Mol. Cryst. Liq. Cryst., Vol. 438, pp. 195/[1759]–204/[1768], 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590958151

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The Interfacial Dipole-to-Dipole Interaction as a Factor of Polar Anchoring in the Cells with Planar Liquid Crystal Alignment

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The frequency of dipole relaxation of liquid crystal (LC) layer at LC- solid interface, f_r, is shown to be in full correlation with the polar anchoring energy W_p; the increase of W_p is accompanied with the decrease of f_r. This correlation is established by the use of the aligning polyimide layers treated with different methods. The anchoring energy increases and the relaxation frequency decreases in the following sequence of processes: rubbing–photoalignment–plasma beam alignment. The correlation between W_p and f_r is an evidence of strong contribution of dipole-to-dipole interaction at the LC-substrate interface to polar anchoring of LC. Based on this correlation new method of polar anchoring measurement can be developed.

1. INTRODUCTION

In phenomenological theory of liquid crystals (LC) the interaction of LC with the boundary substrates is described by surface energy (surface tension) γ. The anisotropic part of γ, F_s, is usually considered in Rapini and Papoular approximation form,

$$F_s = -\frac{1}{2}W(\vec{n}\vec{n}_l)^2$$

where $\vec{n}_l$ is the "easy" axis corresponding to direction of LC director $\vec{n}$ in the absence of all other external fields (i.e., direction in which F_s

These studies are supported by INTAS foundation (grant 03–51–5448) and, in part, by the National Academy of Sciences of Ukraine (project "Ordering regularities and properties of nano-composite systems"). Authors thank O. Lavrentovich and Yu. Nastishin for advising on polar anchoring measurement.

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minimizes), and W is an anchoring coefficient [1]. W has dimension of energy and physically can be interpreted as energy per unit area needed to deviate LC director from the easy direction $\vec{n}_l$. Considering in-plane and out-of-plane deviations (with regard to the plane of aligning substrate) one can select azimuthal and polar anchoring coefficients, W_a and W_p. These anchoring parameters determine director field in the cell, as well as their electro- and magneto-optics performance [2], anchoring transitions [3] and many other effects.

From microscopic point of view, the anchoring energy is an integral parameter determined by many forces acting at the LC interface. The dispersive and elastic anisotropic interactions at the LC – substrate interface are most frequently discussed as the major contributors to the azimuthal anchoring [4–6]. The surface memory caused by adhesion of LC molecules on the boundary substrates may be also a factor of azimuthal anchoring, especially in case of low W_a [7]. The factors of polar anchoring are studied poorer, because of big variety and strong specificity of LC – substrate interactions, that makes identification of a specific mechanism rather difficult. The common factor, which considerably affects W_p, is electrical charging of the aligning layers due to selective adsorption of ions from the LC bulk. The adsorbed ions and the diffuse layer oppositely charged constitute an intrinsic double layer depending only on the aligning material and LC. The thickness of this double layer is comparable with the Debye screening length λ_D. Within double layers arises surface electric field $\vec{E}_s$, which changes surface energy, including anisotropic term F_s:

$$F_s = -\frac{1}{2}\left[W(\vec{n}\vec{n}_t)^2 + \frac{1}{2}\varepsilon_a \lambda_D (\vec{n}\vec{E}_s)^2\right] \tag{2}$$

where ε_a is dielectric anisotropy. Expression (2) shows that coupling of $\vec{E}_s$ with dielectric anisotropy gives the rise to F_s renormalizing finite anchoring energy [8–11].

