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Mechanism in determining pretilt angle of liquid crystals aligned on fluorinated copolymer films

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Abstract
This work explores the surface treatment of copolymer materials with fluorinated carbonyl groups in various mole fractions by ultraviolet irradiation and ion-beam (IB) bombardment and its effect on liquid crystal (LC) surface alignments. X-ray photoemission spectroscopic analysis confirms that the content of the grafted CF_2 side chains dominates the pretilt angle. A significant increase in oxygen content is responsible for the increase in the polar surface energy during IB treatment. Finally, the polar component of the surface energy dominates the pretilt angle of the LCs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Surface alignments of liquid crystals (LCs) are essential to the fabrication of LC displays (LCDs) and other LC devices. They determine the boundary condition of molecular orientation at the surface. The rubbing method is frequently adopted in the LCD industry, which employs a velvet rubbing process on polyimide (PI)-coated substrates. Despite its success, this approach has some shortcomings, such as leaving debris and electrostatic charges on the rubbed surfaces, as well as uniformity issues [1]. Non-contact alignment methods are highly desirable to improve the quality of LC products.

An IBM group reported on one of the alternative alignment techniques, ion-beam (IB) alignment [2–5]. They realized this non-contact alignment technique by integrating low-energy IB equipment and diamond-like carbon (DLC) thin films in an LCD manufacturing processes. The mechanism of this alignment involves the anisotropic change in bonding between carbon atoms under IB bombardment [5]. Over the past decade, numerous works have addressed the IB bombardment of DLC and PI films [6–8]. Gwag *et al* found that both homogeneous and homeotropic alignments can be obtained when organic alignment layers are bombarded by IBs with various energies and current densities [6]. Wu *et al* presented a similar idea, but working in an opposite manner [7]. Treatment with a low-energy IB homogeneously align the LCs while high-energy IB bombardments homeotropically align them. Another remarkable result is that homeotropic alignment can be achieved using fluorinated DLC thin films as the alignment layer and the pretilt angle can be controlled by choosing various IB parameters or the concentrations of fluorine dopant in the films [8].

Wu and Pan also described an approach for aligning LC using IB-sputtered thin films that comprise magnetic nanoparticles, regardless of the pre-coating on the substrates [9]. High-quality homeotropic alignments and promising electro-optical performance are obtained. Both the polar anchoring strength and the saturation magnetization are found inversely related to the thickness of the sputtered γ-Fe_2O_3 film [10].

Another alternative alignment method, photo-irradiation, has attracted substantial interest during the last two

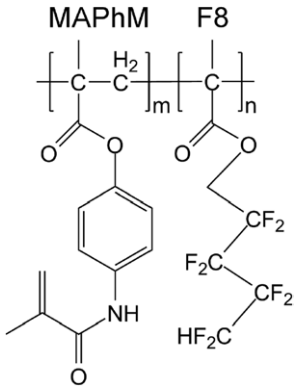

Figure 1. Chemical structure of the fluorinated polymer MAPhM-F8.

decades. The photoreactive polymers have been extensively investigated as a photo-alignment layer. They include photo-decomposable polymers, photocrosslinkable polymers and photo-isomerizable polymers [11–13]. However, none has radically solved the problems of low anchoring strength and insufficient alignment stability. The photoreaction of the PI has received considerable attention because of its extensive use in the LCDs industry [11, 14–16]. A long exposure time or a high-dosage of ultraviolet (UV) irradiation is required to achieve significant surface alignment because of the low photoreactive efficiency of PI.

The copolymer 4-(N-methacryloylamino)phenylmeth acrylate with 2,2,3,3,4,4,5,5-octafluoropenthylmethacrylate (MAPhM-F8), whose structure is as presented in figure 1, was recently developed jointly by Syromyatnikov's group from the Taras Shevchenko Kyiv National University of Ukraine, Yaroshchuk's group from the Institute of Physics of NASU in Ukraine and Lee's group from the Industrial Technology Research Institute, Taiwan [17, 18]. It has good photostability because of its high transparency in the visible and near UV spectral ranges. The 4-(N-methacryloylamino)phenyl methacrylate contains O- and NH-methacryloyl groups, causing the compound to be thermally stable and capable of photocrosslinking. The copolymerization of methacrylic monomers with fluorinated fragments of various concentrations or lengths in polymer promotes a gradual change in the pretilt angle from planar to vertical alignment.

