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Highly Ordered In-Plane Photoalignment Attained by the Brush Architecture of Liquid Crystalline Azobenzene Polymer

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ABSTRACT: We newly prepared liquid crystalline (LC) polymer brushes containing an azobenzene (Az) mesogenic moiety on a quartz or silicon substrate by surface-initiated atom transfer radical polymerization (ATRP). The grafted chain length was controlled by polymerization time and initial monomer concentration. The grafted chain film adopted a smectec LC phase and the molecular orientation of Az mesogens in the grafted chain was nearly parallel to the substrate plane. The in-plane photo-orientation behavior of LC polymer brushes was evaluated by polarized UV−vis absorption spectoscopy and grazing incidence X-ray diffraction measurements. Highly ordered in-plane photoalignment of Az mesogens in the grafted chain was readily provided by the irradiation with linearly polarized visible light due to the effective light absorption of the Az mesogens aligned parallel to the substrate. The highest degree of in-plane orientation was generated at a temperature slightly above T_g of the polymer. As a result, monodomain LC polymer films were readily obtained by the linearly polarized light irradiation.

1. Introduction

The photoinduced optical anisotropy in polymer films has been extensively studied from fundamental interest in polymer physics and also from the practical viewpoints of the applications to optical data storages and processing.[1−4] The optical anisotropy is induced by irradiation with linear polarized light (LPL) to a polymer film. The reorientation of azobenzene (Az) is caused by repeated photoisomerization to provide the orthogonal orientation of the chromophores to the polarization plane of the light. Stumpe et al.[5−7] reported that the storage stability of photoinduced optical anisotropy in spin-coated films and Langmuir−Blodgett multilayers[8] of liquid crystalline (LC) polymers bearing an Az mesogenic group in the side chain. They found that, in spin-coated films, the photoinduced optical anisotropy is enhanced by thermal annealing above the T_g. Han and Ichimura studied of the photomanipulation of two- and three-dimensional orientations of LC Az polymers by irradiation with 436 nm LPL,[9] nonpolarized 436 nm light,[10] and polarized 365 nm light.[11] Recently, attempts to photoalign the microphase separation structures of LC block copolymers, i.e., the hierarchy of larger feature size, have been made in this principle.[12−14] All these film systems so far investigated are prepared with “free” polymers by conventional processing means such as spin-casting and the Langmuir−Blodgett technique.

For the study of functional polymer thin films, on the other hand, brushes have currently constituted fascinating and prominent research areas. Polymer brushes are defined as dense layers of end-grafted polymer chains confined to a solid surface or interface.[15] High-density and well-defined polymer brushes have been synthesized by utilizing surface-initiated “living” polymerization techniques such as atom transfer radical polymerization (ATRP).[16−21] Since various functionalized monomers are tolerable in the ATRP method, many types of polymer brushes have been explored introducing the ionic groups,[22,23] thermoresponsive molecules,[24,25] photofunctional units,[26,27] electrochemical units,[28] and LC groups.[29] Such polymer brushes show deviated properties in various aspects such as the thermophysics,[30] tribology,[31−33] adhesion,[34] wettability,[35] and crystallization process.[36]

In the above contexts, the preparation of photoresponsive LC polymer brushes containing a photoresponsive Az mesogenic group in the side chain by using the surface-initiated grafting polymerization seems to be an alluring approach in view of the creation of new photofunctional smart surfaces. Our recent work has shown the successful synthesis of the Az LC polymer brushes on a solid substrate.[37] The brush films essentially possess the identical thermotropic LC properties as for cast films of a polymer of the identical chemical structure, whereas the molecular and smectic layer orientations are thoroughly different. Such unique orientation features are anticipated to provide different photoresponsive properties.

In this article, we report the detailed synthetic procedures and the orienting properties of the Az LC brushes induced by the LPL. The photoinduced orientation of the mesogenic groups and the smectic layer are investigated by means of UV−vis absorption spectroscopy and grazing-incidence X-ray diffraction (GI-XRD) measurements. It is demonstrated here that highly in-plane ordered structure and orientations that are not obtained in a conventional cast film are realized in these end-grafted polymer brushes.

