



# Surface and interface designs in side-chain liquid crystalline polymer systems for photoalignment

Shusaku Nagano<sup>1</sup>

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## Abstract

In side-chain liquid-crystal (SCLC) polymer systems, the liquid crystalline (LC) mesogenic groups preferentially orient normal to the substrate plane due to the excluded volume effect (homeotropic alignment). Photoresponsive azobenzene (Az) mesogens have a transition moment parallel to the molecular long axis. Light irradiation for photoreactions is generally applied perpendicular to the film surface. Therefore, a homeotropic orientation inhibits efficient photoreactions and photoalignments in Az SCLC polymer systems. This review focuses on new approaches to induce a random planar orientation in Az SCLC polymer systems by interface and surface molecular design. The mesogens in a high-density SCLC polymer brush formed by surface-initiated living radical polymerization adopt a random planar orientation. In the film of an SCLC block copolymer with an amorphous block, a random planar orientation is induced via surface segregation of either of the blocks. The random planar orientations of SCLC polymer systems are thermally stable and offer efficient in-plane photoalignment and photoswitching with hierarchical LC molecular architectures, forming, e.g., microphase-separated (MPS) SCLC block copolymers and layered polymer LC systems. These surface and interface molecular designs are expected to provide new concepts and possibilities for LC polymer devices.

## Introduction

One primary goal for polymer nanotechnology is to construct versatile, organized structures with precise arrangements and orientations of the polymer molecules. Therefore, alignment methods for polymer molecules are crucial. Liquid crystalline (LC) systems can exhibit long-range molecular order, which offers a significant advantage for controlling the alignment of molecules and polymers [1–16]. LC displays (LCDs) are excellent examples of molecular devices using thermotropic LC nature of molecules [1, 2, 17]. The initial LC alignment in LCDs is precisely carried out by rubbed polyimide films [1, 18] or, recently, photoalignment layers [19–27], and the optical transmission is controlled by switching the LC orientation with an electric field. The tough fiber materials used in bulletproof jackets and fishing lines are obtained via

orientation technique by injection molding utilizing the lyotropic LC nature of highly soluble rigid-rod polymers [1, 4, 5, 28]. Highly and efficiently oriented molecular-organized structures can be constructed by combining self-assembly (spontaneous) aggregations of the LC nature with self-organizing alignment by external stimuli, such as mechanical shear [1, 4, 5, 17, 28], electric fields [1, 17], and light [19–22, 29–33].

However, the LC characteristics are not often useful for molecular alignment in thin films. In some situations, unfavorable self-assembly orientations, against the desired LC alignment direction, are formed, as the LC orientation is strongly influenced by the surface or interface. In particular, side-chain LC (SCLC) polymers strongly tend to exhibit homeotropic orientation in free-standing films, such as cast films, Langmuir-Blodgett films, and layer-by-layer films, due to the excluded volume effect [31, 32, 34–37]. Homeotropic orientation inhibits homogeneous (in-plane) alignment by surface alignment and photoalignment processes. In photoresponsive SCLC polymer films containing azobenzene (Az) mesogenic units especially, it is evident that a homeotropic orientation is unsuitable for in-plane photoalignment because the transition moments of the Az units are oriented normal to the light absorption and the

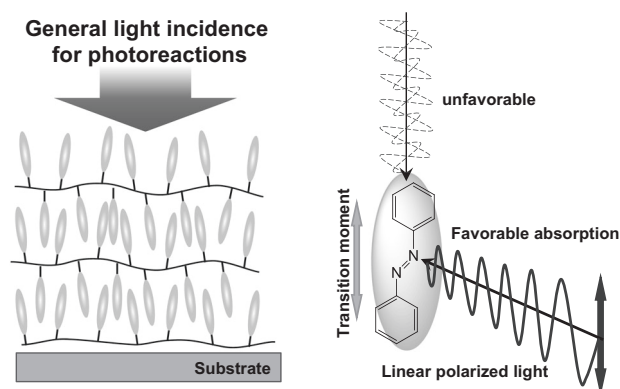
✉ Shusaku Nagano  
snagano@chembio.nagoya-u.ac.jp

<sup>1</sup> Nagoya University Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

mesogens are in a direction opposite (normal) to the in-plane (Fig. 1). Therefore, to adopt photoirradiation for LC molecular alignment, it is required to control the molecular orientations in which the LC nature effectively acts. This review focuses on surface and interface designs to induce a random planar orientation in photoresponsive SCLC polymer thin films for efficient LC photoalignment. The molecular designs at the surface and interface of polymer thin films are critical to realize an advantageous molecular orientation for in-plane LC alignment. In this context, molecular LC orientations in surface-grafted SCLC polymer films (Fig. 2a) and at the surface/interface in MPS domains of SCLC block copolymers (Fig. 2b, c) are discussed.

