method for the realization of small TBAs is the appli-

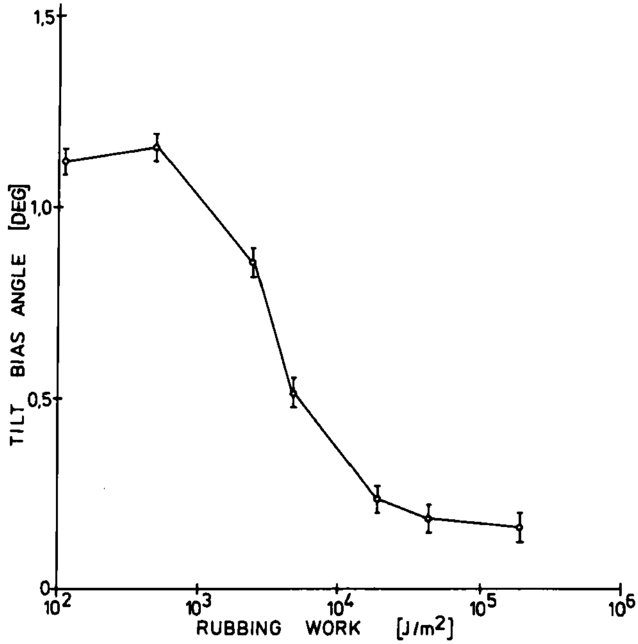

FIGURE 4: Tilt bias angle as a function of the rubbing work (*configuration* 3) for a PAI layer rubbed with teflon coated mohair velour. Liquid crystal material: ZLI 1132 (Merck).

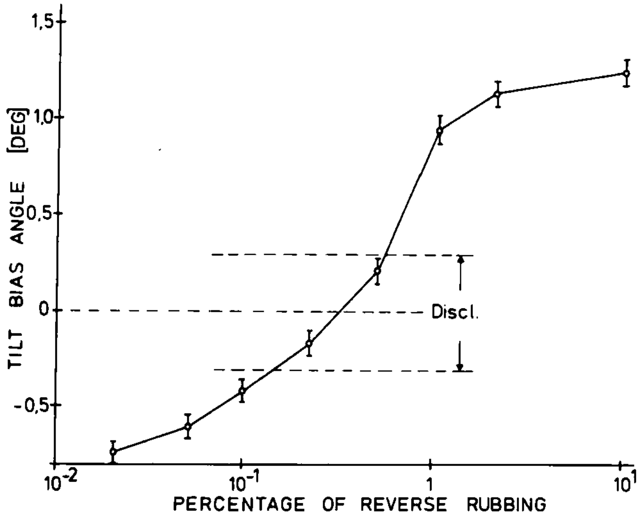

FIGURE 5: Tilt bias angle as a function of the reverse rubbing work (percentage of the bias rubbing work) for a PAI layer rubbed with mohair velour (*configuration* 3), liquid crystal material: ZLI 1132 (Merck).

cation of bidirectional rubbing, where the first "bias" rubbing is followed by a second rubbing in the opposite direction. This reverse rubbing lowers the value of the TBA until it changes sign and reaches saturation with increasing rubbing work as shown in Figure 5. The saturation value is slightly lower than the maximum value in the respective case of unidirectional rubbing.

Several bistability effects as described by Berreman and Heffner,[10] Thurston,[11] Scheffer[12] and others require high TBAs in the range of 20° to 40°. Such values of the TBA have been realized with adequate combinations of rubbed polymer surfaces and surfactants normally used for homeotropic orientation. The value of the TBA may be adjusted by the nature and the concentration of the surfactant, choice of rubbing parameters and the sequences of coating with surfactant and rubbing.

On rubbed PAI layers with identical treatment and rubbing work the TBA increases from 0.6° to 1.6° with increasing dielectric anisotropy of the LC materials shown in Figure 6. This effect is due to the interactions between permanent and induced electric dipole moments in the LC molecules and the dielectric anisotropy of the polymer layer.