2. Experimental Section

2.1. Materials. The synthesis rout is shown in Scheme 1. All reagents for the syntheses were purchased from TCI Inc., Aldrich Co., and Kanto Kagaku. Copper bromide (CuBr) was washed with acetic acid and diethyl ether for several times and dried in vacuum.[38,39] Tetrahydrofuran (THF) and toluene were dehydrated by distillation over sodium in the presence of benzophenone. Other compounds were used without further purification. The Az chromophore containing an methacrylate monomer, 4-(10-methacryloydecyloxy)-4′-pentylazobenzene (5Az10MA), was synthesized according to the method previously reported.[40−42] The homopolymer of 5Az10MA ($M_n = 9800$, $M_w/M_n = 1.14$) was obtained by the ATRP method as described previously.[37] This polymer shows the thermal transitions as glass−51 °C−smectic A−108 °C−isotropic.[37] The spin-cast films were obtained from a toluene solution after rotation at 2000 rpm for 30 s.

2.2. Measurements. ^{1}H NMR spectra were recorded on a JEOL 270GXS instrument spectrometer using tetramethylsilane as the internal standard for deuterated chloroform solutions. The melting point (uncorrected) was measured with a Yanaco MP-S3 melting-point apparatus. Molecular weight and polydispersity of the

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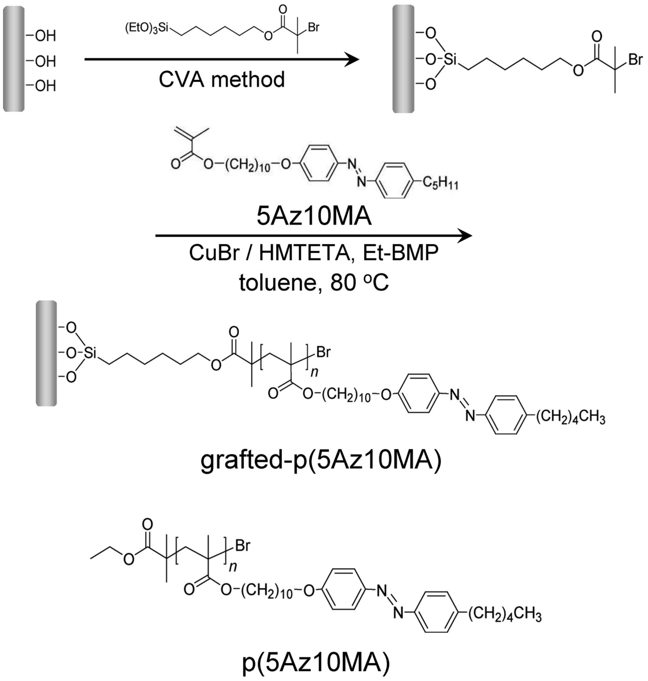
Scheme 1. Synthetic Procedures of Liquid Crystalline Polymer Brushes Bearing Az Moiety on Substrate by Surface-Initiated ATRP (Grafted-p(5Az10MA)) and the Structure of the Free Polymer of the Identical Structure (p(5Az10MA))



polymers were evaluated by gel permeation chromatography (GPC) using a Shodex liquid chromatography system calibrated with standard polystyrenes. THF was used as an eluent at a flow rate of 1.0 mL/min. X-ray photoelectron spectroscopy (XPS) was measured by ESCA-3300 (Shimadzu Corp.) to confirm the formation of the initiator monolayer on the substrate surface. All binding energies were referenced to Si 2p at 99.34 eV. Atomic force microscopy (AFM) was carried out on a SPA400/SPI3800N system (Seiko Instruments) for the observation of surface morphologies of initiator-modified substrates and roughness. The static contact angle was measured with a FACE CA-XP (Kyowa Interface Science). The data of contact angle were determined by averaging the data of five measurements. Layer thickness was measured by an ellipsomater (Philips PZ2000) equipped with a He−Ne laser (632.8 nm). The incident angle was 70°. The refractive index of the graft layer was assumed to be 1.561, the identical value for a spin-cast film. GI-XRD measurements were performed with a Rigaku NANO Viewer operating with Cu $K\alpha$ radiation (0.154 nm). Their scattering profiles were recorded on an imaging plate.

2.3. Immobilization of ATRP Initiator on the Substrate. A silane coupling reagent for the ATRP initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE), was synthesized according to the previous literature.[43] The BHE-modified substrate (quartz or silicon wafer) was prepared by the chemical vapor adsorption (CVA) method.[44−46] Quartz plates (1 cm × 1.5 cm) were washed with a saturated potassium hydroxide ethanol solution, followed by washing with pure water under sonication. The static contact angle of water was 8 ± 2° (hydrophilic plates). Silicon wafer substrates (1 cm × 1.5 cm) were washed with acetone under sonication for 5 min. Both kinds of substrates were finally subjected to exposure to UV ozone cleaning for 45 min (Nippon Laser & Electronics). Cleaned silicon wafer or quartz substrates were placed into a Teflon container. The container was sealed and placed in an oven maintained at 150 °C for 1 h. Then, a glass reservoir filled with BHE liquid (ca. 50 mg) was placed together and maintained at 150 °C for 3 h. BHE in the vessel was vaporized and reacted with the hydroxyl groups on the sample surface. Subsequently, the container was opened and maintained at 150 °C for another 1 h. The resultant substrates were dipped into dehydrated toluene and ethanol successively and washed in an ultrasonic bath for 5 min. Finally, the samples were dried under vacuum and stored in a nitrogen atmosphere.

