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Engineering the Anchoring Behavior of Nematic Liquid Crystals on Solid Surface by Varying the Density of Liquid Crystalline Polymer Brush

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Abstract

Controlling the orientation of liquid crystal (LC) molecules towards contacting surfaces is a crucial requirement for the development of LC displays, as well as passive electro-optical devices. To date, research has focused on photo response of LC azobenzene polymer system to obtain either planar or homeotropic orientation of LCs. It remains a challenge, however, to tune the polar angle of LC molecules on solid surface and gain more insights about the polymer chain conformation extending in LC medium. Here, we deposit a liquid crystalline side chain polymer brush, poly(6-(4-methoxy-azobenzene-4'-oxy) hexyl methacrylate) (PMMAZO), onto the solid surface with film thickness varying between ~3 nm and 13 nm, therefore, the grafting density of brush layer ranges from 0.0219 to 0.0924 chains per nm^2. When LCs are confined in hybrid cells with a top surface eliciting uniform homeotropic anchoring and a bottom surface covered by PMMAZO brush, the out-of-plane polar angle of 4-pentyl-4'-cyanobiphenyl (5CB) on brush layer gradually changes from ~0° to ~62° by simply increasing the grafting brush density. Surface force apparatus (SFA) measurement is used to determine 5CB as a good solvent for PMMAZO brush and understand the relationship between chain conformation in 5CB and the anchoring behavior of LC molecules on polymer brush layer. For high grafting density, the polymer chain in 5CB extends significant away from substrate, making the side chain mesogens on average almost parallel to substrate; for the low-density case, main chain extends in the narrow region around the surface to align the mesogens perpendicular to substrate.

Introduction

The alignment of nematic liquid crystals (NLCs) confined between surfaces in the liquid crystal displays and devices (LCD) without external field, called the ground state, is of both fundamental and applied interest. The equilibrium director configuration of the confined NLCs is highly dependent on the chemical and physical properties of the interfaces. The interface could align the nearby LC molecules and thus transfer certain director orientation into the bulk due to the long-range orientationally order property of NLCs. The nematic director fixed by the interface, known as anchoring, could be homeotropic (perpendicular), planar (parallel), or with certain tilted angle to the surface.

Polymeric thin film surfaces, such as alkylsilane self-assembled monolayers[1-3], chemisorbed thiols on gold[4, 5], and monolayer coverages of carbohydrate-based giant surfactants[6], are commonly used to orient the LCs to be homeotropic or planar with only limited control over intermediate tilt angles.

Polymer brush, with a dense layer of polymer chains end-grafted onto a solid surface, could be used to manipulate the anchoring behavior based on their various functionalities. This is especially applicable when mesogenic monomers are introduced into such surface grafted chains connecting by flexible spacer groups, known as liquid crystalline polymers (LCP). Halperin and Williams firstly studied main chain LC polymer brushes in nematic LC solvents from theoretical aspects[7-9]. In such case, densely grafted chains in a good solvent are strongly stretched along the normal to the surface, favoring homeotropic orientation, while the bare substrate with planar anchoring aligned the LC molecules parallel to the surface. A competition between the chain stretching in a dense polymer brush and the alignment favored by the uncovered surface was created here. A second-order anchoring transition between planar alignment at low grafting density and titled alignment at higher grafting density was predicted. Subsequently from experimental realization of such scenario, Peng et al.[10, 11] used the free radical polymerization to synthesize side chain-type surface-initiated polymer brushes as the alignment layer. Higher polydispersities and longer polymer chains in their case result in a higher conformational freedom of the chains and their side groups, so that the combination of brushes and rubbed surface could achieve preferred planar alignment. However, the homeotropic alignment is not observed. Hamelinck and Huck[12] synthesized side chain liquid crystalline polymer brushes by surface-initiated ATRP and obtained homeotropic alignment of nematic liquid crystal. They assumed that the brush backbones are not totally stretched out but exhibit a certain amount of coiling, which makes the side chains mesogens orient vertically to the surface and induces the homeotropic alignment. Because the photoisomerization of azobenzene (Az) mesogen group is the most widely used in application studies for photo-functional materials, Nagano et al.[13-15] prepared the LCP brush bearing the Az mesogen group in the side chains by adopting surface-initiated ATRP, which attained parallel alignment of the Az units. In contrast, the Az mesogen would adopt homeotropic alignment to the substrate through spin cast films and annealing. The planar aligned photoresponsive Az side chain LCP films lead to an effective in-plane photoalignment under linearly polarized light irradiation[16, 17]. Furthermore, the non-photoresponsive LCP films could also be controlled through photoalignment by commanding a photoresponsive LCP thin layer at the free surface.

So far, the LC polymer brushes were studied at sufficiently high grafting densities, resulting in the polymer backbone stretching away from the surface, without overlapping among the neighboring chains. Homeotropic anchoring was predicted by stretching the main-chain LCP backbones, and the tilted alignment was introduced by the competition between vertical chain stretching and the planar anchoring of the uncovered substrate [7]. Within side-chain LCP brushes, the mesogenic side groups are perpendicular to the polymer main chain[18], the planar alignment is the favored state when the chain stretched away from the substrate. Hamelinck and Huck[12] observed the homeotropic anchoring from side chain LCP, however, the interrelation between chain conformation and anchoring behavior has not been fully explored, and especially when the grafting density is low, uniform homeotropic anchoring could not be achieved because the uncovered portion of the substrate may provide a planar anchoring component. On the other hand, the miscibility between the LCP layer and the nematic medium has to be considered. The miscibility studies from Halperin and Williams[8] showed the main-chain LCP brushes can be theoretically swollen to a limited extent by low molecular weight nematic compounds with similar chemical structure. However, the extending behavior of the LCP in the nematic medium from experiments has not been reported. It is expected that the LCP chain conformation under extending state will have effect on the transition of anchoring behavior.

