Reprinted from

JAPANESE JOURNAL OF
APPLIED
PHYSICS

RAPID COMMUNICATION

Perfluoropolymer as Planar Alignment Layer for Liquid Crystal Mixtures

Tatipamula Arun Kumar, Hideo Takezoe, and Surajit Dhara

Jpn. J. Appl. Phys. **50** (2011) 040203

Japanese Journal of Applied Physics **50** (2011) 040203 **RAPID COMMUNICATION**
DOI: 10.1143/JJAP.50.040203

Perfluoropolymer as Planar Alignment Layer for Liquid Crystal Mixtures

Tatipamula Arun Kumar, Hideo Takezoe[1], and Surajit Dhara*

School of Physics, University of Hyderabad, Hyderabad 500046, India
[1]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan*

Received October 29, 2010; accepted January 20, 2011; published online April 5, 2011

We report a perfluoropolymer (CYTOP) provides planar alignment to liquid crystal mixtures (e.g., ZLI-2293) that are used in display. We found that the anchoring energy of ZLI-2293 on CYTOP is almost eighteen times less and the pretilt angle is slightly larger than on AL-1254. It is expected that the low surface anchoring and high transmission in CYTOP cell will make CYTOP a suitable aligning agent for LC displays as well as many other LC devices. © 2011 The Japan Society of Applied Physics

The molecular alignment of liquid crystals (LCs) on the treated surfaces of solid substrates is of great importance for the basic understanding of the interfacial phenomena as well as technological applications.[1)] The bulk LC and the interfacial properties strongly influence the electro-optic properties of liquid crystal displays (LCDs).[2,3)] It is well known that weak anchoring of the LC director at the interface with alignment layer can in principle reduce the operating voltages and can improve the steepness of the electro-optic response of LCDs.[4)] For the performance of multistable optical switching, weak anchoring is also desirable. Fast response times less than several hundreds of microseconds are desired for high performance LCDs. The main objective of this work is to show that a perfluoropolymer (CYTOP) which is commonly used as an antireflection coating in organic light emitting devices provides good planar alignment to a liquid crystal mixture (ZLI-2293). We measured some surface and bulk physical properties like anchoring energy, pretilt angle and rotational viscosity at room temperature and compared with results using another alignment layer AL-1254.

The nematic mixture ZLI-2293 was obtained from Merck. We used amorphous perfluoropolymer poly[perfluoro-(4-vinyloxy-1-butene)] (PPFVB, commercially known as CYTOP). It has been used widely for antireflective coatings and optical fibers because of its low refractive index (1.34) and high transmittance over a wide wavelength range (200 nm to 2 μm).[5,6)] High solubility in fluorinated solvent makes it suitable for easy coating on substrate for various applications in photonics such as nanoimprint lithography (NIL), organic light-emitting diodes (OLEDs[7,8)]), lasing, and in biological applications.[9)] Very recently we reported several interesting physical phenomena related to anchoring transition[10,11)] in nematic liquid crystals and also demonstrated bistability in dye-doped samples.[12,13)] In case of smectics it was shown to provide a shock-free homeotropic alignment.[14)]

The glass plates with indium–tin-oxide (ITO) were spin-coated with polyimide AL-1254 or perfluoropolymer (CYTOP), and were cured at 180 and 100 °C for 1 h or 30 min, respectively. After curing, the plates were rubbed by using a homemade rubbing machine in which commercially available soft velvet cloth with long fibres was used. The plates are assembled such that the rubbing directions were set antiparallel. The rubbing strength were kept fixed for all the plates by adjusting the distance between the plate and the roller. Milar spacers and glass beads were used to make thick (~100 μm) and thin (~10 μm) cells. The thickness of the cell is measured using fiber optic specrometer (Ocean Optic). The cell of thickness ~10 μm was used for measuring anchoring energy and rotational viscosity. Cells of thicknesses in the ranges 100 to 150 μm were used for measuring pretilt angle. The sample was injected into the empty cell through the capillary action in the nematic phase at room temperature.

