Orientation of Lyotropic and Thermotropic Liquid Crystals on Plasma-Treated Fluorinated Surfaces

Noushine Shahidzadeh,* Abder Merdas, and Wladimir Urbach

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, URA 1306 du CNRS, associé aux Universités Paris VI et VII, 24 rue Lhomond, 75231 Paris Cedex 05, France

Farzanch Arefi-Khonsari, Michael Tatoulian, and Jacques Amouroux

Laboratoire de Génie des Procédés Plasmas, ENSCP-UPMC, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

A carbon tetrafluoride plasma discharge using a grafting mechanism and very short treatment times (a few milliseconds to a few seconds) was used to obtain high-quality reproducible surfaces that permit the homeotropic alignment of lyotropic as well as thermotropic liquid crystals. The intermolecular interactions between the fluorinated surfaces and the lyotropic liquid crystals, molecules with polar heads, and hydrophobic chains, were studied using different analytical techniques. The results show that the interaction responsible for the homeotropic anchoring occurs through the formation of hydrogen bonds between the polar heads of the molecules and the grafted polar fluorine groups.

Introduction

Lamellar phases (L_α) consisting of surfactant bilayers are smectic liquid crystalline structures also called lyotropic liquid crystals. The elastic properties of these lyotropic liquid crystals are generally defined using the layer compressibilty modulus (B) and their elasticity (K). These two constants can be evaluated by using, for instance, dynamic light scattering measurements.[1–3] However, the major problem in performing these measurements is that one has to have perfectly oriented samples, since the theoretical treatment of this method is based on oriented lamellar phases.[1–3] The amphiphilic molecules have to be oriented perpendicular to the surface (homeotropic anchoring) or, equivalently, the bilayers should be parallel to the surface. Also, for many display applications that use thermotropic liquid crystals, a regular orientation on planar surfaces is required.[4–7] It is therefore very important to know the characteristics the surface should possess to yield a planar, homeotropic, or tilted alignment.

We show here that an almost perfect alignment can be obtained by fluorinated plasma treatment of the solid surfaces on which the lamellar phases are deposited. The physicochemical basis of plasmas relies on the excitation of molecules in the gaseous phase by collisions with accelerated electrons in an electric field. This mechanism of energy transfer allows one to obtain excited molecules, ions, radicals, and atoms in the gaseous state. The interaction of such species with substrates gives rise to the modification of surface characteristics by three different mechanisms. Plasma polymerization of organic precursors results in highly cross-linked polymeric thin films on various kinds of substrates. Second, plasma grafting consists of incorporating new functional groups (polar or nonpolar, depending on the gas used) at the substrate. Finally, the plasma degradation or etching technique permits the ablation by the formation of volatile species resulting from the reaction of the excited species in the gaseous phase and the surface. These different processes can take place simultaneously in the case of plasmas produced in fluorocarbons.

The interaction of electrical discharges generated in fluorinated gases with substrates gives rise to the fluorination of the treated surfaces in two different ways: plasma polymerization or plasma grafting.[8,9] Generally in fluorinated plasmas, the CF_x radicals formed in the discharge are considered to be the building blocks for polymerization.[10,11] The CF_x/F ratio of the species resulting from the decomposition of the plasma gas plays an important role in the predominant mechanisms that take place: plasma polymerization, grafting of fluorine groups, or etching. A low CF_x/F ratio, such as is the case for carbon tetrafluoride (CF_4) used in our study, produces fluorination through a direct grafting of F atoms to the surface. Simultaneoulsy, F atoms, can give rise to the etching of the fluorinated layer. It is also well-known that for very short treatment times, the grafting process is much more significant than the ablation process since long treatment times favor the bombardment of the surface with highly energetic ions leading to the ablation of the surface.[12]

Studies done by Watanabe et al.[13] on plasma-polymerized films as an orientation layer for thermotropic liquid

(1) Nallet, F.; Laversane, R.; Roux, D. *J. Phys. II (France)* **1993**, *3*, 487.
(2) Nallet, F.; Roux, D.; Prost, J. *J. Phys. (Paris)* **1989**, *50*, 3147.
(3) Martin, P. C.; Parodio; Pershan. P. S. *Phys. Rev. A* **1972**, *6*, 2401.
(4) Gray, G. W. *Molecular structure and the properties of liquid crystals*; Academic Press: London/New York, 1962.
(5) Nicot, C.; Waks, M.; Ober, R.; Gulik-Krzywicki, T.; Urbach, W. *Phys. Rev. Lett.* **1996**, *77*, 3485.
(6) Kitzerow, H. S.; Jérôme, B.; Pieranski, P. *Physica A* **1991**, *174*, 163.
(7) Pieranski, P.; Jérôme, B. *Mol. Cryst. Liq. Cryst.* **1991**, *199*, 167.