2. Experimental

To understand the mechanism by which the fluorinated carbonyl groups affect the pretilt angle, MAPhM films copolymerized with three mole fractions of the F8 side chain, 0, 1/2 and 2/3, are used. They are labelled X_0, $X_{1/2}$ and $X_{2/3}$, respectively. The indium–tin-oxide coated glass substrates of size 20 mm × 10 mm are spin-coated with these copolymers, as described elsewhere [19]. The coated MAPhM-F8 films are then treated by both the linearly polarized ultraviolet light (LPUVL) irradiation and IB bombardment because their mechanisms of interaction with the surface of the film differ from each other.

2.1. Surface treatments

For photo-alignment, the LPUVL is obtained from a 1000 W xenon arc lamp (Model 6269 Oriel) through a liquid filter, a convex lens and a Glan–Taylor prism in sequence. The photo-induced alignment is a two-step irradiation process, which includes exposure to LPUV with an intensity of 2.4 mW cm^{-2} followed by exposure to unpolarized UV light with an intensity of 12.7 mW cm^{-2} for another 1 min to remove the degeneracy of the pretilt angle. The angle of incidence of the UV light is 45° throughout the process.

For IB bombardment, a direct-current (dc) diode-type IB sputter (model IB-2 from EIKO Engineering Co., Ltd.) is employed, as described elsewhere [7]. Sputtering is performed in etching mode, the bottom electrode acts as the cathode. The substrates are etched by IBs from the induced glow discharge close to the top electrode. A sample holder is attached; the angle of incidence, duration of bombardment, current density and the energy of ions are all controllable parameters. The incidence angle, the current density and the dc bias between the electrodes are fixed at 60°, 255 μA cm^{-2} and 560 V, respectively. Before the IB process begins, the chamber is pumped down to a base pressure of 30 mTorr and then filled with argon gas to a target pressure of 120 mTorr.

2.2. Alignment characterization

Following surface treatments, two substrates are combined but separated by a 23 μm Mylar spacer to form an empty cell with an anti-parallel arrangement. The empty cell is then filled with LC 4′-n-pentyl-4-cyanobiphenyl (5CB, Merck) with a nematic range between 24.0 and 35.3 °C to characterize the alignment and measure the pretilt angle.

After the LC cells have been annealed, the alignment direction and uniformity of each cell are checked using a pair of crossed polarizers. The pretilt angle of 5CB molecules near the surface is measured using the 'crystal rotation method' [20].

2.3. X-ray photoelectron spectroscopy

Surface-sensitive x-ray photoelectron spectroscopy (XPS, PHI-1600 from Physical Electronics, Inc.) was utilized to determine the chemical compositions of the treated film surfaces. A PHI dual-anode monochromatic source of x-ray irradiation from Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) lines and a PHI 10-360 precision energy analyzer were used. Only the Mg Kα line was adopted in this work. The base pressure during acquisition was below 5.0 × 10^{-9} Torr. The anode voltage was set at 15 kV. (The x-ray power was 250 W.)

2.4. Surface energy

The surface energy was measured using the contact angle method to determine its relationship with the alignment properties of the treated films. The polar, dispersive and total surface energy were deduced according to the Owens–Wendt method [21]. In this method, liquid drops are put on the surface and the contact angles are measured. The total surface energy