We adopted the crystal rotation method (CRM)[15)] to measure the pretilt angle. The transmitted intensity was measured with photodiode as a function of the incidence angle from −45 to +45° about the axis perpendicular to the light beam and the rubbing direction. The transmitted intensity was fitted to the theoretical equation.[15)]

In order to measure anchoring energy we adopted a high field technique proposed by Yokoyama and Sprang.[16)] A computer controlled setup was used to measure the optical retardation (R) and sample capacitance (C) simultaneously. A He–Ne laser of wavelength 632.8 nm was used as source for optical measurements and the cell is placed between two crossed Glan Thampson polarizers. A photoelastic modulator (PEM-100) was used to measure the retardation very accurately. The temperature of the cell was maintained by a Instec (mK 1000) temperature controller. A LCR meter (Agilent E4980A) was used to measure the cell capacitance as a function of voltage. The transmitted light intensity I was measured using a photodiode. The anchoring strength (W) is estimated from the following equation:[16,19)]

$$\frac{R}{R_0} = \frac{\xi I(\gamma, \kappa, \nu)}{CV} - \frac{2K_{11}}{Wd}, \quad (1)$$

where R_0 is the retardation at $V = 0$ and R/R_0 is the normalized phase retardation. The parameters γ, κ, and ν are related to dielectric constants, elastic constants and refractive indices respectively. Hence $I(\gamma, \kappa, \nu)$ depends on the material parameters. Here, ξ is a constant dependent on the geometrical factor of the cell (the area and the thickness). K_{11} and d are the splay elastic constant and thickness of the sample respectively. W can be determined from the intercept of the plot R/R_0 as a function of $1/CV$, provided that K_{11} and d are known.

To measure rotational viscosity (γ_1) we adopted relaxation method.[17)] We measured the transmitted light intensity through a planar aligned LC cell, to obtain the optical phase as a function of time. The phase change $\delta(t)$ as a function of time t was measured from the time dependent intensity, $I(t)$, using the following equation: $I(t) = I_0 \sin^2[(\Delta_{tot} - \delta(t))/2]$,

*E-mail address: sdsp@uohyd.ernet.in

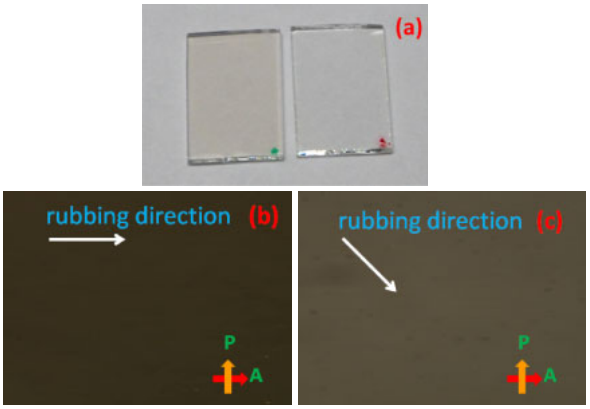

Fig. 1. (Color online) (a) ITO plates coated with AL-1254 (left plate with green dot at the right corner) and CYTOP (right plate with red dot at the right corner). Photomicrographs of CYTOP coated cell at room temperature: (b) rubbing direction $\psi = 0^\circ$ and (c) rubbing direction $\psi = 45^\circ$.

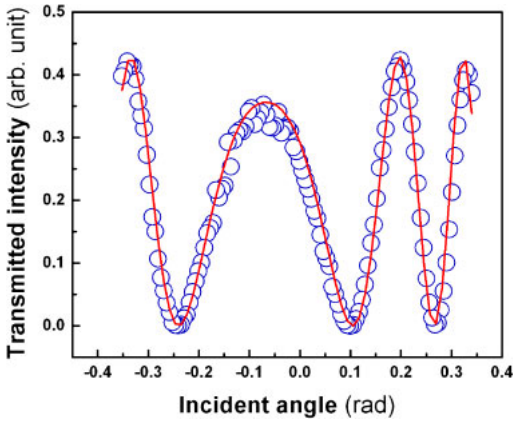

Fig. 2. (Color online) Transmitted intensity versus incident angle for ZLI-2293 in a CYTOP coated cell at room temperature. The circles represent the experimental data points and the solid line denotes the best fit to the theoretical equation.[15)]