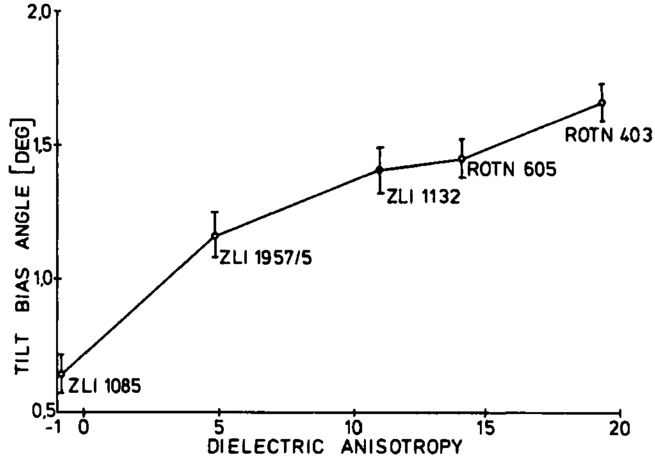

FIGURE 6: Tilt bias angle as a function of the dielectric anisotropy of the liquid crystal materials listed. ROTN: liquid crystal materials by Hoffmann-la Roche. ZLI: liquid crystal materials by Merck. Polymer material: PAI, rubbing material: mohair velour and the rubbing work was 10^4 J/m^2. Dielectric anisotropies of the LC materials according to data sheets of the manufacturers: ZLI 1085 = −0.9, ZLI 1957/5 = +4.5, ZLI 1132 = +10.3, ROTN 605 = +13.2 and ROTN 403 = +19.2.

Relaxation experiments

With the relaxation time T defined as the time difference between normalized birefringences of 50% and 90% (as shown in Figure 7), an increase of the relaxation time of 9.3% has been observed for a change of rubbing work from 10^3 J/m^2 to 3.6×10^5 J/m^2 with corresponding TBAs of 1.05° and 1.45° respectively. The effect of this

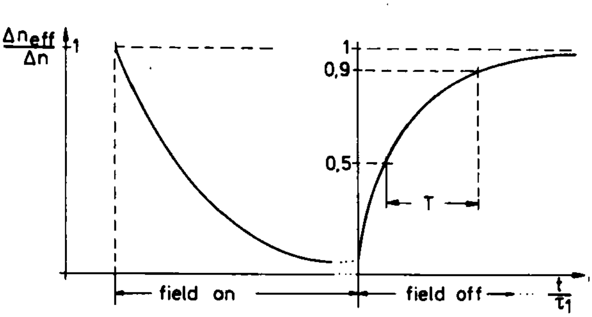

FIGURE 7: Definition of the relaxation time T: After a field induced deformation corresponding to a normalized birefringence of 0.12 the field is switched off and T is the time difference between a normalized birefringence of 50% and 90% in units of τ_1.

TABLE III

Relaxation times as a function of increasing surface time constant (at constant bulk time constant) for $\lambda = 0.01$

τ_o / τ_1	1	10	100
$(T / T_o) - 1$	1.5%	2.2%	18.8%

difference of TBAs on the relaxation times was shown to be negligible by numerical calculations of the relaxation.[13] In order to explain these observations we assumed an elastic coupling of the LC molecules on the substrate surfaces with a value of the normalized coefficient of coupling $\lambda = \pi \cdot K_1/(C \cdot d) = 0.01$ corresponding to an anisotropic surface energy C of about 2×10^{-5} J/m^2 for a cell spacing of d = 13 μm. In the mathematical model of the relaxation an elastic boundary coupling requires the introduction of a surface viscosity γ_o which is dimensionally different from the bulk viscosity γ_1.[14] The time constant of surface relaxation is defined by

$$\tau_o = (\gamma_o \cdot d)/K_1$$

and the time constant of bulk relaxation by

$$\tau_1 = (\gamma_1 \cdot d^2)/K_1.$$

Raising this surface time constant with respect to the bulk time constant results in increased relaxation times as observed in the experiments. The tendency of the increase of relaxation times with increasing ratio of surface to bulk time constant is shown in Table III. The first value of 1.5% represents the effect of an elastic boundary coupling compared to the case of rigid anchoring (i.e. $\lambda = 0$). Raising the elasticity of the surface coupling (increasing λ) also effects increasing relaxation times as shown in Table IV for the case of identical surface and bulk time constants.