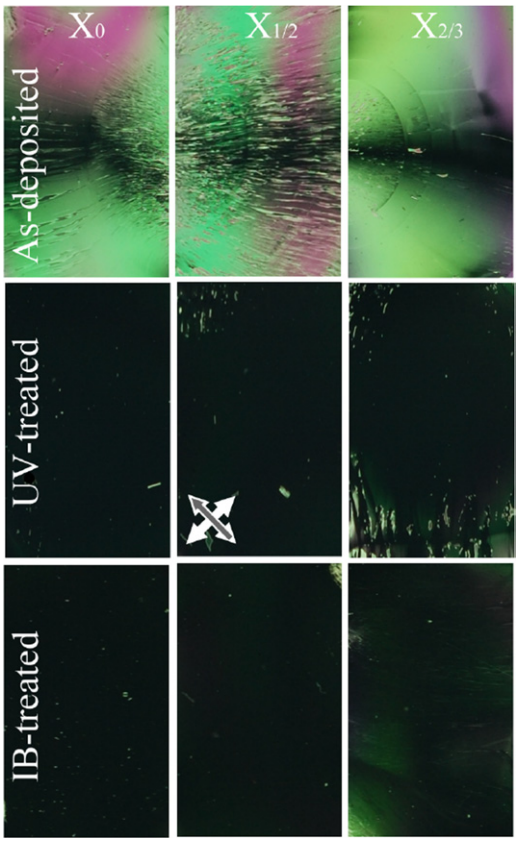

Figure 2. 5CB cells viewed with crossed polarizers in the dark state. The cells are aligned with surface-treated X_0, $X_{1/2}$ and $X_{2/3}$ films by LPUVL irradiation and IB bombardment for 10 min. (Grey arrow: LC director and white arrow: polarizers)

of a solid γ_s can be resolved into a dispersion component γ_s^d and a polar component γ_s^p with contact angle θ,

$$1 + \cos\theta = \frac{2}{\gamma_l}\left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}\right), \qquad (1)$$

where γ_l^d and γ_l^p are the two corresponding components of the surface tension γ_l of the liquid in contact with the solid surface. To deduce the surface energy γ_s, two liquids, water and glycerol, are utilized. The surface energies of these two liquids, $\gamma^d_{water} = 21.8\,mJ\,m^{-2}$, $\gamma^p_{water} = 51.0\,mJ\,m^{-2}$, $\gamma^d_{glycerol} = 37.0\,mJ\,m^{-2}$ and $\gamma^p_{glycerol} = 26.4\,mJ\,m^{-2}$ are taken from the literature [22].

3. Results and discussion

Our earlier work demonstrated that even the highest pretilt angle induced by the IB-treated fluorinated polymer surface is still much smaller than that provided by the LPUVL-irradiated surface [19]. The pretilt angle is proportional to the fluorine content.

Figure 2 shows the photographs of the LC cells in the dark state when the X_0, $X_{1/2}$ and $X_{2/3}$ films are treated with LPUVL irradiation and IB bombardment for 10 min. Both treatments of this copolymer film result in good alignment effects. The alignment directions of each LC sample are either parallel to the incidence plane of IB or perpendicular to the polarization of UV light. The UV-treated surfaces have more defects, especially when the content of the fluorinated agent is high. However, increasing the duration of the LPUVL irradiation significantly reduces the number of defects.

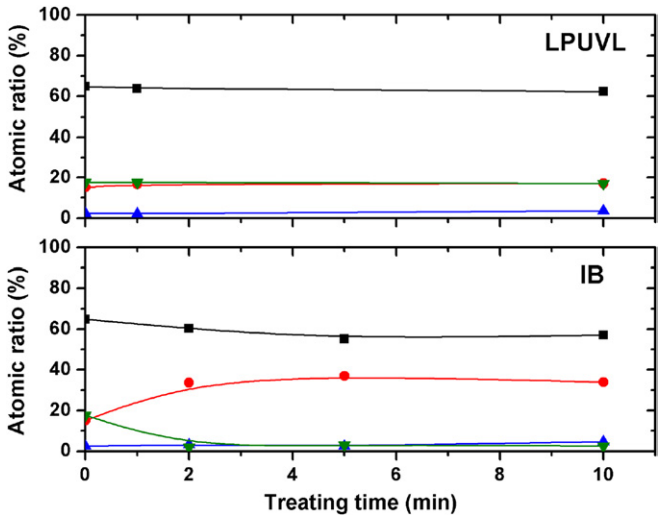

Figure 3. Variation of chemical composition of the $X_{1/2}$ film surface following treatment by LPUVL irradiation and IB bombardment with treatment time for elements: C (■), O (●), N (▲) and F (▼).

Figure 3 plots the variation of the chemical composition of the $X_{1/2}$ film that has been surface-treated by LPUVL irradiation and IB bombardment with the treatment time. No significant change in the element content was observed after the LPUVL irradiation, suggesting that photo-crosslinking dominated the photoreaction mechanism, as mentioned by Vretik *et al* [17]. However, the IB bombardment dramatically destroyed the fluorine element, but a large increase in the amount of oxygen element is observed.