where I_0 is the maximum intensity change. The decay time is given by the following equation:[17,18)] $\delta(t) \cong \delta(0)\exp(-2t/\tau_0)$, where $\delta(0)$ is the total phase change of the LC cell under a bias voltage V_B. The slope of the linear plot $\ln[\delta(0)/\delta(t)]$ is $2/\tau_0$, which yields the relaxation time (τ_0). The rotational viscosity (γ_1) of the sample is given by $\gamma_1 = \tau_0 K_{11}\pi^2/d^2$. All the experiments were performed at room temperature (27 °C).

Figure 1(a) shows the visible difference between the AL-1254 and CYTOP coated on ITO substrate. CYTOP coated plate appears more transparent than AL-1254 due to the high transmission of CYTOP. The texture of nematic phase of ZLI-2293 in rubbed cell under polarizing optical microscope with the rubbing direction $\psi = 0$ and 45° are also shown in Figs. 1(b) and 1(c), respectively. A complete dark state ($\psi = 0^\circ$) and a uniform bright state ($\psi = 45^\circ$) indicate good uniform alignment of director in the entire nematic phase.

In order to determine pretilt angle, transmittance intensity through a thick cell was measured as a function of incident angle. The result on a CYTOP coated cell is shown in Fig. 2. A good fit to the theoretical equation gives pretilt angle $\alpha \sim 2^\circ$. In case of AL-1254 it is $\alpha \sim 1^\circ$, which is negligibly smaller than CYTOP coated cell. To measure the anchoring energy, the retardation (R) and the sample capacitance (C) were measured simultaneously. Typical variation of normalized retardation (R/R_0) and capacitance C/C_0 as a function of applied voltage is shown in Fig. 3. We obtain the threshold voltage $V_{\text{th}} = 1.16\,\text{V}$ and estimated splay elastic constant $K_{11} \simeq 8.9 \times 10^{-12}\,\text{N}$. In Fig. 4 we show the variation of R/R_0 with $1/CV$ in the voltage range of 8–17 V. Good linear fits were obtained in the above voltage range. From the intercept to the ordinate axis we obtain the anchoring strength; $W \simeq 1.0 \times 10^{-4}\,\text{J/m}^2$ in a CYTOP cell and $W \simeq 18.3 \times 10^{-4}\,\text{J/m}^2$ in a AL-1254 cell. Note that W in a CYTOP cell is more than eighteen times smaller than W in a AL-1254 cell. Similar values of anchoring energy ($W \sim 17 \times 10^{-4}\,\text{J/m}^2$) of ZLI-2293 on other polyimide at room temperature was reported by You *et al.*[19)] Low surface anchoring properties of 4-cyano-4′-pentyl-1,1′-biphenyl (5CB) on Langmuir–Blodgett films of similar polymer (perfluoropolyether) was reported by Russel-Tanner *et al.*[20)]

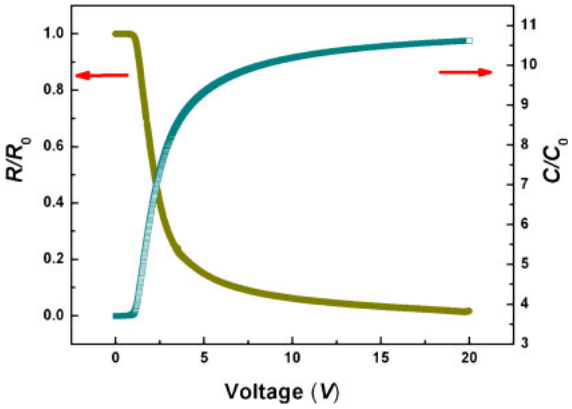

Fig. 3. (Color online) Variation of normalized retardation (R/R_0) and the ratio of the sample capacitance to the empty cell capacitance (C/C_0) as a function of voltage in a CYTOP coated cell at room temperature.