In the present work we pay attention to the specific microscopic mechanism of the electric origin, which might contribute to LC anchoring in the cells containing LC with $\varepsilon_a >> 0$ planarly aligned. The condition $\varepsilon_a >> 0$ means that LC molecules possess strong dipole moment along the molecule's axis. In the bulk these molecules are usually dimerized with an antiparallel dipole orientation in the dimers [12]. In this case summary dipole moment of LC bulk is zero. In contrast to bulk, the dimerization process is weak at the interface so that boundary LC layer possesses uncompensated dipole moment revealed in a number of studies [13–14]. The reasons of this surface polarization may be adhesion and self-assembling of LC molecules on the solid substrate, as well as their poling in the field $\vec{E}_s$ created by double electric layers. The relaxation of the uncompensated dipole moment of LC at the substrates may explain new relaxation process described in References [15,16] preceding, if one moves to deeper frequencies, the relaxation caused by a charge transfer through the LC-electrode boundary [17,18]. This relaxation occurring in the frequency range $f_r = 1$–$20\,\text{Hz}$ is observed only in the planarly aligned layers of LC with $\varepsilon_a >> 0$. There are several reasons to believe that relaxation frequency of the described process f_r is substantially influenced by the solid-LC interaction. The interaction of dipole molecules with charged substrate reduces their ability to reorient in phase with the alteration of the applied electric field. Thus the stronger is the interfacial interaction, the lower relaxation frequency should be observed. This dipole relaxation can be pronounces only if uncompensated dipole of LC boundary layer is considerably high, which, in turn, can be achieved for strong interaction at the interface.

The described interaction of LC dipoles with the aligning substrate may be important mechanism of polar anchoring in the planarly aligned LC layers with substantial $\varepsilon_a > 0$. On the other hand, since dipole relaxation is influenced by the interfacial interaction, the characteristic frequency of this process might be considered as a measure of polar anchoring strength. To demonstrate this, we carry out comparative studies of polar anchoring energy and the frequency of dipole relaxation at the substrates treated with different methods. As we revealed, both W_p and f_r are sensitive to the treatment of the aligning substrates. In consent with explanations above, the observed increase of W_p is accompanied with the decrease of f_r. The dependence of LC-solid interaction on the alignment treatment of solid substrates is discussed.

2. EXPERIMENTAL

2.1. Samples

The cells were made of ITO coated glass slides with the size of $3 \times 2\,\text{cm}^2$. To prevent any cell edge effects, ITO coating was removed from the edges of the slides used for cell gluing. The slides were cleaned and coated with polyimide (PI) 2555 from Dupont. The choice of this PI was stipulated by its use in LC photoalignment [19]. In our experiments, the following alignment treatments procedures were applied:

1. Rubbing. The PI coatings were manually rubbed by means of slide translation on the plate covered by velvet cloth. The translation

direction was about 10 cm. After rubbing, the slides were blown by a pressed air.

2. Photoalignment. The substrates were irradiated with a UV light from mercury lamp (500 W). The irradiation consisted of two steps; the substrates were irradiated normally with a polarized light (50 mW/cm^2, 30 min) and then obliquely with a non-polarized light (100 mW/cm^2). On the second stage, used to break two-fold degeneracy of pretilt angle, the incidence angle of UV light (accounted from the substrate's normal) was about 45°.
3. Plasma beam alignment. The substrates were obliquely (incidence angle of about 60°) treated with a beam of accelerated Ar plasma generated by anode layer thruster. The details of this procedure can be found in our recent publications [20–21].

The substrates were pressed and glued by an epoxy adhesive. The cell gap 10 μm was maintained with spacer balls. The cells were filled with nematic LC 5CB from Merck. The time period between the alignment treatment and LC filling was about 2 h. The pretilt angle of 5CB measured by crystal rotation method was close to zero in case of UV light and plasma beam treatment and about 2° in case of rubbing.

2.2. Methods

The *dielectric measurements* were carried out in a frequency range 10^{-1}–10^6 Hz by the use of oscilloscope method [22,23]. The measured signal was delta shaped with a maximum value of 0.25 V. All measurements were carried out at 293 K. We defined capacity C and resistance R of samples by analysis of the oscillogram obtained. The C and R data allows us to calculated real ε' and imaginary ε'' parts of dielectric permittivity. In these calculations, the electrical field along the thickness of the sample was considered as homogeneous.