In this work, we synthesized a side-chain LC polymer brushes, poly(6-(4-methoxy-azobenzene-4'-oxy) hexyl methacrylate) (PMMAZO), bearing azobenzene mesogenic groups in the side chains attached to the polymethacrylate main chain. Different grafting densities of PMMAZO surfaces were fabricated by tethering the different concentration of PMMAZO solutions on the cleaned Si surface. Their anchoring behavior of 4-pentyl-4'-cyanobiphenyl (5CB) was investigated. The out-of-plane tilt angle of 5CB from the surface gradually changed from perpendicular to planar by increasing grafting density, producing an effective way to tune the anchoring behavior of NLCs. In this system, the surface effect from Si was screened even in the lowest grafting density. A phenomenological model was considered to explain the anchoring mechanism of the PMMAZO layer. For the first time the extending behavior of the LC polymer brush in the good solvent, nematic medium, was investigated by surface force apparatus (SFA). The extending direction of PMMAZO chain in the good solvent depended on the grafting brush density: the polymer chain expanded perpendicular to the silica substrate on the high-density surface, while, in the low-density case the chain extended in the narrow region around the surface.

Results and discussion:

To investigate and control the anchoring of the nematic 5CB, we used substrates coated with a polymer brush, hydroxyl-terminated poly(6-(4-methoxy-azobenzene-4'-oxy) hexyl methacrylate) (PMMAZO) (Fig. 1a), containing 4-methoxy-azobenzene moieties which served as tethered mesogens to control the anchoring properties between the LC and polymer brush surfaces. To form brushes on the substrate, a series of ~3 to ~13 nm thick films of PMMAZO were coated onto clean silicon wafer substrates and annealed at 250 °C for 5 min to create covalent bonds between the hydroxy end groups of PMMAZO and the silicon substrates[19]. Unbound polymers were removed by repeated sonication in chlorobenzene. The durable attachment of PMMAZO brush to the substrate was created to overcome the dissolution of the alignment layer. The film thickness of grafted polymer brush layer keeps the same range (~3-~13nm) after the above process. The absolute molecular weight of PMMAZO sample was ~110 000 g/mol with PDI of ~1.12. Glass surfaces functionalized with octadecyltrichlorosilane (OTS) were prepared to impose uniform homeotropic anchoring on the 5CB molecules.

Fig. 1b shows a schematic of the process used to assemble LC cell with the uniform PMMAZO brush coated surface as the bottom substrate and an OTS modified glass as the top surface. The separation distance between the top and bottom surfaces, namely the thickness of the cells, was controlled as 1.5 μm by the Mylar film spacers. The two substrates were pinched by binder clips to fix the cell gap. 5CB was injected into the cells above its isotropic temperature to avoid any initial flow orientation and allowed to fill the cell by capillary action. The morphology of PMMAZO brush surfaces with two different limited film thickness that we tested in our system, the thinnest (right) and the thickest (left), were investigated using atomic force microscopy (AFM) (Fig. 1c). The PMMAZO coated surfaces shows many protuberances but are constructed as a uniform continuous film. The height profiles of each condition are shown besides the morphology images, which are almost identical to each other with the root-mean-square (RMS) surface roughness as 2.5 nm and 3.0 nm, respectively. The average height of protuberances is within 1.0 nm for both cases. The surface topographic difference between two thickness conditions can be ignored and the randomly distributed topographic features on the film surface wouldn't be the main reason to induce different anchoring behaviors of 5CB on such surfaces.

Due to the molecular interactions between liquid crystal molecules, the orientation of them at the surface can propagate through the bulk, giving rise to complex optical structures, which can be used as an amplifier that translates chemical surface effects into macroscopic, optically observable phenomena. The anchoring behaviors of 5CB on different polymer brush layer were analyzed by observing the birefringence phenomenon of the LC cell between crossed polarizers using polarized light microscopy (PLM). Normally, homeotropically anchored 5CB appears optical extinction under crossed polarizers, due to the long axis of 5 CB molecules being anchored perpendicular to the surface of cells without any birefringence effect. However, the 5CB with planar anchoring gives rise to bright features when not oriented parallel to either the polarizer or the analyzer, which is associated with large birefringence. Figure 2a shows the birefringence difference for the 5CB LC over PMMAZO brushes, and the angle of the LC cells on the stage are fixed in order to obtain the maximum brightness. When the thickness of the PMMAZO brush layer is ultra-thin as 3.2 nm, the cell exhibits a dark state, indicating the homeotropic orientation in the cell. By increasing the thickness of the PMMAZO brush layer, a gradual transition from dark state of minimum film thickness to colored (state) associated with the larger birefringence of thicker films is observed. In order to quantify the change of anchoring by different film thickness, the tilt polar angle of the brush surfaces was calculated[20] from the measured retardance as shown in Figure 2b. The bare Si surface without any brush grafted shows 84° of polar angle as the planar anchoring. Once a very thin layer (~3 nm) of side chain mesogen brush is grafted onto the Si surface, the polar angle is dramatically dropped to almost 0° behaving as the homeotropic anchoring. Then after the 5.3 nm film thickness transition point, the polar angle appears to begin to vary linearly with film thickness.