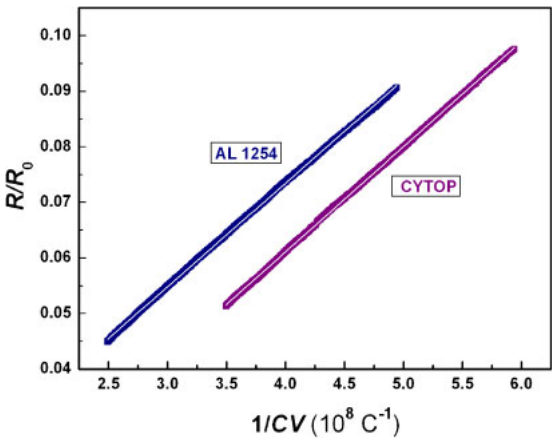

Fig. 4. (Color online) The variation of R/R_0 versus $1/CV$ in AL-1254 and CYTOP coated cells at room temperature. The data are well fitted to eq. (1).

Furthermore, CYTOP also provides perfect homeotropic alignment of smectic liquid crystals exhibiting its low surface anchoring properties.[14)]

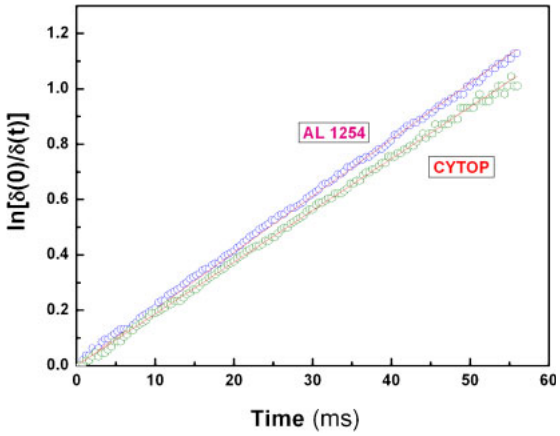

Fig. 5. (Color online) $\ln[\delta(0)/\delta(t)]$ versus time t for ZLI-2293 at room temperature. The open circles represent the experimental data for both alignment layers and the solid lines represent the best fit to the theoretical equation $\ln[\delta(0)/\delta(t)] = -2t/\tau_0$. Cell thickness $d = 9.5 \pm 0.5\,\mu m$ (AL-1254) and $10.6 \pm 0.5\,\mu m$ (CYTOP), respectively.

In Fig. 5 we show the variation of $\ln[\delta(0)/\delta(t)]$ as a function of time t. A good fit of the experimental data with the theoretical equation is obtained. The slope of this linear plot is $2/\tau_0$, which yields the relaxation times 107 and 99 ms in CYTOP and AL-1254 coated cells, respectively. The calculated rotational viscosities are 0.08 ± 0.01 and 0.10 ± 0.01 Pa s respectively, and agree within an experimental error due to the cell thickness measurement, the accuracy of which is within $\sim\pm5\%$. Rotational viscosity of this compound was also measured by using a transient current method by Imai *et al.*[21] and was slightly larger (0.14 Pa s) than our results. Finally we present the summary of the obtained quantities, anchoring strength (W), pretilt angle (α), and rotational viscosity (γ_1) in cells coated with CYTOP and AL-1254 in Table I. It is noted that the anchoring energy in CYTOP coated cell is significantly low compared to AL-1254 coated cell.

In conclusion, our measurements show that CYTOP is a good candidate for planar alignment of ZLI-2293. It provides much lower surface anchoring energy than AL-1254. The low anchoring energy is attributed to the low surface free energy and is supported by the fact that CYTOP provides larger contact angle than other alignment layers for liquid crystals.[14] The pretilt angles are not significantly different and hence suitable for the application. It is expected that the advantage of high transmission through CYTOP cell will be very useful for better performance. However, display performances using many other nematic mixtures should be studied for further details.