2.4. Surface-Initiated ATRP. Typical procedures are as follow. 7 mg (0.05 mmol) of Cu(I)Br, 492 mg (1.0 mmol) of the Az containing monomer 5Az10MA, 1 mg (0.005 mmol) of ethyl 2-bromoisobutyrate as a free initiator, and 11.5 mg (0.05 mmol) of 1,1,4,7,10,10- hexamethyltriethylentetraamine as a Cu ligand were dissolved in 1.25 mL of dry toluene and purged with nitrogen gas. The mixture was then degassed by freeze−pump−thaw cycle three times. The initiator-modified quartz or silicon substrates were added in a polymerization solution and sealed in a glovebox. The flask was placed in the oil bath at 80 °C for several hours. After the polymerization procedure, substrates were washed with THF several times to remove unreacted monomer and the free polymer and then dried in vacuum at room temperature.

2.5. Photoinduced Orientation. UV−vis absorption spectra for the grafted substrates and spin-cast films at room temperature were taken with a Hewlett-Packard diode array spectrometer 8452A or an Agilent Technology 8453 spectrometer. To obtain polarized spectra, a polarizer was mounted in a rotating holder in front of the sample. The UV and visible light irradiation of the samples was performed using an Hg−Xe lamp (SAN-EI Electric UVF-203S) equipped with appropriate combinations of color filters (Toshiba glass: UV-35/UV-D36A and V-44/Y-43 for 365 and 436 nm light, respectively). LPL was obtained by passing through a polarizer. Light intensity was measured by an optical power meter (Advantest TQ8210). Temperature of the sample plate was controlled with a Mettler FP82HT.

3. Results and Discussion

3.1. Synthesis of Surface-Grafted Polymer Films. The silylation with a trifunctional silane compound onto a substrate in a solution phase often leads to a rough surface of the modifying layer due to the self-condensation reaction. The surface morphology and roughness should influence the property and orientation of the LC brush polymer film. To avoid this, the CVA method was adopted to prepare a smooth monolayered film of organosilane compound of the initiator.[45,46] The typical water contact angle of the silicon wafer surface or quartz plate one cleaned after the UV/O$_3$ treatment was smaller than 5°. In contrast, the contact angles after the modification with BHE by CVA were significantly increased and became more hydrophobic. The contact angles of water were 54.8° (silicon wafer) and 58.7° (quartz) when treated at 100 °C and increased to 70.8° (silicon wafer) and 66.1° (quartz) at 120 °C. These values do not indicate a satisfactory coverage, judging from the value reported in the literature (79°), for Br-terminated self-assembled monolayers (SAMs).[47,48] The full coverage was attained after the CVD treatment at 150 °C. The contact angles became 79.7° (silicon wafer) and 75.2° (quartz), which exactly agree with those of the reported values.[47,48] For this BHE-SAM on the silicon wafer, the AFM evaluation elucidated a flat surface morphology at a molecular level. The root-mean-square roughness (R_{rms}) in the scan area of 5 μm^2 was 0.83 nm. On the quartz surface, the R_{rms} became slightly larger ($R_{\text{rms}} = 1.8$ nm), probably reflecting the larger roughness of the bare surface of the quartz plate. XPS measurements revealed the formation of the initiator layer. The bromide 3d peak and the carbon 1s peak were observed in the narrow scan mode around 70 and 286 eV, respectively. The carbon 1s signals attributed to C=O and C−O bonds were also observed. These results are indicative of the formation of a BHE-SAM on the silicon wafer.