A histogram distribution was performed on the contact angle measurements with water on all different film thicknesses (Fig. 2c), showing the average value was ~73.0 degree with a standard deviation of 0.7 degree. The tight distribution of contact angles indicates that the chemistry and wettability of the films are all the same when not swollen in nematic solvent. The different anchored behaviors could be attributed to the different grafting densities of polymer brush, which associated with the film thickness. The different grafted density determines the stretched direction of polymer chains, and therefore the orientation director of side chain mesogens, which are the reason to induce 5CB to anchor homeotropic or planar on the brush surface.

The radius of gyration can be used to define the conformation of a grafting polymer chain[21]. In a mushroom conformation, the polymer chains do not cover the whole surface, and the substrate effects may take over the anchoring behavior. This occurs when the polymers are spaced farther apart than 2 R_g, or when the reduced grafting density Σ is less than 1. When the polymers are attached within 2 R_g of each other, or $1 < \Sigma < 5$, the polymers become a brush. As the polymers become closer, and Σ increases to 5 or greater, a highly stretched brush forms. The radius of gyration was computed from the following equation[22]:

$$R_g = \sqrt{\frac{C_\infty n l}{6}} \qquad (1)$$

where C_∞ is the characteristic ratio of the polymer (8 for PMMAZO)[21], n is the number of C-C bonds in the polymer backbone (n=559), and l is the length of a single C-C bond (l=0.154 nm). So the R_g of PMMAZO here is 10.7 nm.

Grafting densities were computed from the ellipsometric thicknesses using the following equation[21]:

$$\sigma = (h\rho N_A 10^{-21})/M_n \qquad (2)$$

where h is the ellipsometric film thickness, ρ is the density of the polymer (1.25 g/mL for PMMAZO), N_A is Avogadro's number, 10^{-21} is a conversion factor, and M_n is the molecular weight (110K for this sample of PMMAZO). So σ is the grafting density, representing the number of chains per unit area. For the film thickness range that we tested here (3.2 nm ~ 13.5 nm), the polymer brush grafting densities ranged from 0.0219 to 0.0924 chains per nm^2, which means the polymer brush extends from 45.7 nm^2 per chain at the lowest density to 10.8 nm^2 per chain at the highest density by using the reciprocals of the grafting densities to compute the area per chain.

Based on the above calculated radius of gyration R_g and grafting density σ, the reduced grafting density (Σ) of the brush[23], calculated from the following equation, is between $\Sigma = 7.89$ to $\Sigma = 33.3$. Both of the lowest and highest reduced grafting densities are greater than 5, which indicates that all films are in the stretched polymer brush regime and the polymer brushes become closer as the film thickness increased.

$$\Sigma = \sigma \pi R_g^2 \qquad (3)$$

The densities at which the anchoring was completely homeotropic were from 0.0219 to 0.0294 chains per nm^2, or from 45.7 to 34.0 nm^2 per chain. This corresponds to a reduced grafting density from $\Sigma = 7.89$ to $\Sigma = 10.6$, meaning that even in the completely homeotropic anchoring regime with the lowest attained grafting densities, the PMMAZO was in the stretched brush conformation, screening any surface effects. As shown in Figure 2, clean Si surface will anchor 5CB planar to the surface with polar angle 84°, with a thin layer of PMMAZO brush the 5CB molecules were screened from the bare surface anchoring effects, giving exactly the opposite anchoring behavior.

Therefore, the expected molecular configuration in the LC cells is illustrated in figure 3. In the low-density condition, the polymer is lying on the silicon surface (figure 3a). The mesogenic groups align perpendicular to the surface, and 5CB molecule obeys their direction. The optical view of a low-density brush LC cell is dark under the crossed nicols setting, and cross pattern emerges in the conoscopic view. These optical images of figure 3a show that homeotropic alignment is obtained on the low-density brush surface. As mentioned before, solid substrate is completely covered by PMMAZO layer, even in the lowest density condition. When the polymer density increases, the main chains start to stretch perpendicular to the solid substrate due to their repulsive interaction. The molecular configuration of the high-density state is schematically illustrated in figure 3b. Since the mesogenic groups orients perpendicular to the main chain on average, 5CB molecules align parallel with the substrate. The optical images of the high-density brush LC cell are consistent with the anchoring model. The tilting states are described as the intermediates between low- and high-density state.

Compared to the main chain LCP brushes, the side-chain LCP brushes show a better miscibility with low molecular weight nematic compounds[11]. Such a side chain LC polymer brush layer will be miscible with the nematic medium resulting in extending. The extending behavior of PMMAZO brush layers in 5CB was measured by surface forces apparatus (SFA)[24, 25]. By using SFA, surface force is measured as a function of the distance, D, between two surfaces in the crossed cylindrical geometry. The measured force $F(D)$ is normalized by the curvature radius of the surface (R) based on the Deljaguin approximation[26], $F/R = 2\pi G_f$. Here, G_f is the free energy of interaction per unit area between flat surfaces. Figure 4a shows profiles of surface force between surfaces modified with PMMAZO layers of low grafting density. As a reference, we measured the dry distance d_0, to be 26.2 nm between two PMMAZO layers without 5CB. The dry distance d_0 corresponds to twice of the dry thickness of PMMAZO layers, indicating the dry thickness of PMMAZO layer here is 13.1 nm. Subsequently, nematic 5CB was injected between the surfaces as a solvent, and the system was equilibrated for 24 hours before the first measurement. As shown in Figure 4a, a repulsive force appears at the distance d of 72.0 nm upon the first approach. Here, the distance d corresponds to the position where the PMMAZO layers on the opposite surfaces start to overlap, which doubles the thickness of the extended PMMAZO layers. After repeating the measurement for several times, the distance d starts to decrease and becomes constant after 5 cycles. In order to avoid the effect of hysteresis of cycles, the result of the 1st run is used for discussion. By decreasing distance D, the repulsion force gradually increases at the beginning and then grows dramatically. Eventually, the separation distance is practically constant with further increasing applied load; the minimum value of such separation distance shifts to smaller number after repeating the measurement for 5 times, and finally becomes constant. During this process, the polymer chain on the surfaces slowly squeezes out the LCs and reaches to equilibrium state under the applied load. We call this minimum distance of the 5th run as "hard wall distance (Hw)". In figure 4a, the value of Hw is defined to be 33.4 nm (Table 1), which is slightly larger than the dry thickness d_0.