Table I. Summary of the physical properties of ZLI-2293 on both alignment layer, CYTOP and AL-1254.

	W ($\times 10^{-4}$ J/m^2)	α (deg)	γ_1 (Pa s)
CYTOP	1.0	2	0.08
AL-1254	18.3	1	0.10

Acknowledgements One of the authors Surajit Dhara gratefully acknowledges the support from the Department of Science and Technology, Government of India for the project number SR/FTP/PS-48/2006 under the Science and Engineering Research Council Fast Track Scheme and Center for Advanced Studies, School of Physics. We acknowledge Ashai Glass for supplying CYTOP. Tatipamula Arun Kumar acknowledges Center for Advanced Studies, School of Physics for the fellowship.

1) K. Takatoh, M. Sakamoto, R. Hasegawa, M. Koden, N. Itoh, and M. Hasegawa: *Alignment Technologies and Applications of Liquid Crystal Devices* (Taylor & Francis, London, 2005).
2) M. E. Becker, J. Nehring, and T. J. Scheffer: J. Appl. Phys. **57** (1985) 4539.
3) L. M. Blinov and V. G. Chigrinov: *Electrooptic Effects in Liquid Crystal Materials* (Springer, New York, 1994).
4) G. P. Bryan-Brown, E. L. Wood, and I. C. Sage: Nature (London) **399** (1999) 338.
5) S. Ando, R. K. Harris, J. Hirschinger, S. A. Reinsberg, and U. Scheler: Macromolecules **34** (2001) 66.
6) K. Yamamoto and G. Ogawa: J. Fluorine Chem. **126** (2005) 1403.
7) S. M. Jeong, F. Araoka, Y. Machida, K. Ishikawa, H. Takezoe, S. Nishimura, and G. Suzaki: Appl. Phys. Lett. **92** (2008) 083307.
8) S. M. Jeong, N. Y. Ha, F. Araoka, K. Ishikawa, and H. Takezoe: Appl. Phys. Lett. **92** (2008) 171105.
9) L. J. Cheng, M. T. Kao, E. Meyhofer, and L. J. Guo: Small **1** (2005) 409.
10) Surajit Dhara, J. K. Kim, S. M. Jeong, R. Kogo, F. Araoka, K. Ishikawa, and H. Takezoe: Phys. Rev. E **79** (2009) 060701(R).
11) T. Arun Kumar, P. Sathyanarayana, V. S. S. Sastry, H. Takezoe, N. V. Madhusudana, and Surajit Dhara: Phys. Rev. E **82** (2010) 011701.
12) J. K. Kim, S. M. Jeong, Surajit Dhara, F. Araoka, K. Ishikawa, and H. Takezoe: Appl. Phys. Lett. **95** (2009) 063505.
13) J. K. Kim, K. V. Le, Surajit Dhara, F. Araoka, K. Ishikawa, and H. Takezoe: J. Appl. Phys. **107** (2010) 123108.
14) S. M. Jeong, J. K. Kim, Y. Shimbo, F. Araoka, Surajit Dhara, N. Y. Ha, K. Ishikawa, and H. Takezoe: Adv. Mater. **22** (2010) 34.
15) T. J. Scheffer and J. Nehring: J. Appl. Phys. **48** (1977) 1783.
16) H. Yokoyama and H. A. Sprang: J. Appl. Phys. **57** (1985) 4520.
17) S. T. Wu and C. S. Wu: Phys. Rev. A **42** (1990) 2219.
18) S. T. Wu: J. Appl. Phys. **60** (1986) 1836.
19) D. H. You and S. D. Lee: Mol. Cryst. Liq. Cryst. **316** (1998) 215.
20) J. M. Russell-Tanner, S. Takayama, A. Sugimura, J. M. DeSimone, and E. D. Samulski: J. Chem. Phys. **126** (2007) 244706.
21) M. Imai, H. Naito, M. Okuda, and A. Sugimura: Jpn. J. Appl. Phys. **33** (1994) 3482.