The method was applied in several stages. On the first stage we estimated frequency dependencies of ε' and ε'' for the cells stored about 8 h after filling. In the following measurements, to ensure, equilibrium state of LC cell after filling [24,25], the kinetic of sample conductivity was measured. In these measurements, the frequency of the applied voltage was fixed at the value well beyond the relaxation range and ε'' (proportional to sample conductivity, σ) was measured as a function of time passed after the sample filling. The $\sigma(t)$ curves obtained were fitted with a function

$$\sigma = \Delta\sigma \exp(-t/\tau_\sigma) + \sigma_\infty \qquad (3)$$

The relaxation time τ_σ obtained was in a range of 3–5 h. This shows that relaxation process caused by ion redistribution within the cell was completed before the measurement of $\varepsilon'(f)$ and $\varepsilon''(f)$ curves.

For the *measurements of polar anchoring energy* we used the retardation versus voltage $(\Phi - \mathrm{V})$ method and corresponding protocol proposed by Nastishin et all [26]. In contrast to classic Yokoyama and van Sprang (YvS) technique [27] based on simultaneous measurement of the capacitance and optical phase, $(\Phi - \mathrm{V})$ method uses only retardation of a nematic cell as a function of applied voltage. This technique allows to measure $\mathrm{W_p}$ in cells with tilted easy axis. Basic equation of $(\Phi - \mathrm{V})$ technique is

$$\frac{\Phi(V-\bar{V})}{\Phi_0} = \tilde{J}_0 - \frac{2K_1}{Wd}(1 + k\sin^2\theta)(V-\bar{V}) \tag{4}$$

where $\bar{V} = \alpha\frac{\varepsilon_a}{\varepsilon_{par}}V_{th}$, $V_{th} = \pi\sqrt{\frac{K_1}{\varepsilon_0\varepsilon_a}}$, $k = \frac{K_3-K_1}{K_1}$, α is a coefficient in the range $(2/\pi, 1), \Phi_0$ is the retardation under no external field, $\tilde{J}_0$ is a constant, $\mathrm{K_1}$ and $\mathrm{K_3}$ is the splay and bend elastic constant of LC, d is the cell gap, θ is the pretilt angle, ε_{par} and ε_{par} are the components of the dielectric tensor that are parallel and perpendicular to the director. In the defined voltage range $(\mathrm{V_{min}}, \mathrm{V_{max}})$ expression (4) can be approximated by linear function $Y = A - BX$. The linear fit yields A and B. The value of $\mathrm{W_p}$ can be estimated from B using known material parameters of 5CB ($\mathrm{K_1} = 6.6510^{-12}$ N and $\mathrm{K_3} = 8.9510^{-12}$ N; $\varepsilon_{par} = 19.5$ and $\varepsilon_{par} = 8.0$). The error of $\mathrm{W_p}$ estimation did not exceed 40%.

3. RESULTS AND DISCUSSION

Figure 1 shows typical $\varepsilon'(f)$ and $\varepsilon''(f)$ curves we obtained. The relaxation corresponding to surface polarization, which is distinctly shown in the offset of Figure 1, is localized in the range 10°–10^{2} Hz. From the side of lower frequencies, it neighbors with the relaxation concerned with a charge transport from LC to electrode. From the side of higher frequencies, it adjoins the relaxation range 10^{5}–10^{6} Hz caused by rotational relaxation of LC molecules along the short molecular axis [2]. The frequencies of dipole relaxation obtained for different kinds of substrates are summarized in Table 1. As one can conclude, any surface treatment procedure reduces this frequency. The treatment effect strengthens in the sequence rubbing–photoalignment–plasma beam alignment.