That means during the repeating force measurements, almost all of the LC molecules are squeezed out of the brush layers but the removing isn't perfect.

The force profile on high grafting density surface is shown in figure 4b. The dry distance d_0 is 49.6 nm, which is approximately twice of the low grafting density case, so the dry thickness of high grafting density layer is 24.8 nm. 5CB was injected and the system was also equilibrated for 24 hours. In the 1st experiment after the equilibration, repulsive force appears at the distance d of 144.2 nm. Therefore, the maximum polymer extension is estimated to be 72.1 nm from the surface. This value is consistent with the average fully stretched length of PMMAZ chain, 70.2 nm. The small amount of long chain could be due to the molecular weight distribution contributing to the thickness[27]. From table 1, the difference between d and d_0 is around 90 nm in the high grafting density layer, which is much larger than the low grafting density case (50 nm). However, the ratio d/d_0 is very close in both cases, indicating the distance of polymer extension in LCs is proportional to the initial dry distance. When the measurement was repeated, the hard wall distance Hw reduced from the 1st approach as 61.8 nm to 52.2 nm of the 5th run and kept constant since the 4th measurement.

Therefore, 5CB acts as a good solvent for PMMAZO brush to allow the polymer chain extension in the LC system for both low- and high grafting density cases. The repulsive force appeared distance d and hard wall distance Hw of the high grafting density case are larger than those of the low grafting density surfaces, indicating the PMMAZO main chain with high grafting density extends more perpendicular away from the solid surface compared to the low grafting density case. This fact directly supports the molecular conformation illustrated in figure 3a and 3b about the polymer extending states in the 5CB.

The thickness of the low and high grafting density layer shown in figure 4 are 13.1 nm and 24.8 nm, respectively, which obtained as a half of the dry distance in surface force measurement. The thickness of PMMAZO obtained in the surface force measurement is significantly larger than those in figure 2, which are 3.2 nm and 13.5 nm, respectively. The roughness of the silica layer (5 μm in thickness) used in this work is 6.5 nm in RMS, considering as the reason for the large thickness difference. When the thickness of silica layer is reduced to 2 μm, the RMS value is usually ca. 0.65 nm which is much smaller than the current condition. We hope to reduce the influence of larger RMS from the silica substrate in the near future by reducing the silica thickness and achieve better agreement with thickness obtained from silicon wafer surface. The orientations of 5CB anchored by the high and low grafting density polymer brush surfaces on the silica are consistent with those on the silicon surface, indicating the grafting ability of PMMAZO brush is identical on both surfaces. The repulsive force in the figure 4 appears around $d > 70$ nm, while the RMS of roughness is estimated to be 6.5 nm in the system. The polymer conformations are discussed based on the distance where the repulsive force appears. Therefore, we expect that the effect of roughness can be negligible in our case.

The results of surface force measurement illustrate the conformation of the polymer chain depending on the polymer density as shown in figure 3. Furthermore, we consider the reason of the polymer chains changing their configuration through estimating entropy.

The free energy of polymer brush in a solvent was discussed previously based on the mean field theory.[28, 29] Based on that, a region on the surface which includes only one polymer chain is picked up for the calculation. The volume of the region is defined as $V = Ad/2$. Here $A = 1/\sigma$ is the area occupied by one polymer, and $d/2$ is the maximum length of PMMAZO chain extending in 5CB. Entropy S is calculated by equation (4):

$$S = -k_{\mathrm{B}} N_{5\mathrm{CB}} \ln \phi_{5\mathrm{CB}} = -k_{\mathrm{B}} \frac{V - V_{\mathrm{P}}}{V_{5\mathrm{CB}}} \ln \frac{V - V_{\mathrm{P}}}{V} \qquad (4)$$