Figure 1a shows the absorption spectra of the grafted-p(5Az10MA) films on quartz obtained with the variations of polymerization time. The peaks around 244 and 340 nm were assigned to the $\phi-\phi^*$ transition of the aromatic ring[49] and $\pi-\pi^*$ long-axis transitions of the Az unit, respectively. A slight hypsochromic peak shift was observed for the $\pi-\pi^*$ absorption band from that in solution (352 nm), showing the partial

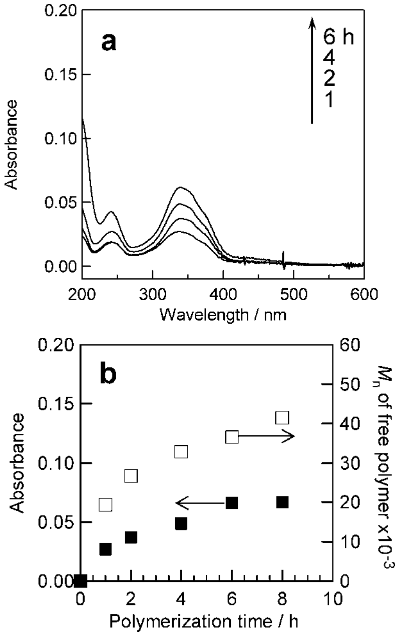


Figure 1. UV−vis absorption spectra of grafted-p(5Az10MA) at various polymerization times (a) and absorbance of grafted-p(5Az10MA) on a quartz plate (■) and M_n of the free polymers of p(5Az10MA) (□) with polymerization time (b). The reaction conditions were $[M]_0 = 0.5$ mol dm^{-3}, $[M]_0/[I]_0 = 200/1$.

formation of H-aggregate in the film. The spectra were not changed by repeated washing with THF, obviously indicating that the polymer chains were chemically tethered onto the substrate. The absorbance gradually enhanced with the increase in the polymerization time; however, the spectral features were unchanged in all cases. Figure 1b displays the plot of the M_n of the simultaneously polymerized free polymer of p(5Az10MA) and absorbance on the quartz plate at the peak top as a function of polymerization time. M_n value increased with the polymerization time and reached 4.0×10^4 after 8 h. The absorbance of the grafted-p(5Az10MA) also increased in the same fashion. In the above manners, the absorbance and the polymerization degree were almost saturated in 6−8 h.

Figure 2a displays the absorption spectra of the grafted-p(5Az10MA) films on a quartz substrate when the initial monomer concentration was varied in the polymerization process. Here, the polymerization conditions were the same for all samples ($[M]_0/[I]_0 = 200/1$, reaction time 12 h), except the monomer concentration. As shown, the absorbance constantly increased with the initial monomer concentration. Figure 2b shows the absorbance at the absorption maximum (λ_{max}, 340 nm) of the $\pi-\pi^*$ long-axis transition of Az as a function of the initial monomer concentration. A nearly proportional relationship was obtained between them, and the concentration of monomer was directly reflected to the chain length. The film thickness obtained at the initial concentration of 2.0 mol dm^{-3} was evaluated to be 20 nm from the ellipsometric and AFM measurements.

In the above manners, the grafted-p(5Az10MA) on the solid substrate were successfully synthesized by the surface-initiated ATRP, and the chain length was precisely controlled by the polymerization time and initial concentration of 5Az10MA monomer.

3.2. Effect of Grafted Chain Length on the Packing State of Az Mesogens.

As previously shown, the molecular orientation of LC Az units in the side chain adopted a nearly parallel orientation to the substrate for the film of ca. 20 nm thickness.[37,50] Since the chain length was successfully controlled, the effect of the grafted chain length on the packing and orientation of the Az mesogen was examined. The relative intensity of absorption at the peak of $\pi-\pi^*$ band (338 nm) to that of $\phi-\phi^*$ one (244 nm) can be a measure of Az mesogen orientation, since the $\pi-\pi^*$ transition is directional dependent while the $\phi-\phi^*$ transition is insensitive to the chromophore orientation.[49]

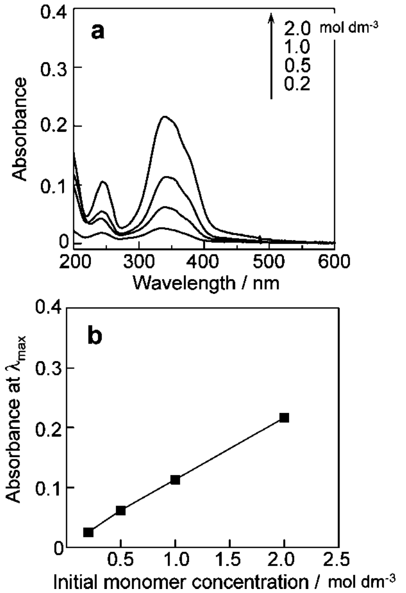


Figure 2. UV−vis absorption spectra of grafted-p(5Az10MA) on a quartz plate at various initial monomer concentrations $[M]_0$ (a) and the absorbance at λ_{max} as a function of $[M]_0$ (b).