In our earlier work, we found that the CF_2 bonds are largely destroyed after IB bombardment [19]. Furthermore, deconvolution of the C_{1s} core-level signal is carried out to evaluate the composition of each carbonaceous bond, for example, the C–O–C, O–C=O, CF_2, N–C=O, etc. Figure 4 shows the C_{1s} spectra of the X_0, $X_{1/2}$ and $X_{2/3}$ films treated by LPUVL irradiation and IB bombardment. It differs from that by LPUVL irradiation, the CF_2 bonds are almost destroyed by IB bombardments but excess C=O bonds increase instead. This explains the origin of the increase in oxygen content that further re-oxidization of dangling bonds occurs after IB bombardments.

Figure 5 plots the measured pretilt angles against the treating time. The pretilt angles induced by IB bombardments are much smaller than those of the LPUVL-irradiated surfaces. The increase in fluorine content of the polymer film improves the pretilt angle remarkably. However, longer treating time will reduce the pretilt angle. The error bar is given by averaging the measured values over different positions on the surface.

Figure 6 plots the measured pretilt angle against the CF_2/C ratio for all of the samples with various treatment times and mole fractions of fluorinated side chains. The logarithm of the pretilt angle varies linearly with the CF_2/C ratio for the

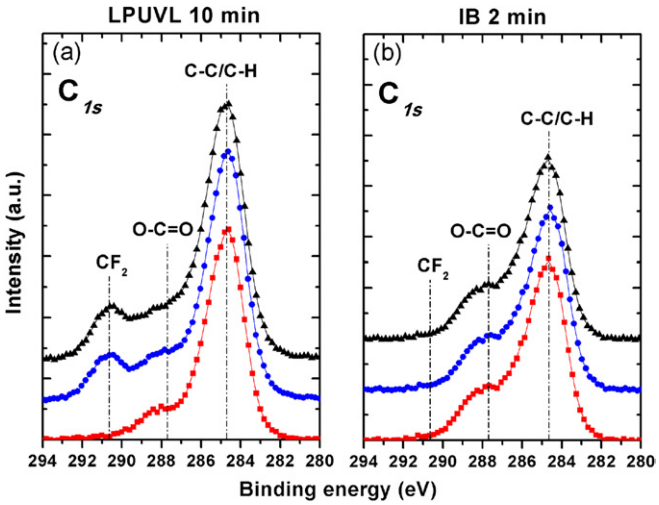

Figure 4. C_{1s} core-level spectra of X_0 (■), $X_{1/2}$ (●) and $X_{2/3}$ (▲) film surfaces treated by (*a*) LPUVL irradiation for 10 min and (*b*) IB bombardment for 2 min.

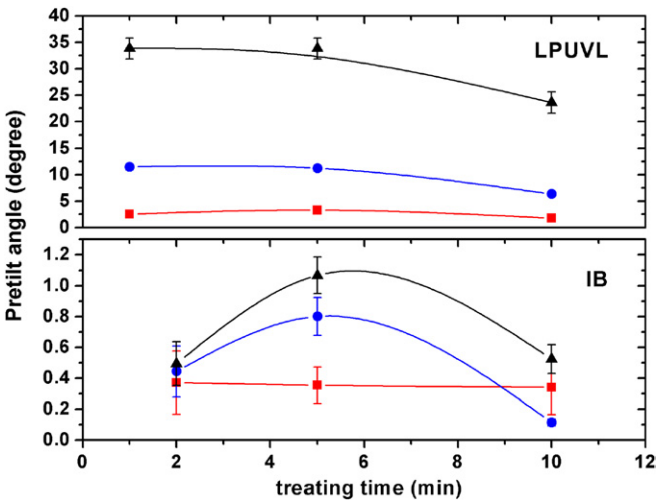

Figure 5. Pretilt angles of X_0 (■), $X_{1/2}$ (●) and $X_{2/3}$ (▲) film surfaces plotted as a function of treating time for LPUVL irradiations and IB bombardments.