In equation (4), k_{B} is the Boltzmann constant, $N_{5\mathrm{CB}}$ is a number of 5CB molecules in the volume, $\phi_{5\mathrm{CB}}$ is a volume fraction of 5CB, V_{P} and $V_{5\mathrm{CB}}$ are the volume of PMMAZO and 5CB respectively. Because only one polymer chain is considered for the calculation, the equation could be simplified as above. The PMMAZO chain is considered to be a flexible cylinder with radius 1.25 nm and length 70.2 nm. The value of V_{P} is estimated to be $V_{\mathrm{P}} = 344.6$ nm^3. In the same way, the 5CB molecule is considered as a cylinder with radius 0.20 nm and length 1.6 nm. The volume of 5CB molecule is $V_{5\mathrm{CB}} = 0.21$ nm^3. When the polymer main chain stretches in the x-y plane, $V = 1.65 \times 10^3$ nm^3 are obtained from results of low density surface ($A = 45.7$ nm^2 and $d/2 = 36.1$ nm). The S value is estimated to be 2.0×10^{-20} J/K in this situation. On the other hand, the polymer chain extends along the z-direction in the high-density case. The volume V is 803 nm^3, here $A = 10.8$ nm^2 and $d/2 = 74.2$ nm is used for the calculation. The entropy is estimated to be $S = 1.7 \times 10^{-20}$ J/K. The system has slightly larger entropy when the main chain stretches in x-y plane. It is more favorable for a single polymer chain to lie on the Si surface as shown in figure 3a. However, the polymer chain prefers to extend in the x-y plane only under the low grafting density condition. In the high-density case, due to the repulsive interaction from neighboring polymer chains, the polymer chains are forced to extend perpendicular to the Si surface. In this way, the chain conformation of PMMAZO has been changed as shown in the figure 3. Here the entropy is roughly estimated based on the mean field theory. Some additional factors, including overlap of polymer chains, initial state of calculation and molecular interaction between mesogenic part and 5CB, have to be considered for more detailed discussion.

Conclusion

In this study we showed gradual anchoring transition of nematic LCs from homeotropic to planar over large areas by changing the grafting density of polymer brush on solid surface, which included azobenzene mesogenic groups in the side chains attached to the polymethacrylate main chain. The alignment of LC molecules is the result of the joint interaction among the mesogen side chains of the polymer brush, the nematic molecules and the extending behaviors of LC polymer brush in the nematic medium. The mesogenic groups are preferentially aligned perpendicular to the main chain, while the stretching director of the main chain surrounded by nematic medium is controlled by the brush grafting density. Both of these two factors contribute to the orientation of the adjacent nematic medium and also to the forming an alignment layer. The out-of-plane polar angle of 5CB on brush layer gradually changes from ~0° to ~62° by simply increasing the grafting density of the polymer brush from 0.0219 to 0.0924 chains per nm^2. For the first time, the extending chain conformations of the LC polymer brush in good solvent, nematic medium, was investigated by surface force apparatus (SFA). The extending direction of PMMAZO chain in the good solvent depended on the grafting brush density: polymer chain expanded perpendicular to the silica substrate with high density surface, while on the other hand, the chain extended in the narrow region around the surface at the low-density case.

Experimental section:

Materials. The thermotropic 4-pentyl-4'-cyanobiphenyl (5CB) liquid crystal was used for the experimental and theoretical analysis. 5CB exhibits a nematic phase between 24 and 35^{o}C. It was purchased from Sigma-Aldrich and used without further purification. Octadecyltrichlorosilane (OTS), heptane, chlorobenzene, isopropyl alcohol (IPA) and dichloromethane (DCM) were purchased from Sigma-Aldrich and used without further purification. Glass microscope slides were purchased from Fisher Scientific in the finest premium grade.

PMMAZO brush synthesis. The monomer, 6-(4-methoxyazobenzene-4'-oxy) hexyl-methacrylate (MMAZO), was synthesized according to the procedure described by Stewart and Imrie[30]. It was then polymerized by nitroxide-mediated controlled radical polymerization (NMP). Specifically, a mixture of initiator NMP (0.0244 g, 0.075 mmol) and MMAZO (2.3160 g, 6 mmol) was degassed by three freeze-thaw cycles. The mixture was heated at 120°C for 24 h in a nitrogen atmosphere. The resulting polymer was dissolved in THF and then precipitated in petroleum ether. The average molecular weight was around 110 000g/mol.

Preparation of PMMAZO brush chemical patterns. A 3.2-13.5 nm thick PMMAZO film was deposited on an oxygen-plasma cleaned silicon substrate by spin-coating from a 0.05-1.0 wt% toluene solution and annealed at 250^{o}C for 5 min under nitrogen atmosphere. During the annealing, hydroxyl groups in PMMAZO reacted with the silanol groups of the native oxide through a dehydration reaction, forming a brush layer on the substrate. Non-grafted PMMAZO was removed by sonication in chlorobenzene and the remaining PMMAZO brush was around 3.2-13.5 nm.

Preparation of optical cells. The glass microscope slides were boiled in a piranha solution (7:3 (v/v) of 98% H_2SO_4/30% H_2O_2) for 30 min, to remove any stains on the surface, washed with deionized water and dried with nitrogen. The cleaned glass slides were immersed in a mixture of 13.8 μL OTS and 120 ml heptane. After 30 min, they were removed from the OTS solution, washed with DCM several times and quickly dried under a nitrogen flow. The OTS glass and the Si substrate with the PMMAZO substrate were placed face-to-face, with a 1.5 μm spacer, to create a cell. The optical cell and the LC were heated above the clearing point and 5CB was injected through capillary action. The system was then slowly cooled down to room temperature.

Characterization. The thickness of the PMMAZO brush was measured by a Woollam VUV-VASE32 variable angle spectroscopic ellipsometer. The morphologies of the polymer brush were inspected with atomic force microscopy (AFM). The optical images of the LC cell were obtained with a BX 60 Olympus polarized light microscope.