(8) Placinta, G.; Arefi-Khonsari, F.; Gheorghiu, M.; Amouroux, J.; Popa, G. *J. Appl. Polym. Sci.* **1997**, *66*, 1367.
(9) Arefi, F.; Andre, V.; Montazer-Rhamati, P.; Amouroux, J. *Pure Appl. Chem.* **1992**, *64*, 5, 715.
(10) d'Agostino, R.; Cramarossa, F.; Fracassi, F. In *Plasma Polymerization of fluorocarbon in plasma deposition, treatment and etching of polymer*; R. D'Agostino: Boston, 1990.
(11) Yasuda, T.; Gazicki, M.; Yasuda, H. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*, 201.
(12) Khairallah, Y.; Arefi, F.; Amouroux, J.; Leaonard, D.; Bertrand, P. *J. Adhes. Sci. Technol.* **1994**, *8*, 363.

crystals showed that when tetrafluoroethylene (C_2F_4) is used as the gas to perform the polymerization, the surface energy of the surface decreases considerably inducing a perpendicular alignment. Moreover, the authors pointed out that in some cases plasma-polymerized ethylene (C_2H_4) films resulted in a perpendicular or tilted alignment of nematic liquid crystals whereas allylamine (C_3H_7N) gives rise to a parallel alignment. The latter was interpreted as being due to the large number of polar groups present on the glass substrate caused by the incorporated nitrogen.

In all papers describing the use of surface-active agents (wet processes)[14-17] and plasma-polymerized films (dry processes)[13,18] for the orientation of thermotropic liquid crystals, the explanations to describe the orientating effect of such surfaces are all based on steric effects or on the thermodynamic properties. The basic assumption is that the ratio of the surface tension of the nematic to that of the substrate allows an estimation of the nematic orientation on that substrate. Moreover, the problem of orientation of lyotropic liquid crystals was not addressed, although for a number of applications a regular homeotropic orientation on plane surfaces is required.

In this paper, we show that by using a plasma discharge with the grafting mechanism, one obtains high-quality reproducible surfaces that orient the lamellar phases and thermotropic liquid crystals. The originality of this work is that for the first time a plasma-grafting mechanism with very short treatment times (a few milliseconds to a few seconds) is proposed. Second, an attempt has been made to understand the microscopic orientation mechanisms involved at the liquid/solid interface, i.e., the effect of intermolecular interactions on the alignment of these molecules, which was not studied before. We are specifically interested in the homeotropic alignment of lyotropic and thermotropic liquid crystals on different types of substrates using carbon tetrafluoride (CF_4) as the gas for the plasma discharge and using very short treatment times (a few milliseconds to a few seconds). We demonstrate which part of the molecule intervenes in the intermolecular interactions at the solid/liquid interface and therefore is responsible for the possible perpendicular orientation.

Materials and Methods

A highly energetic low-frequency 70 kHz discharge[8] with CF_4 as the plasma gas was used to treat the substrates. The bell jar reactor and the whole experimental setup are detailed elsewhere.[9] The nonsymmetrical configuration of electrodes used in the reactor (hollow electrode-earthed cylinder) allows for very short treatment times and, in this respect, simulates continuous surface treatments used in the industry. Substrates to be treated (glass plates, polypropylene films, and mica samples) were attached to the earthed cylinder. The treatment time of the substrate was measured by multiplying the rotation time of the cylinder by the ratio of the plasma width on the substrate over the perimeter of the cylinder. The power of the discharge was 20 W, and the CF_4 gas flow rate in the reactor was 100 cm^3 min^{-1} during the experiments.