Figure 2 shows relaxation of sample conductivity after LC filling caused by ion adsorption onto the aligning substrates. This curve corresponds to the cell based on rubbed PI substrates; however, it is

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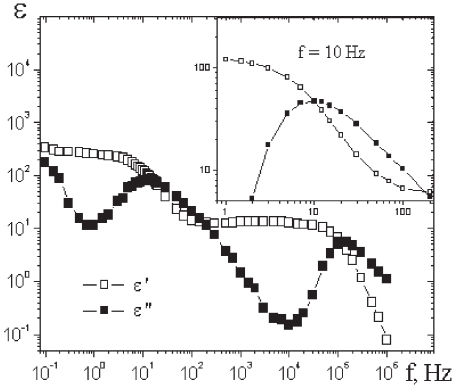

FIGURE 1 The frequency dependencies of real ε' and imaginary ε'' parts of dielectric permittivity for 5CB layer aligned on rubbed PI substrates.

typical for all samples. It is fitted well with the formula (3). The relaxation time of conductivity, τ_σ, is varied within 15–30 min for different samples and poorly depends on alignment treatment. The other two fitting constants $\Delta\sigma$ and σ_∞ are in the range $\Delta\sigma = (1\text{–}3)\,10^{-7}\ \text{A/cm}^2$ and $\sigma_\infty = (3-5)10^{-7}\,\text{A/cm}^2$. The value of $\Delta\sigma$ can be used to obtain surface concentration of the adsorbed ions following the formula [24]:

$$n_s = \frac{\Delta\sigma d}{e\mu}, \tag{5}$$

where e is an electron charge, μ is ion mobility, d is a thickness of LC layer. In our calculations we used the value $\mu = 8\,10^{-11}\,\text{m}^2/\text{Vs}$ obtained from References [28]. The averaged values of n_s estimated for different treatment procedures are presented in Table 1. The accuracy of n_s is about 30%. One can see that amount of free charges adsorbed from LC onto aligning substrates is quite similar for different alignment treatments; the difference in n_s does not exceed 1.5 times and so is practically within the accuracy of measurement. This

TABLE 1 The values of surface concentration of ions n_s, relaxation frequency f_r and anchoring energy $\mathrm{W_p}$ obtained for different alignment procedures

Aligning material	Aligning method	n_s, $10^{17}\,\text{m}^{-2}$	f_r, Hz	W_p, $10^{-4}\,\text{J/m}^2$
PI2555(Dupont)	No treatment	0.72	15	–
	Rubbing	1.14	12	0.9
	Photoalignment	0.82	10	1.23
	Plasma alignment	1.06	3	2.95

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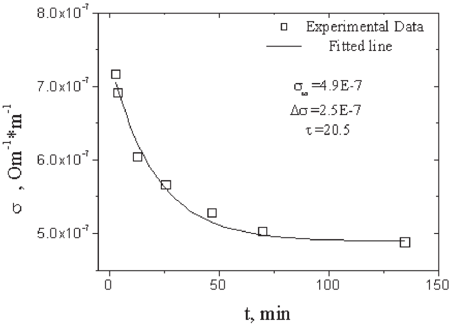

FIGURE 2 Measured (symbols) and fitted (line) dependencies of dielectric conductivity σ of LC cell based on rubbed PI substrates on the time passed after the sample filling with LC 5CB.

result looks strange if we assume that different procedures generate different amount of charges on the aligning substrates. If this assumption is true, the substrates of different treatment should attract LC ions with different intensity. The discrepancy of this expectation with experimental results can be explained by low concentration of charges generated on the substrates and/or by the processes of their recombination in air. One more sophisticated model assumes that LC ions are surrounded with the polarized LC molecules forming solvate covering and so ions adsorb on the substrates together with these solvates [16]. The latter process of adsorption should be much less sensitive to the surface charging as the adsorption of pure ions. It is necessary to mark that detection of charges generated on the aligning substrates and comparison of their concentration for different methods of alignment was not a subject of the present work. The study of this problem requires the methods more sensitive to surface charging. Such methods as Kelvin probe technique [24] and electron paramagnetic resonance [29] are recently used for this purpose.