Surface force measurement. The surface forces measurement was performed using the home-built surface forces apparatus (SFA) at Kurihara laboratory[31, 32]. Two cylindrical disks with curvature radius $R = 0.02$ m were used for this measurement as substrates. The disks were coated with silica layer for grafting PMMAZO. The details of the procedure were shown in a reference[33]. In short, chromium and gold layers were deposited on the disc surfaces by vapor deposition (the thickness are approximately 5 nm and 40 nm, respectively). The silica layer was then prepared on the gold surface by sputtering process and annealed at 600℃ for 2 hours. These disks were treated by piranha solution (7:3 (v/v) of 98% H_2SO_4/30% H_2O_2) for 30 min at room temperature to add the hydroxy groups to the silica surface. These disks were mounted on the SFA chamber with crossed cylindrical geometry. The bottom disc is supported by the double cantilever springs with spring constant k ~ 200 N/m and driven by a pulse motor. The thickness of silica was measured by fringes of equal chromatic order (FECO) at a resolution of 0.1 nm. White light was used for the measurement. The value of silica thickness was typically 5 μm.

These silica surfaces were coated by 1 wt% and 0.05 wt% of PMMAZO chlorobenzene solutions by spin coating process (4000 rpm for 60 s). After annealing (250℃ for 5 min in N_2 atmosphere) and sonication in chlorobenzene, we obtained high and low density of PMMAZO surfaces respectively. The procedure after spin coating was the same as the case of silicon wafer.

Two surfaces with the same grafting density were mounted on the SFA. The distance between two surfaces was measured by FECO on a monochrometer (OPS-500T, OLE Systems), which was was recorded for every 0.5 s through a CCD camera (Neo 5.5 sCMOS, ANDOL) mounted on the equipment. The distance between surfaces and motor speed (~11 nm/s) were obtained. The surface force, $F(D)$, was calculated as a function of the separation distance, D. First measurement was held in dry condition without 5CB. Thickness of dry PMMAZO layer was measured by this experiment. After the measurement in dry condition, a droplet of 5CB (~ 10 μL) was injected between the top and bottom surfaces. After 24 hours, surface force was measured under the swollen condition. Approaching and separating process was repeated for 5 times (shown as day1_1st and 5th). The same experiments were repeated for 3 times on the different surfaces.

Figures and captions:

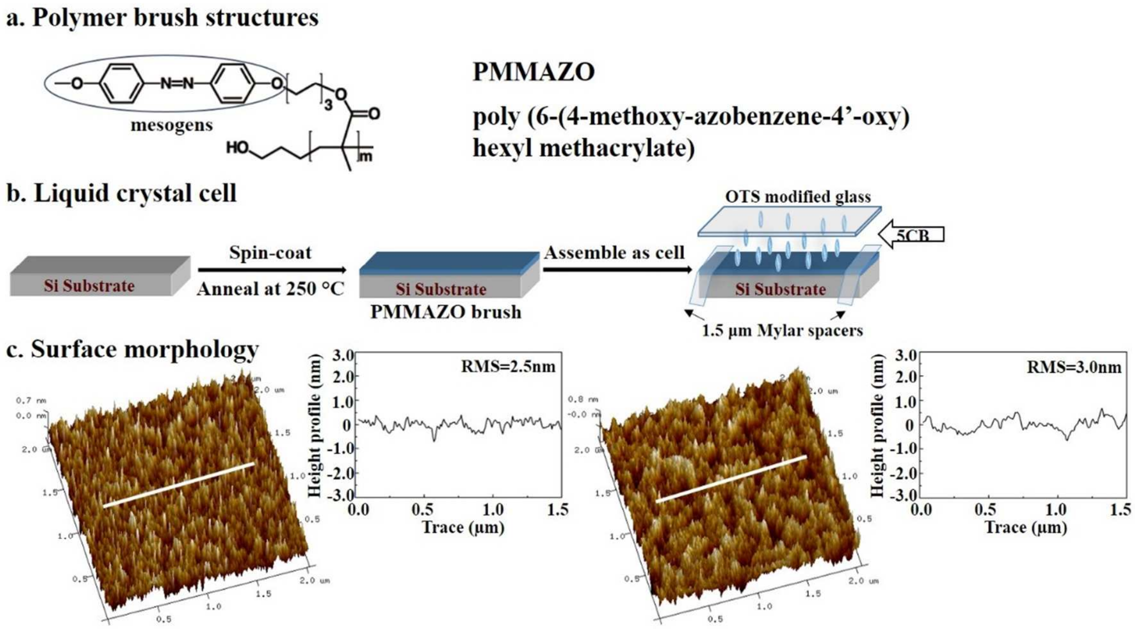

Figure 1. Illustration of materials and LC cell process. (a) The chemical structure of PMMAZO containing the azobenzene mesogen, which, after forming a brush layer, induces the homeotropic/planar anchoring of 5CB by different grafting density on the substrate. (b) Schematic representation of the fabrication process to create liquid crystal cell by PMMAZO brush substrates, OTS modified glass and spacer in between. The 5CB was injected into the cell by capillary action. (c) 3D topographic AFM images and their corresponding height profiles of pure PMMAZO brush layer of low grafting density (left) and high grafting density (right).