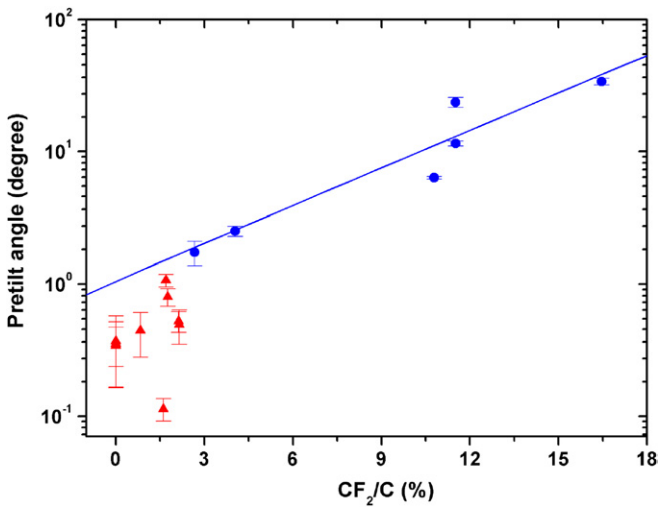

Figure 6. Logarithm of pretilt angle as a function of CF_2/C ratio following LPUVL (●) and IB (▲) treatments.

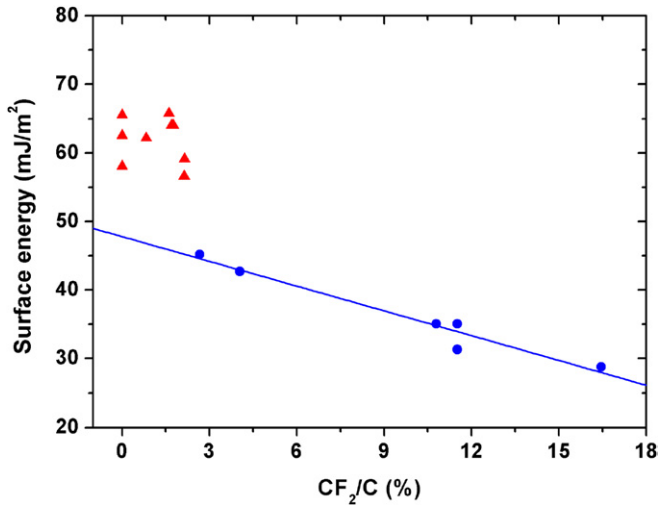

Figure 7. Surface energy as a function of CF_2/C ratio following LPUVL (●) and IB (▲) treatments.

LPUVL-irradiated surfaces. The points for IB-treated surfaces basically follow this line only a little lower. The difference may be associated with the destruction of the photoactive group MAPhM by IB bombardments, which is followed by a large increase in the oxygen content of the surface. Accordingly, the CF_2 group is primarily responsible for the high pretilt angle. To understand how the CF_2 group takes effect in determining the pretilt angle, the surface energy of each treated surface is measured for comparison. Figure 7 plots the surface energy against the corresponding CF_2/C ratio. A linear relationship is similarly found for LPUVL-treated surfaces. A higher concentration of the fluorinated carbonyl group lowers the surface energy effectively.

Figure 8 plots the pretilt angle as a function of surface energy. The open and solid circles represent the samples treated by LPUVL irradiation and IB bombardment, respectively. A dashed line represents the surface energy of an as-deposited X_0 film. As described in the literature, the incorporation of fluorine in a polymer film typically reduces its surface energy [23]. This is because fluorine atom has the highest electronegativity among all elements; therefore, its electron dipole is small [24]. As a result, the intermolecular van der Waals forces between fluorinated compounds are small. Measurements made for all the LPUVL-treated films are consistent with this point. The IB-treated films have a higher surface energy mainly because they contain less fluorine. However, the reduction in the amount of fluorine element cannot cause the surface energy to exceed that of an as-deposited X_0 film (45.4 mJ m^{-2}). A remarkable increase in oxygen content upon IB bombardment explains the further increase in the surface energy. Figure 8 also plots the oxygen content, which increases linearly with the surface energy. Since the bond-breaking process is dominant in IB treatments, numerous dangling bonds are expected to be formed. Then, the re-oxidization of these dangling bonds increases the C=O carbonyl group content. These newly formed polar groups can increase the surface polar force.