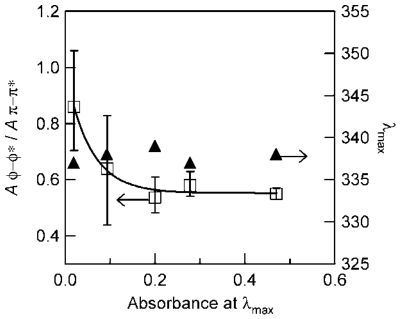
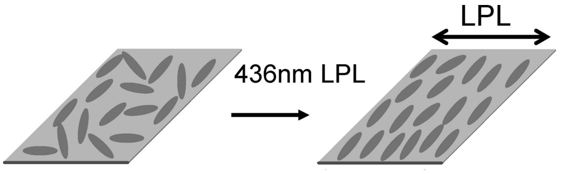


Figure 3. Molecular orientation parameter ($A_{\phi-\phi^*}/A_{\pi-\pi^*}$) and the aggregation parameter (position of λ_{max}) versus grafted chain length expressed as the absorbance at λ_{max} of grafted-p(5Az10MA).

Figure 3 shows the ratio of $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ and position of λ_{max} as a function of absorbance at λ_{max} of the grafted-p(5Az10MA). When the absorbance was 0.02, the $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ value was around 1.0. With increasing the absorbance above 0.2, the ratio reduced a saturated value of ca. 0.6. Above this length, the Az orientation is regarded to be unchanged. With respect to λ_{max} of the $\pi-\pi^*$ band, the spectrum essentially showed no shift at any chain length, indicating that the aggregation state is not altered by the change in the chain length.

With the above knowledge, mesogen orientations in the grafted chains were interpreted as follows. In the initial stage of polymerization, Az mesogens oriented randomly because the polymer chains were short and mesogens possess a higher flexibility and orientational freedom. This situation is implied by the large range of error bar. With increasing the length, the polymer chains start to orient perpendicular to the substrate because of a spatial confinement. Thus, Az mesogens are oriented preferentially perpendicular to the main chain, namely nearly parallel to the substrate plane.



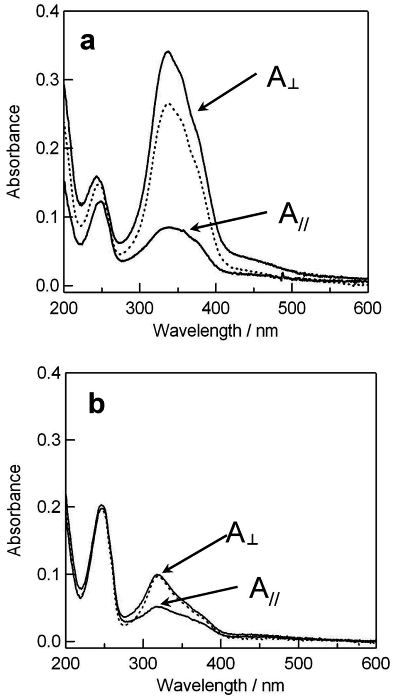


Figure 4. Polarized UV−vis absorption spectra of the grafted-p(5Az10MA) film (a) and the spin-cast film of p(5Az10MA) (b) before and after exposure to LPL at 436 nm at 60 °C. Dotted and solid lines are spectra taken with nonpolarized beam and polarized ones set perpendicular ($A_\perp$) and parallel ($A_{||}$) to the actinic LPL at 436 nm, respectively. The film thickness was ca. 20 nm for both cases.

In contrast, such thickness dependency was not observed in spin-cast films of the identical free polymer (data not shown). The relationship between the ratio of $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ and the absorbance at $\lambda_{\max}$ (Figure 3) stayed constant for all thickness investigated (thickness: 10−50 nm). It is thus concluded that the parallel molecular orientation of Az groups in the surface-grafted chain system is attained only by anchoring the one terminal onto the substrate.