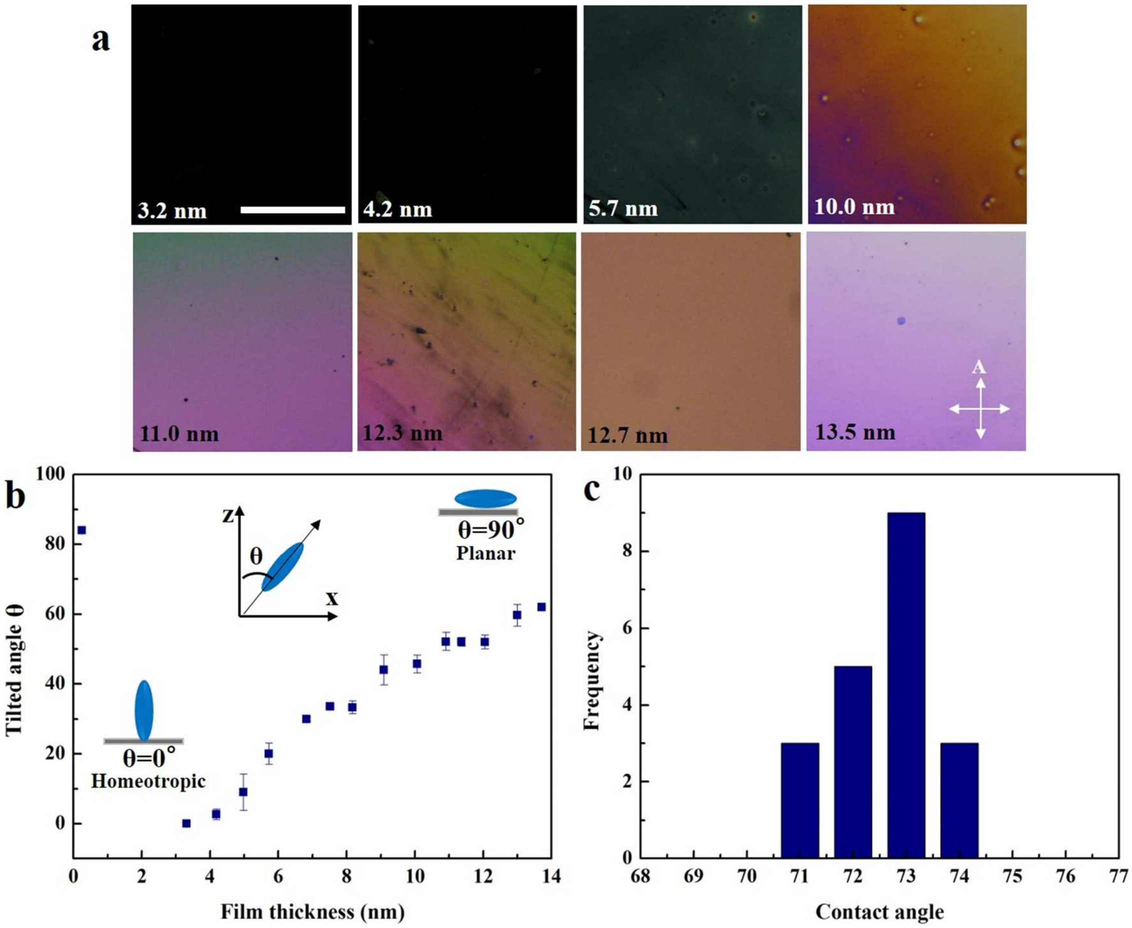

Figure 2. Reflective light microscope images of the 5CB cell under crossed polarizers. (a) The anchoring behavior of different film thicknesses or grafting density are shown with PMMAZO brush layer. The crossed polarizers are marked. The scale bar is 500 µm. (b) The tilted angles of 5CB on different grafting density brush surface of PMMAZO brush layer. (c) The contact angle distribution was measured based on PMMAZO brush layer with different grafting density.