The surface modifications created by the CF_4 plasma were studied by means of image processing contact angle measurements,[19] X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

(13) Watanabe, R.; Nakano, T.; Satoh, T.; Hatoh, H.; Ohki, Y. *Jpn J. Appl. Phys.* **1987**, *26* (3), 337.
(14) Porte, G. *J. Phys. (Paris)* **1976**, *37*, 1245.
(15) Proust, J. E.; Ter. Minassian-Saraga; Guyon, L. *Solid State Commun.* **1972**, *11*, 1227.
(16) Creagh, L. T. Kmetz, A. R. *Proceedings of the 4th International liquid crystals conference*, Kent, OH, 1972.
(17) Kahn, F. J.; Taylor, B. N. *Proc. IEEE 61*, **1973**, 823.
(18) Sprokel, G. J.; Gibson, R. M. *J. Electrochem. Soc.: Solid State Sci. Technol.* **1987**, *124*, 557.
(19) Montazer-Rhamati, P.; Arefi, F.; Borrin, R.; Delacroix, A.; Amouroux, J. *Bull. Soc. Chim. Fr.* **1988**, *5*, 811.

The XPS technique provides a total elemental analysis, except for hydrogen and helium, and chemical bonding information on the top 5 nm of any solid surface that is vacuum stable or can be made vacuum stable by cooling. Its basic principle is the photoelectric effect. X-ray photons interact with the electron in the atomic orbitals such that there is complete transfer of the energy of the photon to the electron. The photon energy is greater than the binding energy of the electron in the atom so that the electron is subsequently ejected from the atom with a certain kinetic energy. Measuring the kinetic energy allows one to calculate the binding energy and thus to identify which atoms are present at the solid surface. The result is a spectrum of photoelectron intensity as a function of binding energy. The XPS spectrum gives information concerning the simple elemental analysis as well as detailed considerations of chemical shifts and nature of chemical bonding in the surface region.[20,21] In this study, the spectra were calibrated with respect to the carbon 1s photoelectron line (C−C, C−H) components placed at 285 eV binding energy. The fractional concentration of a particular element A ($A\%$) was computed using

$$A = \frac{I_A/s_A}{\sum (I_n/s_n)} \times 100$$

where I and s are the integrated peak area and the sensivity, respectively, for a given element and n stands for the nth element considered in the quantitative analysis.[22]

The orientation (anchoring) of the thermotropic liquid crystal E-8 (cyano group with biphenyl with a hydrophobic chain containing 8 carbons) and lyotropic liquid crystals, lamellar phases of the system dodecane + water + the nonionic surfactant $C_{12}E_4$ (HO−(−CH_2−CH_2−O−)$_4$−(CH_2)$_{11}$−CH_3), were examined under a polarizing microscope. The alignment of lamellar phases was observed in a sandwich-type cell consisting of plasma-fluorinated glass plates. When the sample was perfectly oriented (bilayers parallel to the walls) and placed between crossed polarizers, no light passes and the sample is completely black. This homeotropic alignment does not depolarize the light since a uniaxially oriented medium appears isotropic when viewed along the optical axis. On the contrary, defects of the alignment do depolarize the light and are thus visible as bright streaks between crossed polarizers.

For the case of a free droplet (i.e. without confining walls) of E-8 liquid crystal deposited on the plasma-treated substrate, when the latter induces a homeotropic alignment, the molecules are oriented perpendicular to the free surface. As the surface of the droplet is curved, the orientation of the molecules follows the curvature of the free surface. This means that when looking through the center of the droplet, the molecules are all aligned in the same way, since they are also perpendicular to the substrate. The curvature of the droplet, on the other hand, implies that the molecules are oriented tangentially to the substrate on the side of the droplet, which induces a birefringence. This birefringence is visible as the well-known "extinction crosses" between crossed polarizers.