## Surface-grafted SCLC polymer brush films

Photoresponsive polymers containing Az chromophores photoisomerizing between *trans*- and *cis*-form are among the most widely explored photofunctional polymers for photochemical and photomechanical applications [20–22, 29–32, 38]. In LC media, the rod-like Az *trans*-form plays the role of a typical LC mesogenic group, whereas the bent *cis*-form behaves as a nonmesogenic structure. The change in the molecular shape of the Az unit due to *trans*-*cis* photoisomerization leads to the light-induced phase transition of the LC phase (photoinduced LC phase transition) [21, 30, 38]. Moreover, linearly polarized light (LPL) irradiation can induce in-plane monoaxial molecular alignment of the Az chromophore [20–22, 29–32, 38]. When irradiated by LPL, Az molecular units oriented parallel to the actinic electric field ( $E$ ) of the LPL selectively undergo photoisomerization and rotate perpendicular to the  $E$  (Weigert effect) [39]. When the angular-selective photoisomerization is carried out in LC media, we can actualize highly efficient molecular photoreorientation systems

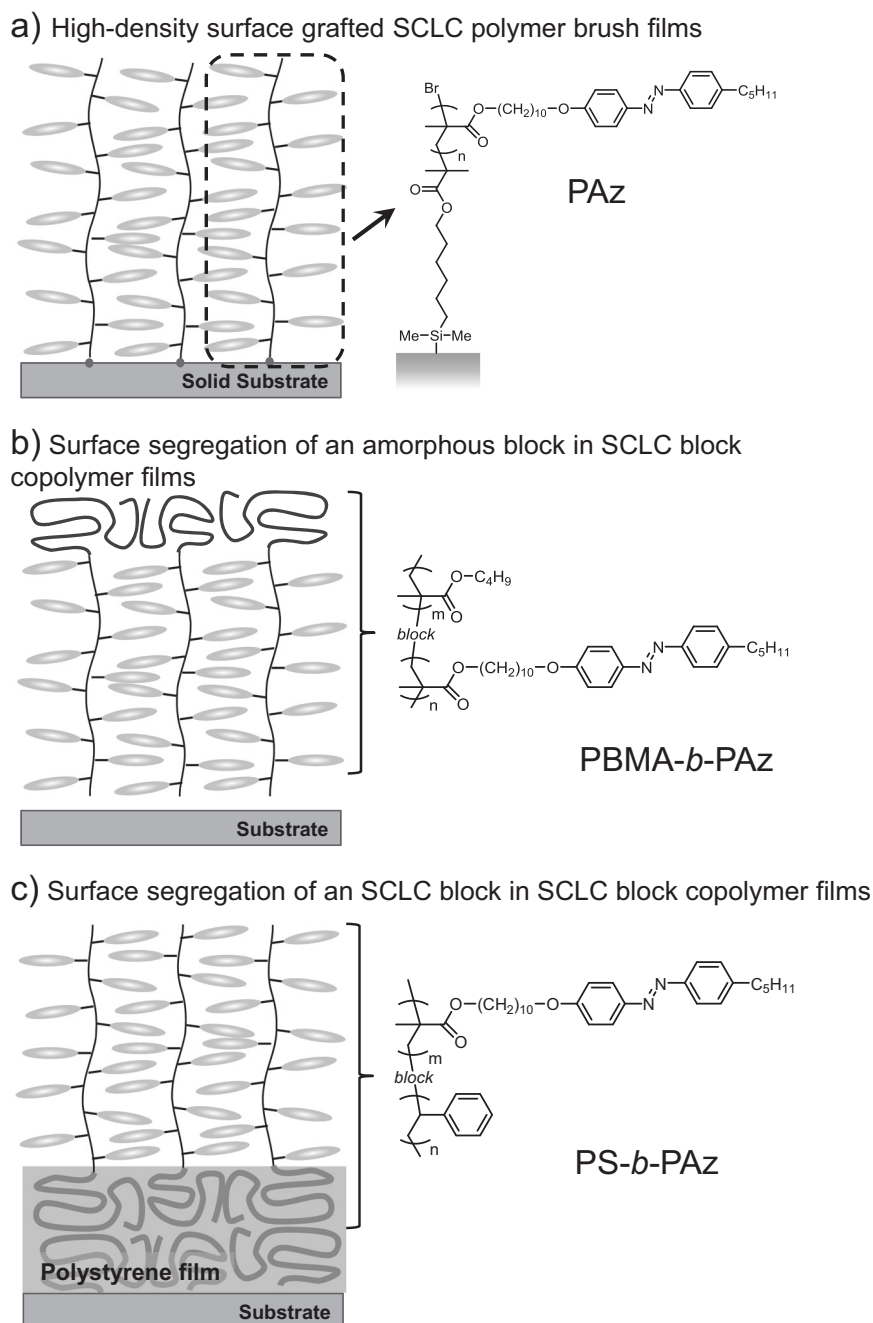


**Fig. 1** Homeotropic orientation of the photoresponsive SCLC polymers (left) and a favorable direction for light absorption in an azobenzene chromophore (right)

[20–22, 29–32, 38]. As mentioned, for Az SCLC polymers, the preferential homeotropic orientation in thin films inhibits efficient photoisomerization and in-plane orientation since light irradiation processes are generally conducted at normal incidence to the film plane (Fig. 1). For efficient photoreorientation, molecular design strategies to induce a planar orientation Az SCLC polymer films are needed.

One strategy for inducing planar orientation uses high-density surface-grafted polymer brushes (Fig. 2a). High-density polymer brushes exhibit vertically oriented main-chain structures. Recently, high-density surface-grafted polymer brushes have been synthesized by surface-initiated living radical polymerizations [40–42]. As radical polymerization can be applied to various functionalized acrylate monomers, many types of polymer brushes have been studied, such as thermoresponsive polymers [43–45], photofunctional molecules [46, 47], electrochemical