3.3. Irradiation with LPL. *3.3.1. Photoinduced Dichroism.* Figure 4 shows polarized UV−vis absorption spectra of the grafted-p(5Az10MA) (20 nm thickness) (a) and the cast film of p(5Az10MA) (b) before (dotted line) and after irradiation (two solid lines) with LPL at 436 nm at 60 °C. Before irradiation, no in-plane anisotropy was recognized at the macroscopic level of spectroscopic measurements. Probably, the mesogens are aggregated to form a polydomain structure. The absorbance of the $\pi-\pi^*$ transition band observed with the polarized light set orthogonal to the electric vector (E) of the actinic LPL ($A_\perp$) became significantly larger than that in the parallel direction ($A_{||}$). The level of photoinduced in-plane optical anisotropy of films was evaluated by the order parameters (S) of the Az in the following equation: $S = (A_\perp - A_{||})/(A_\perp + 2A_{||})$, where $A_\perp$ and $A_{||}$ denote absorbances at $\lambda_{\max}$ (=338 nm) obtained by measurements using polarized light with E perpendicular and parallel to that of actinic polarized light. S reached ca. 0.5 in the grafted polymer film.

For a spin-cast film, annealing at the LC temperature also brought about the perpendicular orientation of Az mesogens with respect to the substrate plane, which can be confirmed by the significant reduction of absorbance of the $\pi-\pi^*$ band. Since the mesogens were oriented preferentially the out-of-plane direction, LPL irradiation at 436 nm induced only a small degree of in-plane dichroism at the same temperature of 60 °C although an excess exposure dose of 2 J cm^{-2} was applied (b, $S = 0.24$). This value is almost in agreement with those for other smectic LC polymers reported ($S < 0.1$).[10] Thus, the in-plane (parallel) mesogen orientation for the grafted-p(5Az10MA) enhances the probability of LPL absorption by the Az groups, which will then cause the large in-plane anisotropy.

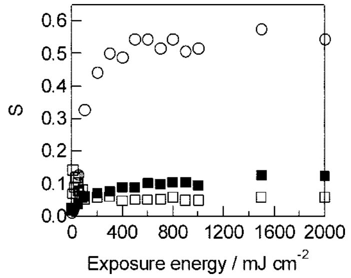


Figure 5. Changes in the order parameters (S) of the grafted-p(5Az10MA) film of 20 nm thickness during irradiation with LPL at 436 nm at room temperature (■), 60 °C (○), and 100 °C (□).

In the above manners, there are essential differences in the degree of in-plane orientational control between the surface-grafted Az polymer film and the spin-cast one. This fact indicates the significant role of the polymer architecture in the film, i.e., free or anchored to the substrate. Since the light irradiation is ordinarily achieved with normal incidence to the substrate, the surface-grafted Az polymer film becomes more sensitive to LPL.

3.3.2. Effect of Temperature. It is known that annealing of spin-coated films of side-chain LC polymers leads to a marked enhancement of the optical anisotropy by LPL.[6] Han et al.[10] reported that S of spin-cast films of smectic LC Az polymers were increased and reached 0.2 at smectic LC temperatures. It should be of importance to comprehend the alignment behavior at various temperatures.

The grafted-p(5Az10-MA) films were exposed to LPL at 436 nm at room temperature, 60 °C, and 100 °C, which correspond to the temperetures below T_g (51 °C), slightly above T_g, and near the isotropidization temperature (105 °C) of p(5Az10-MA), respectively. The change in S with exposure energy is indicated in Figure 5. At room temperature, S value increased at an early stage of irradiation and reached a saturated level at ~200 mJ cm^{-2}. The induced in-plane anisotropy was low as below $S <$ 0.1. The evaluation of S at elevated temperatures of 60 and 100 °C was performed by exposure to LPL at the given temperature followed by immediate cooling to ambient temperature for the absorption spectral measurement. The profile of S at 60 °C exhibited a rapid and drastic increase of S until ca. 500 mJ cm^{-2} and reached a saturation value above this exposure dose (open circle). The final value of S (=0.56) is significantly higher than that obtained at room temperature.

In the case of the even higher temperature of 100 °C, the complex behavior was observed. The S value increased abruptly at an early stage (50 mJ cm^{-2}) of the photoirradiation, and a rapid reduction of S was observed to be leveled off above ~150 mJ cm^{-2}. The reduction in S at the later stage seems to be caused by the thermal segmental relaxation (randomization) of the polymer chains.

The photoinduced dichroism could be fully erased by thermal annealing at 140 °C, i.e., the temperature above the isotropidization temperature (105 °C). It is worth mentioning that even at the isotropic state the film remained stable and showed no

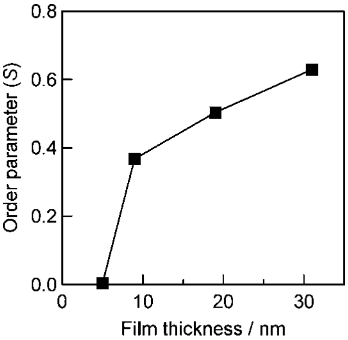


Figure 6. Changes in the order parameter (*S*) of the photoinduced alignment with increase in the thickness of the grafted-p(5Az10MA) film.

dewetting. The spin-cast film of a comparable thickness shows an unstability at this temperature. The thermal and mechanical stability are the further advantages toward applications for device fabrications.