Results and Discussion

The surface topographies of untreated and CF_4 plasma treated mica were studied by AFM. Mica was used as the substrate because of its smooth surface, which is taken as reference before treatment. After CF_4 treatment a granular structure can be observed (Figure 1). From AFM measurements it follows that the height of the grains remains fixed around 20 nm whereas their diameter varies with the plasma treatment times (16−100 nm). Actually, silicon-containing substrates give rise to the etching process in the presence of a CF_4 plasma by the formation

(20) Andrade, J. S. *Surface and Interfacial Aspects of Biomedical Polymers*; Andrade, J. S., Ed.; Plenum Press: New York, London, 1985; Vol. 1, Chapter 5.
(21) Chehimi, M. M. *Handbook of Advanced materials testing*; Cheremisinoff, Ed.; Marcel Dekker: New York, 1994; Chapter 33.
(22) Watts, J. *Vacuum* **1994**, *45*, 653.
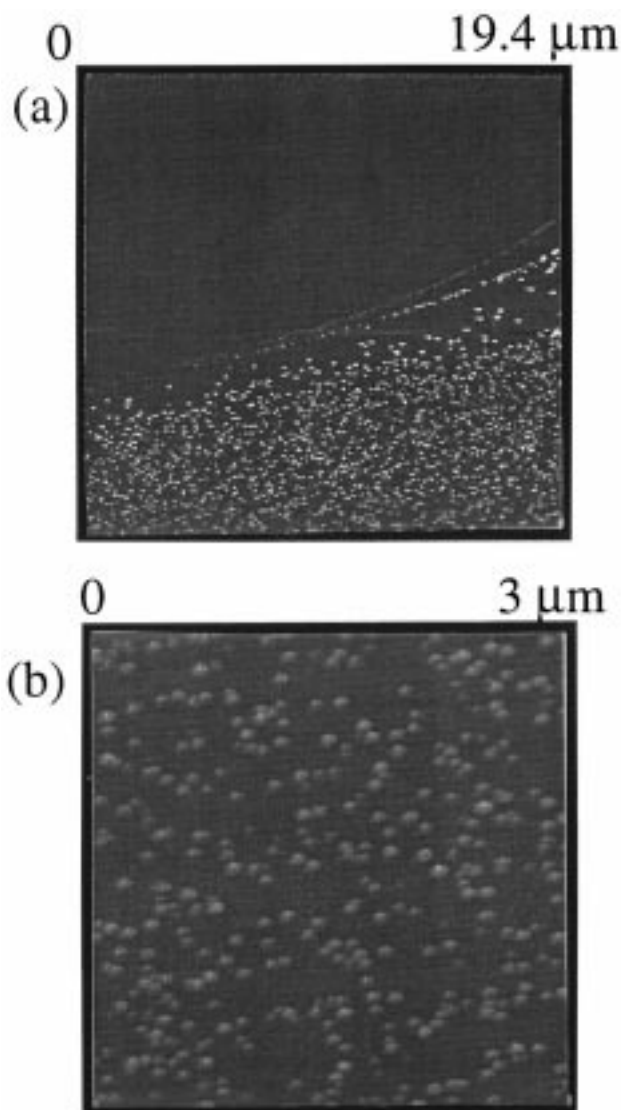
Figure 1. AFM micrographs of (a) the surface of mica half masked and treated by CF_4 plasma ($t = 0.046$ s). In the treated part the appearance of granular structures can be clearly observed. (b) CF_4 plasma treated mica ($t = 0.138$ s).

Table 1. Advancing Contact Angle Measurements (deg) of Water (pH = 5) on Nontreated and CF_4 Plasma Treated Surfaces of Glass Plates and PP Films for Different Treatment Times

	water contact angle ($\theta \pm 2°$)			
	nontreated	0.023 s	0.046 s	0.115 s
glass plate	26	43	87	97
PP film	97	79	76.2	84.5

of volatile SiF_4 etch products. At the same time the ions that bombard the surface can ablate the fluorinated surface and the nodular structure observed is probably due to the redeposition of the low molecular weight fluorocarbon fragments of the surface.

The advancing contact angle of water (θ) was measured on two different surfaces, polypropylene (PP) and glass, before CF_4 plasma treatment using a direct visualization apparatus based on an image-processing system.[19] θ is equal to 97° for polypropylene (PP) films and equal to 26° for glass showing, respectively, the hydrophobic and hydrophilic properties of these surfaces before the CF_4 plasma treatment (Table 1).