units [48], ionic polymers [49–51], and LC polymers [52–54]. SCLC polymer brushes have been investigated on non-photoresponsive LC brushes [52–54]. However, thorough investigations into LC characteristics such as LC orientation and phase transitions have not been conducted. We synthesized an Az SCLC polymer (PAz) brush by surface-initiated atom-transfer radical polymerization (SI-ATRP), which is a living radical polymerization technique (Fig. 2a) [55, 56]. In the surface-grafted film, UV absorption by the Az side chain suggested the in-plane (random planar) orientation of the LC mesogens after annealing at an isotropic temperature. Moreover, grazing incidence small-angle X-ray scattering (GI-SAXS) measurements revealed that the smectic lamellar structure in the Az SCLC polymer grafted film oriented vertically to the substrate plane (Fig. 3a), unlike the homeotropic orientation of spin-cast films of the same free PAz not affixed to a substrate (Fig. 3b). The vertical smectic phase indicates the normally oriented main chains and the random planar orientated side-chain mesogens. Therefore, SI-ATRP gave a sufficient polymer brush density to induce a random planar orientation in the SCLC polymer smectic phase by self-assembly. The planar orientation of the Az SCLC polymer brush film has an excellent advantage for in-plane photoalignment by angular-selective photoisomerization and photoreorientation since Az side chains are oriented in a favorable direction for efficient light absorption and in-plane alignment. In fact, a highly ordered in-plane alignment was attained by LPL irradiation of the Az SCLC polymer films (Fig. 3c, d) [56]. The optical order parameter  $S$  is useful for evaluating the in-plane anisotropy of the photoaligned Az films.  $S = (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$ , where  $A_{\parallel}$  and  $A_{\perp}$  are the absorbance at the peak of the  $\pi$ - $\pi^*$  transition band (approximately 336 nm) measured with polarized light set parallel and perpendicular to the realigned actinic LPL light, respectively. The SCLC polymer brush film attained  $S > 0.55$  by LPL irradiation at

**Fig. 2** Surface and interface molecular designs for inducing a random planar orientation in photoresponsive SCLC polymer systems