TABLE IV

Relaxation times as a function of increasing surface coupling elasticity for equal surface- and bulk time constants

λ	0	0.01	0.05	0.1
$(T / T_o) - 1$	0	1.5%	9.9%	28.3%

DISCUSSION

The observed dependence of the coefficient of kinetic friction μ on rubbing pressure and velocity (see Figure 2) and the formation of a "liquid" interfacial layer may be explained by the model of Adamson[15] which was applied to the rubbing of substrates for LC alignment purposes by Castellano.[2] According to this model the action of rubbing causes a very high local heating resulting in the melting of the material with the lower melting point or both if their melting temperatures are close to each other. The rubbing forces tangential to this layer will align the polymer chains in the direction of rubbing as may be concluded from birefringence measurements.

If hard materials like glass, tin-indium-oxide or SiO_2 are rubbed with soft materials (cotton or nylon cloth) the action of rubbing will melt the rubbing material and a certain amount of highly stretched (anisotropic) deposits will stick to the hard surface. The case of ITO rubbed with a cloth (of undefined material) has been studied by Nakamura[1] who concluded from Auger spectroscopy data that the stringlike structures visible on the ITO surface represent wear of the rubbing material.

The alignment properties of stretched polymer films (adhesive tape, stretched PVA films) or carefully rubbed PAI layers on which no surface topography could be observed with SEM lead to the conclusion that the existence of surface structures (assymmetric and anisotropic deposits or grooves) is not necessary for the alignment of LC molecules but is sometimes hard to avoid. SEM observations of PAI surfaces carefully rubbed with nylon velour (*configuration 2*) reveal smooth surfaces with the exception of several scratches caused by dust particles. Increasing the rubbing work results in the generation of assymmetric, scale-like structures (the crosscut exhibiting a gentle rise and an abrupt decrease), similiar to the observations of Nakamura,[1] and their surface density and size increase with increasing rubbing work. These changes of the surface topography may cause the increase of the TBA with the rubbing work and its final value of saturation is determined by the plastic and thermal properties of the polymer materials.

Quite different structures have been observed on PAI surfaces rubbed with teflon coated fibers: the number of scratches is considerably reduced as well as the smoothness of the areas between the scratches, but the stringlike structures on the surface (deposits of teflon) are much more symmetric in the direction of rubbing. This difference of the surface topography effects the decrease of the resulting TBA.

The use of wedge materials of different hardness, in *configuration 1* at the same rubbing load, yields increasing TBAs with increasing hardness of the rubbing material caused by different anisotropies of the surface structures.

The experiments of bidirectional rubbing provide further evidence for the importance of the surface structures determining the direction and the value of the TBA: once the bias rubbing is applied to yield good in plane alignment of the LC molecules, only a small percentage of the bias rubbing is necessary to reverse the sign of the TBA, indicating that this second rubbing just changes the upper (structured) part of the layer.

Since numerical calculations show the tendency of decreasing relaxation times with increasing coupling strength (compare with Ref. 14), we measured the relaxation times for different values of the rubbing work, in order to obtain information on the respective variation of the coupling strength.

The measured increase of birefringence of the polymer layers with increasing rubbing work was expected to cause decreasing relaxation times, but the experiments yield just the opposite trends. As shown by the numerical calculations, this may be explained either by a reduced surface coupling strength or by an enhanced surface viscosity. The variation of both of these with the rubbing work may be connected with the surface structures (roughness) generated by strong rubbing of the polymer layer.

These results suggest that in the process of manufacturing TN cells the rubbing work applied to the polymer coated surfaces should be just high enough to avoid the formation of disclinations thereby ensuring low values of the TBA and low relaxation times.

SUMMARY

The introduction of the rubbing work applied to the polymer surface seems to be a reasonable choice as parameter describing the induced plastic deformation. The tilt bias angle may be adjusted by adequate combinations of liquid crystal and polymer material, rubbing material and rubbing work. The tilt bias angle is affected by the dielectric anisotropy of the liquid crystal material. A reduction of the tilt bias angle with a fixed combination of liquid crystal and polymer material is possible by the application of bidirectional rubbing or by the use of teflon coated fibers as rubbing material. An increase of the tilt bias angle is given by combinations of rubbed polymer surfaces and homeotropic surfactants.

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