Table 2. XPS Characterization of the Functional Groups Present on the CF_4-Treated PP[a]

treatment time (s)	F_{1s}/C_{1s}	O_{1s}/C_{1s}	% $C-CH$	% $C-CF$ and/ or $C-OH$	% CF	% CF_2	% CF_3
nontreated			100				
0.023	0.09	0.08	78	14			
0.046	0.28	0.04	78	15	3		
0.069	0.41	0.04	75	10	7	3	3
0.23	0.7	0.04	71	10	7	6	4
1	1.05	0.06	50	5	14	14	6
5	1.05	0.06	49	11	14	16	5
12	1	0.07	54	11	10	11	5

[a] $P = 10^2$ Pa; $Q(CF_4) = 100$ cm^3 min^{-1}; $P_w = 20$ W; $f = 70$ KHz.

After CF_4 plasma treatments, for both surfaces, the contact angle increases with treatment time showing the increase of the hydrophobicity of the fluorinated surfaces. However, in the case of the PP films for very short treatment times ($t < 0.046$ s) one can note a loss of hydrophobicity of the surfaces upon treatment, i.e., the decrease of θ from 97° for the nontreated film (reference) to 76.2° for the 0.046 s treated one. This result shows the hydrophilic character of the surface induced by the particular grafted fluorinated functional groups (discussed in the next paragraph) at the first stages of the treatment.

To determine the stability of grafted fluorine groups at the surface after CF_4 plasma treatment, the contact angle of water was measured on a CF_4 plasma treated glass plate ($t = 0.23$ s) after washing with water and drying in air. The results show pratically the same contact angle ($\theta = 45°$) as the one measured on a freshly treated glass plate ($t = 0.23$s, $\theta = 43°$).

For both kinds of substrates (glass plates and PP films) fluorinated functional groups were detected and identified by XPS. Table 2 shows the results obtained for the case of PP films for different treatment times. A CF_4 plasma generates a number of fluorinated moieties, CF and CF_2. Up to 0.046 s of treatment time only polar groups (CF) were present. For longer treatment times (>0.115s), nonpolar groups (CF_2 and CF_3) were formed, which constitute together the predominant groups. This is in good agreement with the contact angle results which show that the wettability of the surfaces increases at the first stages of the treatment and then decreases with increasing treatment time.

The alignment of the lyotropic and thermotropic liquid crystals is determined for different substrates (PP films, glass plates, mica) for different plasma treatment times. Samples are observed between crossed polarizers using a polarizing microscope. A homeotropic anchoring is obtained on CF_4 plasma treated surfaces for short treatment times (0.023 and 0.069 s) (Figure 2). For long treatment times (>0.2 s) the anchoring exhibits some flaws. On combination of these results with the XPS data, the presence of CF groups seems to play an important role in the homeotropic alignment.

Once the orientation of the lamellar phase had been observed between crossed polarizers (Figure 3b), the cell formed by the treated glass plates was opened. The rest of the lamellar phase solution was removed using filter paper, and the glass plates were dried in air for 30 min (evaporation of dodecane and water). The contact angle of water is then measured on these glass plates; a drop of water deposited on these surfaces spreads showing complete wetting of the surface ($\theta = 0°$) by water (Table 3).