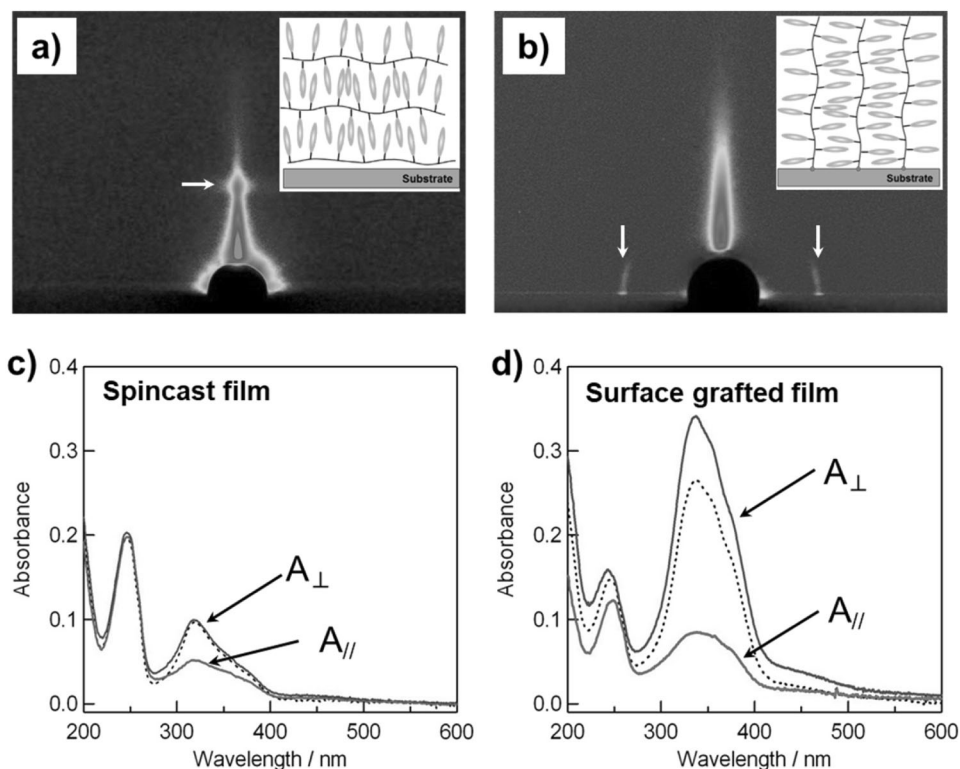


436 nm for  $300 \text{ mJ cm}^{-2}$  (Fig. 3d), whereas the spin-cast film of the same free PAz exhibited a low dichroism ( $S = 0.24$ ) due to the homeotropic orientation (Fig. 3c). The in-plane aligned smectic phase (homogeneous orientation) was confirmed by the highly anisotropic scatterings in the GISAXS measurements with two X-ray incident directions parallel and perpendicular to the LPL electric field [56].

Az SCLC polymer brush films have been adopted in block copolymer systems with amorphous polymer blocks laid between the Az SCLC polymer block and substrate [57–59]. Amorphous blocks, such as poly(hexyl

methacrylate) (PHMA), poly(butyl methacrylate) (PBMA), and poly(methyl methacrylate) (PMMA), were introduced by two-step ATRP. These diblock copolymer brush films exhibit the same structure and orientation as the Az homopolymer brush film directly attached to a solid substrate. However, contradictory to the same LC structure, the photoalignment behaviors were strongly influenced by the glass transition temperature ( $T_g$ ) of the in-between amorphous block layers [57]. The block copolymer brush with rubbery amorphous polymer blocks, such as PHMA and PBMA, exhibited highly ordered in-plane anisotropy upon

**Fig. 3** 2D GI-SAXS images of the spin-cast free PAz film **a** and the surface-grafted PAz film **b**. The scattering is indicated by white arrows in **a** and **b**. Polarized absorption spectra of the free PAz spin-cast film **c** and the surface-grafted PAz film **d** before and after exposure to LPL at 436 nm at 60 °C. The dotted and solid lines are the spectra taken with a nonpolarized beam and polarized beams set perpendicular ( $A_{\perp}$ ) and parallel ( $A_{\parallel}$ ) to the actinic LPL at 436 nm, respectively. Adapted with permission [56]. Copyright 2008, American Chemical Society