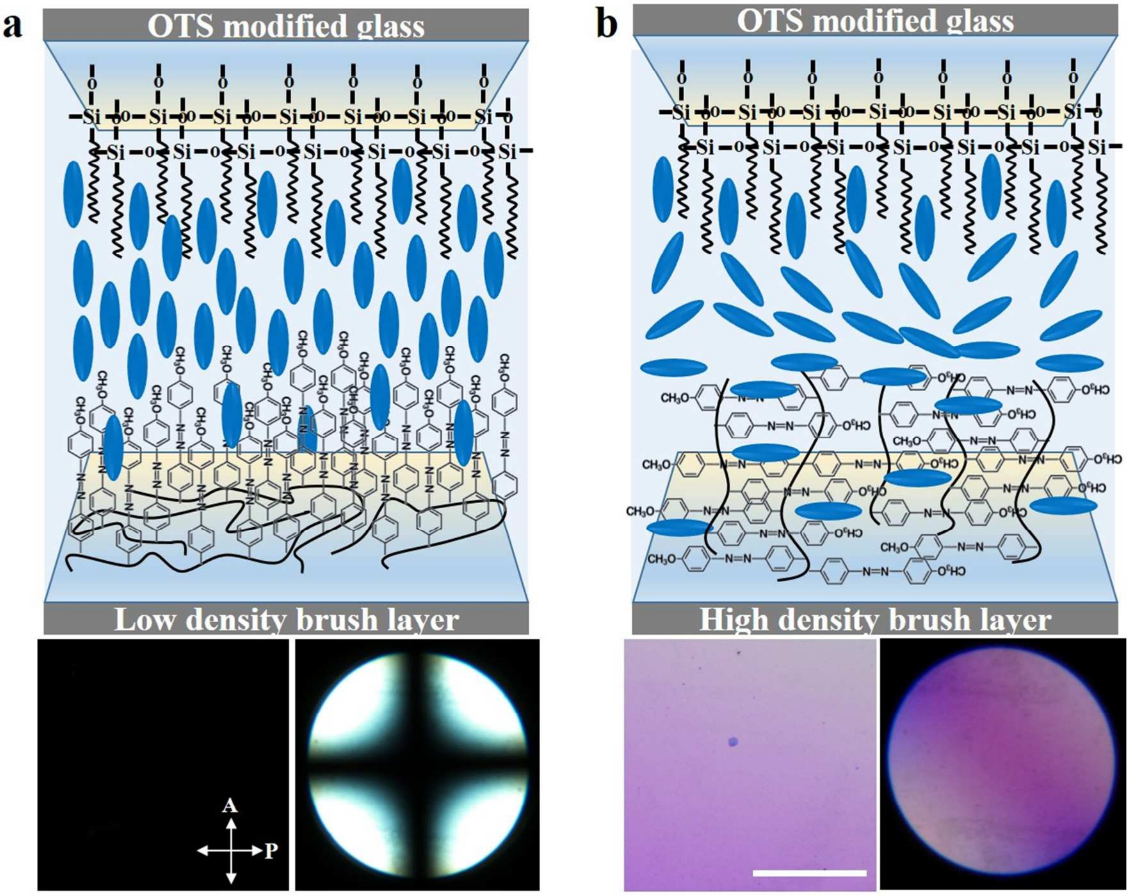

Figure 3. Schematic illustrations of the 5CB alignment on (a) homeotropic anchoring substrate by grafting low density of PMMAZO brush, and (b) planar anchoring substrate by grafting high density PMMAZO brush. The corresponding crossed polarizers images and conoscopic images are shown at the bottom. The crossed polarizers are marked. The scale bar is 500 μm.

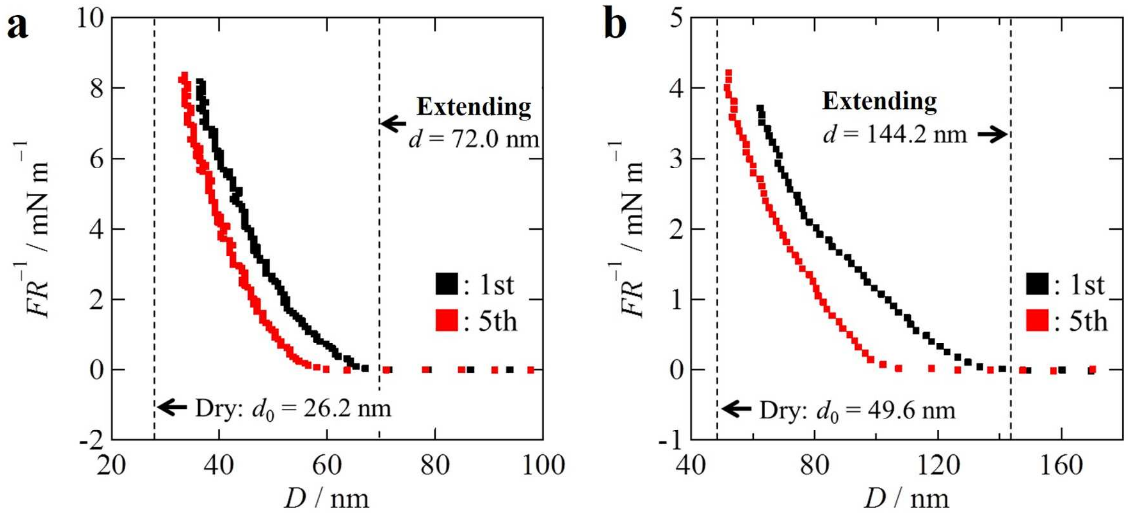

Figure 4. Surface force is plotted as a function of distance, measured by SFA. Two graphs represent the results of (a) low grafting density and (b) high grafting density. Dry distance is the thickness of PMMAZO layers without 5CB (dry condition). Extending distance is defined as the position where the repulsive force starts to take hold. Here the dry distance is 26.2 nm and extending distance is 72.0 nm in (a). Dry distance is 49.6 nm and extending distance is 144.2 nm in (b).

Solvent	**PMMAZO thickness**	d_0**(nm)**	d**(nm)**	**Hw(nm)**	d/d_0
5CB	**LD**	**24.7(±1.7)**	**72.2(±6.6)**	**33.9 (±3.1)**	**2.1**
	HD	**56.1(±6.5)**	**148.4(±15.8)**	**69.1 (±8.9)**	**2.6**

Table. 1 The thickness of PMMAZO layer in dry condition and in 5CB. They are the average of three experimental data including the results on figure 4. HD and LD represent the results for high density and low density PMMAZO layer respectively. The d_0 is the distance in dry condition (dry distance), d is the maximum thickness on 1st experiment at 24 hours after 5CB injection (extending distance), and Hw is the hard wall thickness on 1st run. The ratio d/d_0 is approximately the same in both cases. All experimental results are contained in the range shown in the brackets. These errors are less than 15 % of the averaged values of d_0, d and Hw.

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Notes

The authors declare no competing financial interests.

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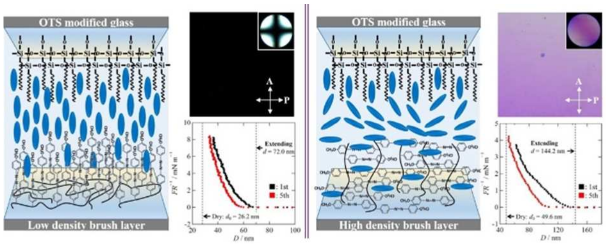

Using liquid crystalline polymer brush to continuously control the anchoring transition of 5CB by simply varying the brush density.