The typical Φ-V curve experimentally measured and the fitting line are shown in Figure 3. The W_p values for the substrates differently treated are summarized in Table 1. The presented ranges of values embrace the W_p values obtained for at least 5 cells equally treated. The difference in the values of W_p corresponding to different alignment processes is less then one order of magnitude; commonly, 1.5–4 times. Nevertheless, this difference is out of accuracy of the method.

One can conclude from Table 1 that W_p increases in the sequence rubbing–photoalignment–plasma beam alignment. The difference in W_p for rubbed and photoaligned substrates is not so big (1.5 times).

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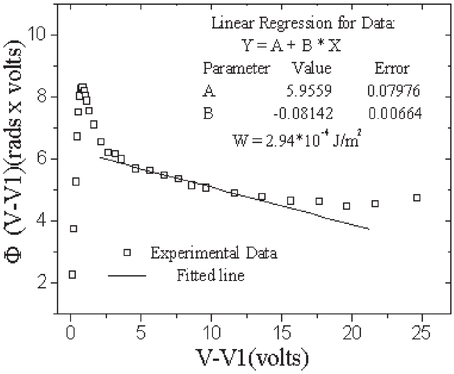

FIGURE 3 $\Phi(V-\bar{V})$ vs $(V-\bar{V})$ curve for the 10 μm cell with plasma beam treated polyimide alignment layers.

However, it is substantial (3 times), if rubbed and plasma treated substrates are compared. Our estimate for rubbed substrates is close to that one obtained in Reference [26]. The increase of W_p under UV irradiation is in good agreement with results of Reference [30] and our previous estimations[31].

Let us discuss now electric mechanisms of polar anchoring mentioned above. According to sample's conductivity measurements, the amount of *free charges* adsorbed from LC bulk onto aligning substrates is pretty much the same for the substrates of different treatment. This implies that surface field mechanism (described by second term in expression (2)) proposed by Barbero and Durand [8–11] is practically independent of treatment procedure. As we believe, the observed difference in W_p is caused by interfacial interaction of *constrained charges*. Indeed, any alignment treatment influences orientational ordering of the polymer chains (at least in the very top layers of the aligning films), which can be accompanied by surface polarization. This polarization in case of rubbing and photoalignment was really confirmed by second harmonic generation [32]. As we mentioned in Introduction, boundary layers of LC are also polarized. For this reason, dipole-to-dipole interaction at the LC-substrate interface can be quite strong, as it is clearly evident in the dielectric relaxation. Logically, this interaction can bring substantial contribution to the polar anchoring. The enhanced anchoring in case of plasma treated substrates can be caused by the particular feature of this procedure; plasma action removes top layer of the aligning film containing ion impurities adsorbed from air, which may screen charges on the polymer surface and so reduce dipole-to-dipole interaction of LC with the substrate.

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CONCLUSIONS

We conducted comparative studies of polar anchoring energy on the substrates treated by different alignment methods. According to results obtained W_p increases in the sequence rubbing–photoalignment–plasma beam alignment. The observed difference in W_p may be caused by different dipole-to-dipole interaction at LC – substrate interface, which might substantially contribute to W_p in case of LC with $\varepsilon_a >> 0$. This interaction is clearly detected in dielectric measurements as a new relaxation process. The frequency of this relaxation is also sensitive to alignment treatment and can be considered as a measure of polar anchoring energy. In contrast to optic methods requiring good LC alignment, dielectric method can be also applied to the samples with no alignment, for instance, to estimate anchoring on the untreated substrates.

Of course we fully realize the fact that we compare now alignment parameters for different alignment procedures without variation of treatment conditions within the same procedure. For instance, anchoring coefficient W_p should depend on rubbing strength or irradiation dose [30,31]. Moreover, the results should be rather sensitive to exposure time of the treated samples to the air [25]. These problems are beyond the scope of present work and will be treated in the future studies.

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