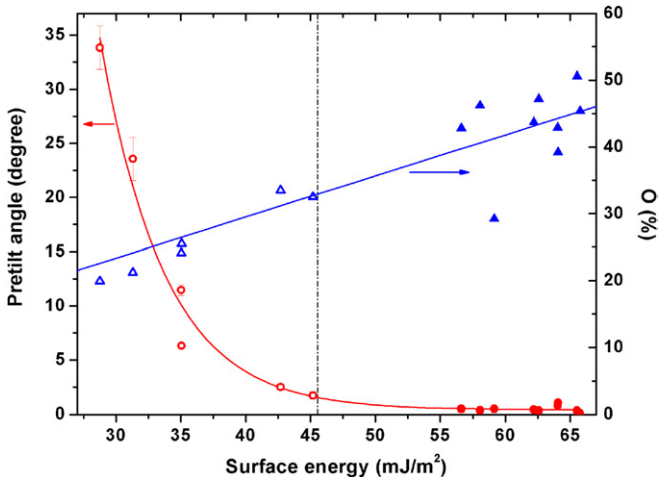

Figure 8. Pretilt angle (circles) and atomic ratio of oxygen content (triangles) as functions of surface energy for all the samples that had been treated by LPUVL irradiation (open) and IB bombardment (solid) for various treatment times.

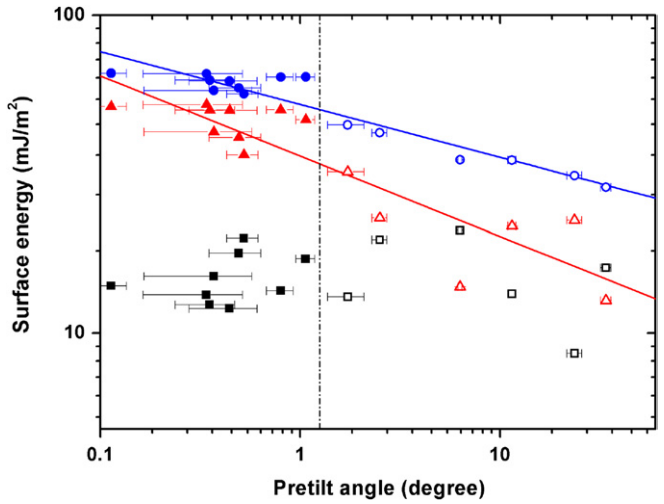

Figure 9. Total surface energy γ_s (circles), polar surface energy γ_s^p (triangles) and dispersion surface energy γ_s^d (squares) as functions of the logarithm of pretilt angle for all samples treated by LPUVL irradiation (open) and IB bombardment (solid) for various treatment times.

Figure 9 plots the logarithm of the polar and dispersion surface energies as functions of the logarithm of the pretilt angle. The decline in the polar surface energy as the pretilt angle increases is clear, whereas the dispersion surface energy γ_s^d remains essentially constant. Apparently, the contribution of the polar force to the surface energy dominates the pretilt angle. Ban and Kim have also described this relationship [25]. As described by Stöhr *et al* [5], the alignment mechanism of LCs on the carbonaceous surface is attributed to the dipole–dipole interaction between the unsaturated π bonding of LC and surface systems. The induced pretilt angle is associated with the orientation of benzene rings in addition to the chemical composition of surface. Herein it is confirmed that the fluorinated carbonyl group is capable of lowering the surface polar force which can be raised by creating additional C=O bonds on the surfaces by IB bombardments. For IB treatments, the polar force is dominant in determining the surface energy. Therefore, the decrease in the pretilt angle is probably due to the enhancement of polar force interaction between the cyano group (C≡N) of 5CB and the surface polar group. In contrast, the non-polar CF_2 group could lessen the surface polar force and increase the pretilt angle further.

4. Conclusion

The content of fluorinated groups CF_2 that are grafted in the F8 side chains dominates the pretilt angle. XPS analyses reveal that the photo-crosslinking and bond-breaking reactions of MAPhM-F8 copolymer dominate in the LPUVL irradiation and IB bombardment, respectively. Following the IB treatment, the C=O carbonyl groups newly formed by the re-oxidization of dangling bonds cause a drastic increase in polar surface energy. The non-polar CF_2 group is capable of mitigating the polar force interaction and increasing the pretilt angle further. The polar component of the surface energy in turn dominates the pretilt angle.

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