3.3.3. Effect of Grafted Chain Length. The relationship between *S* value and film thickness before LPL irradiation is shown in Figure 6. At 5 nm, no dichroism was admitted. With increase in the film thickness, the *S* value was enhanced. Thus, the level of in-plane dichroism obviously depends on the grafted chain length. With increasing the thickness from 5 to 9 nm, *S* value was drastically enhanced to ca. 0.4, and the thickness increase above 10 nm led to a simple increase in *S*. These facts imply that the molecular cooperativity becomes manifested above ca. 10 nm thickness and that the orientational order improved for the thicker films due to the larger cooperative behavior of the Az mesogens. When the thickness is less than 5 nm, the lack of assembling cooperativity and strong interactions with the substrate surface seem to impede the photoalignment.

3.4. Photoalignment of the Smectic LC Layer Structure. As described above, the highly ordered photoinduced in-plane orientation of the Az mesogenic groups was confirmed. The orientation of smectic LC layers in the grafted-p(5Az10MA) films after exposure to 436 nm LPL was evaluated by GI-XRD measurements. The configuration of the incident X-ray beam was schematically shown in Figure 7a. The direction of the beam incidence is expressed as A and B, which are parallel and orthogonal to *E* of the actinic LPL, respectively. Parts b and c of Figure 7 show 2D GI-XRD scattering images of the photoaligned grafted polymer film recorded on an imaging plate in the incident direction of A and B, respectively. An intense comet-tail-like image running orthogonal to the substrate is an artifact of specular reflection.

When the incident beam was set in the A direction, diffraction patterns were observed in the in-plane direction as shown with two arrows. Thus, the periodic layer structure of the smectic LC phase was formed perpendicular to the substrate plane with the LC Az mesogenic groups aligned parallel to the substrate. This exhibits a clear contrast with the cases for the ordinary spin-cast films with which the diffractions are observed in the out-of-plane direction. The mesogen orientation is in agreement with the data of the polarized UV−vis absorption spectroscopy (Figure 4). From the 1D XRD profile monitored in the in-plane direction, a peak was observed at $2\theta = 2.43°$, which corresponds to the layer spacing of 3.63 nm (inset of Figure 7b). The value of the layer spacing suggests the formation of interdigitated structures of Az side chains.[13,40] On the other hand, when the X-ray beam was set in the incident direction of B, no diffraction peak was observed in any direction (Figure 7c), indicating that no obvious regular structures derived from the smectic LC layer were observed in this direction. The above data clearly show that not only the Az mesogenic groups are aligned by LPL but the smectic LC layers of the larger assembly hierarchy are also aligned to form a monodomain films over the irradiated area.