This result implies that the drop of water should be in the contact with a very hydrophilic surface and thus emphasizes two important points. First, there is not only
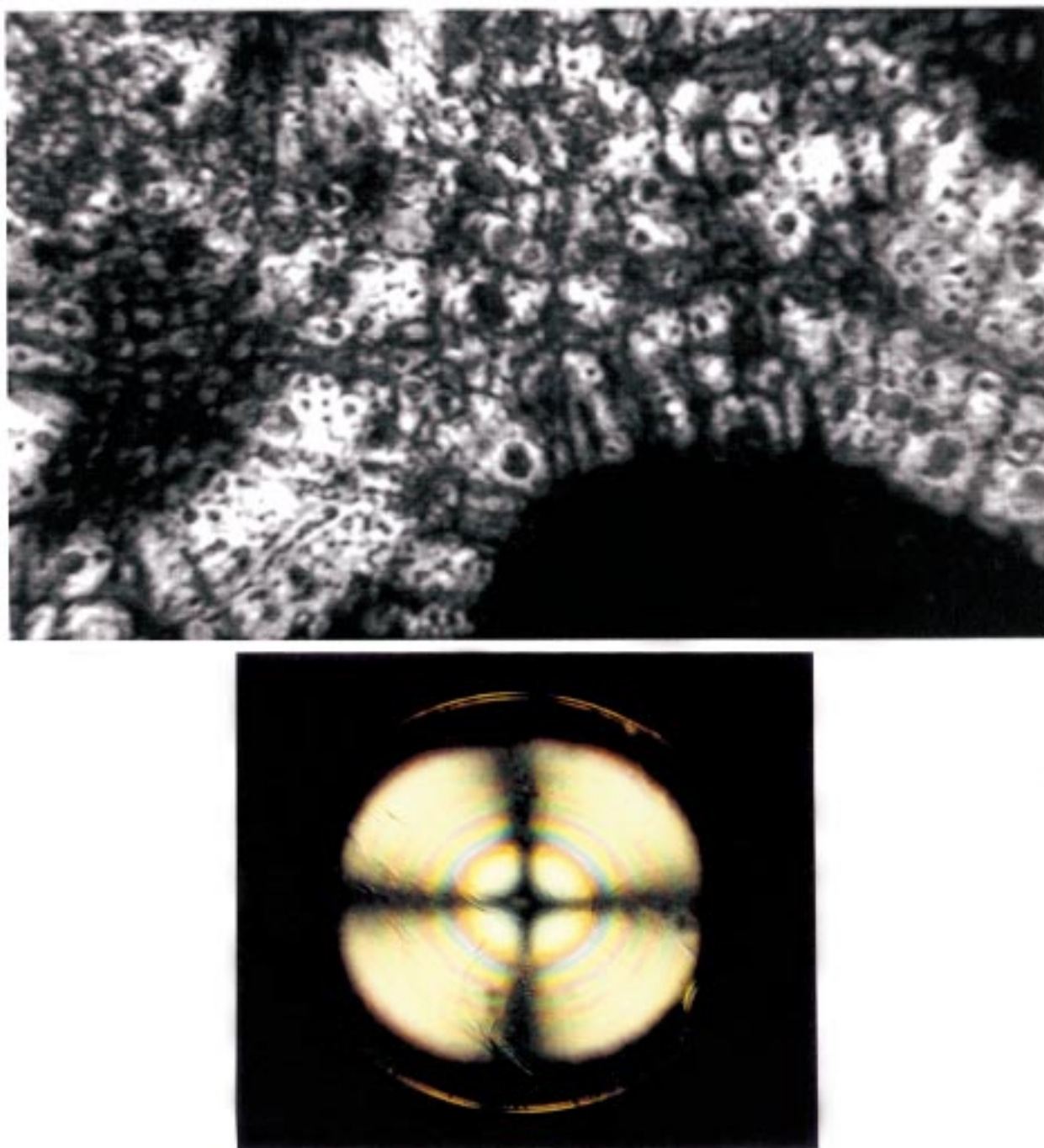
Figure 2. Observation of the homeotropic alignment of lyotropic and thermotropic liquid crystals under a polarizing microscope. (a, top) Flaws in the lamellar phase: water + dodecane + $C_{12}E_4$ introduced in a sandwich-type cell formed with untreated glass plates. With CF_4-treated glass plates ($t < 0.069$ s), a perfect oriented sample can be observed (the sample is completely black and not worth showing). (b, bottom) A high-quality homeotropic anchoring of a drop of E-8 nematic liquid crystal deposited on CF_4 plasma treated glass surface (0.069 s).

a physisorption of the surfactants at the surface. A stronger interaction (chemical or hydrogen bonds) with fluorine-grafted groups keeps the molecules at the surface. The hydrophilic character of the surface should be due to the interactions of surfactant polar heads with water which induces the complete wetting (Figure 3c). Moreoever, when dodecane (aliphatic chains) was deposited on the CF_4-treated surfaces, washed with hexane, and dried, no difference was observed on the contact angle of water compared to a freshly treated surface. These results show that no strong interactions exist between the aliphatic chain and the surface and confirm the hypothesis of

interaction between polar heads of liquid crystals molecules and the treated surface.