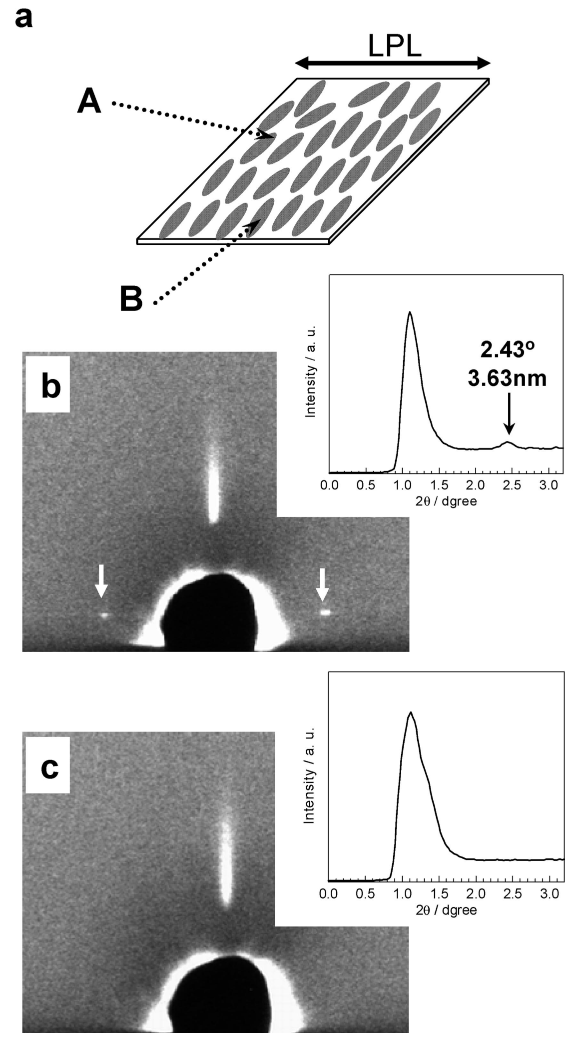


Figure 7. Schematic indication of the incident beam direction A and B for the GI-XRD measurements of the grafted-p(5Az10MA) film (a) and 2D GI-XRD patterns of the grafted polymer film recorded on an imaging plate taken with the incident direction A (b) and B (c). 1D profiles in the in-plane direction extracted from the 2D XRD pattern are shown as the inset. A strong comet-tail-like line running in the perpendicular direction is a specular reflection.

The reorientation of the molecular and layer orientation by a subsequent exposure to LPL with another polarization direction was further examined. LPL irradiation at 1000 mJ cm^{-2} at 60 °C fully changed the orientations of both Az mesogens and the perpendicular smectic layer. The order parameter of *S* after the subsequent LPL irradiation reached over 0.5. Therefore, a complete rewriting process was demonstrated without an orientational memory effect.

4. Conclusion

Liquid crystalline surface-grafted polymer films containing the photoreactive Az unit have been synthesized by the surface-initiated ATRP method. The chain length of the graft chain was controlled by both polymerization time and initial monomer concentrations. In contrast with the cases of ordinary prepared spin-cast films, the Az mesogenic groups adopt a nearly parallel orientation to the substrate surface. This feature leads to the smectic layer orientation directing perpendicular to the substrate. This orientation feature enhances the probability of light absorption, leading to the highly ordered in-plane photoalign-

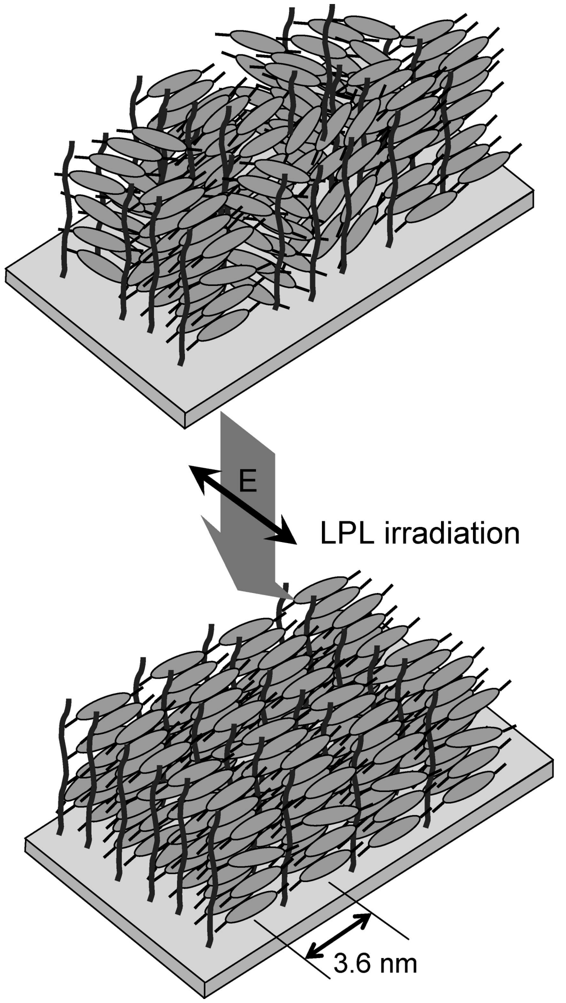


Figure 8. Schematic illustration of the photoinduction of orientations of Az mesogens and smectic layers in the grafted-p(5Az10MA) film. Note that the unique orientations and the strong in-plane anisotropy are realized by tethering one end of the polymer chain to the substrate.

ment of Az mesogens when exposed to LPL. Figure 8 displays a schematic illustration of the photoinduced alignment of Az mesogens and smectic layers after irradiation with LPL. The in-plane dichroism is most effectively generated at 60 °C, a slightly higher temperature above T_g of the polymer. This level of high orientational order is not attained for the spin-cast film with the smectic layers orienting parallel to the substrate. Further investigation should involve the effect of chain density on the orientation of the Az mesogenic groups and photopatterning. We expect that the surface-grafted polymer films with highly in-plane LPL-responsive mesogenic groups will provide new types optically functional surfaces, alignment layers for liquid crystals, and smart surfaces that show anisotropic friction properties.

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