The CF_4 plasma treated surface in contact with L_α, the lamellar phase washed with *n*-hexane and dried at 60 °C, was analyzed by XPS. The XPS spectra showed an increase in the carbon content and a decrease of the fluorine content of the surface, confirming the presence of the $C_{12}E_4$ molecules at the treated surface. Moreover, the detection of surfactants at the surface in the vacuum of the XPS analysis chamber (5×10^{-6} Pa) confirms our earlier interpretation of the existence of a strong interac-
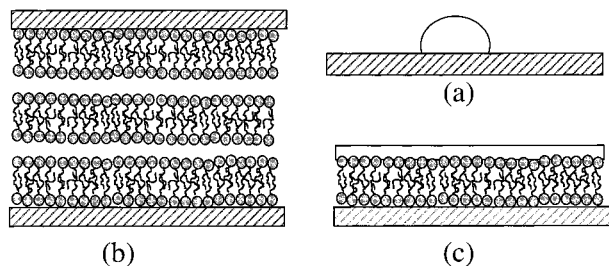
Figure 3. Schematic presentation of (a) the hydrophobic character of a plasma-fluorinated glass plate observed by contact angle of water on the surface and (b) a sandwich-type cell formed with plasma-fluorinated glass plates and the completely oriented lamellar phase. (c) A drop of water completely spreads on the plate obtained by opening the cell, in part (b), and after drying.

Table 3. Contact Angle Measurements (deg) of Water (pH = 5) on CF_4 Plasma Treated Glass Plates (0.023 s): (1) on As-Treated, (2) on Washed (with Water) and Dried (25 °C) Treated Substrate, (3) on Treated Samples after Being in Contact with a Lamellar Phase and Then Dried (25 °C)

CF_4-treated glass plate (0.023 s)	CF_4-treated glass plate (0.023 s) washed and dried	CF_4-treated glass plate (0.023 s) $+L_\alpha$ and dried
43	45	0

tion between the treated surfaces and the surfactant molecules.[23]

This strong interaction could be due to either an acid—base interaction or a hydrogen bond. The latter is likely to occur for the case of the lamellar phase, between the alcool group of the $C_{12}E_4$ surfactant and the $C-F$ grafted groups or the adjacent carbon (C_α) of the CF groups, i.e., *CH*–CF. For the case of thermotropic liquid crystal E-8, it is likely that the cyano groups of the molecules interact with the carbon adjacent to CF or *CH*–CF groups.

Indeed, experiments carried out on model polymers such as conventional PVDF (polyvinyline difluoride) and PTFE (poly(tetrafluoroethylene)) show the homeotropic anchoring of the lamellar phase only for the former.[23] Moreover,

(23) Arefi-Khonsari, F.; Tatoulian, M.; Amouroux, J.; Venot, S.; Bertrand, P.; Shahidzadeh, N.; Merdas, A.; Urbach, V. *J. Appl. Polym. Sci.* To be submitted for publication.

the chemical modifications of the CF_4-treated surface + L_α was also studied by the static secondary ion mass spectrometry (SSIMS).[23] The molecular specificity of SSIMS, its high surface sensivity (1 ppm against 1% for XPS), and a lower analytical depth (1 nm against 5 nm for XPS) have demonstrated the presence of C_n groups with a mass close to the molecular weight of the nonionic surfactant C_nE_m. As this method is based on the fragmentation of the surface in ionic groups, the detection of C_n groups close to the molecular weight of the surfactant molecule demonstrates that the interaction is probably not of a strong acid—base type. For the latter case more energy would be needed to break the interface bonds that would exist between the fluorinated groups and the surfactant molecules.

Therefore, the intermolecular interactions responsible for the orientation of lyotropic and thermotropic liquid crystals are likely to occur through the formation of hydrogen bonds between the polar heads of molecules and the CF or CHCF groups at the fluorinated surfaces.

Conclusion

A plasma-grafting mechanism using a CF_4 discharge has been proposed for the first time in order to obtain a homeotropic orientation of lyotropic liquid crystals on plasma-fluorinated surfaces. The results have shown that functionalization times of fluorine-containing groups as short as fractions of a second were enough to give rise to the orientation of the liquid crystalline molecules.

The microscopic interactions involved at the liquid—solid interface, responsible for the orientation, were investigated by complementary methods of analysis. The results of these differents techniques suggest that the orientation of lyotropic and thermotropic liquid crystals probably occurred through the formation of hydrogen bonds between the polar heads of the molecules and the CF or CHCF groups at the fluorinated surfaces.