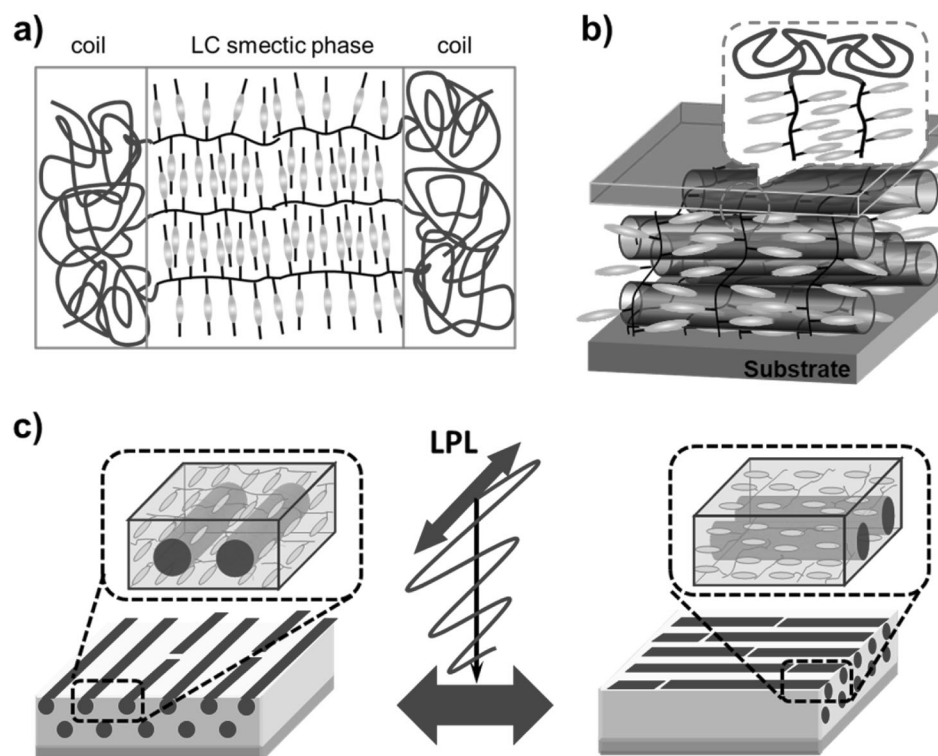
LPL irradiation, similar to the Az SCLC homopolymer brush film. By contrast, the glassy PMMA layer largely suppressed development of the dichroism more than the homopolymer brush did. These results imply that the interfacial rubbery amorphous polymers act as an elastic buffer for LC motions (lubricant effect). In addition, longer rubbery amorphous chains led to a higher  $S$ -value [59]. Recently, an Az SCLC polymer brush with a norbornene main chain was realized by surface-initiated ring-opening metathesis polymerization using the fourth-generation Grubbs catalyst [60]. The Az SCLC polymer brush adopted a random planar orientation in the smectic phase and showed high in-plane anisotropy upon LPL irradiation. These results indicate that production of a highly photoresponsive SCLC polymer brush is not limited to the SI-ATRP method.

The SCLC polymer brushes can induce a random planar orientation in the smectic LC phase by self-assembly and have the potential for the highly efficient in-plane photo-realignment of Az SCLC polymers. Although the LC orientations of the brush and spin-cast films are quite different, the LC temperature and structure are essentially identical. The highly photoresponsive SCLC polymer brush films are new classes of photofunctional surfaces, LC alignment layers, and smart surfaces that exhibit anisotropic friction properties. Recently, Az SCLC polymer brushes were further applied to photoswitchable surfaces and photomechanical materials [61–65].

### Surface segregation in SCLC block copolymer films

Block copolymers are promising candidates for nanolithographic patterning by self-assembly because they spontaneously form nano-ordered structures (MPS structures) such as spheres, cylinders, and lamellae [66–70]. Therefore, alignment methods for MPS structures are directly connected to applications for nanotemplating and nanopatterning. The alignment of MPS structures has been intensively studied by applying external fields, such as mechanical shear and flow, and electric and magnetic fields [66–70]. Topographical and wetting nanopatterns can also provide well-patterned MPS films [68–71]. Block copolymers linked with a thermotropic LC polymer block can offer mesogenic molecular order and direction in MPS structures. In SCLC block copolymers with an amorphous block (SCLC-coil block copolymers), the interfaces dividing the polymer blocks are inevitably faced parallel to the molecular direction of the side-chain mesogens (Fig. 4a) [72–76]. Thus, the orientation of the MPS structure in SCLC-coil block copolymers is dominated by the SCLC block orientation [72, 74]. Iyoda and colleagues [77–79] achieved a highly reliable vertical cylinder structure over a large area with a homeotropically oriented Az polymer matrix in films of an amphiphilic Az SCLC block copolymer with a polyethylene oxide block by self-assembly. The

**Fig. 4** Schematic images of the interfacial molecular orientation of SCLC-coil block copolymers **a** and orientation of the LC phase and MPS structures in a PBMA-*b*-PAz thin film **b**. The low-surface free-energy PBMA block preferentially segregates at the surface. Schematic illustrations of the in-plane photoswitching of MPS cylinders in a PBMA-*b*-PAz film (c, active photoalignment)



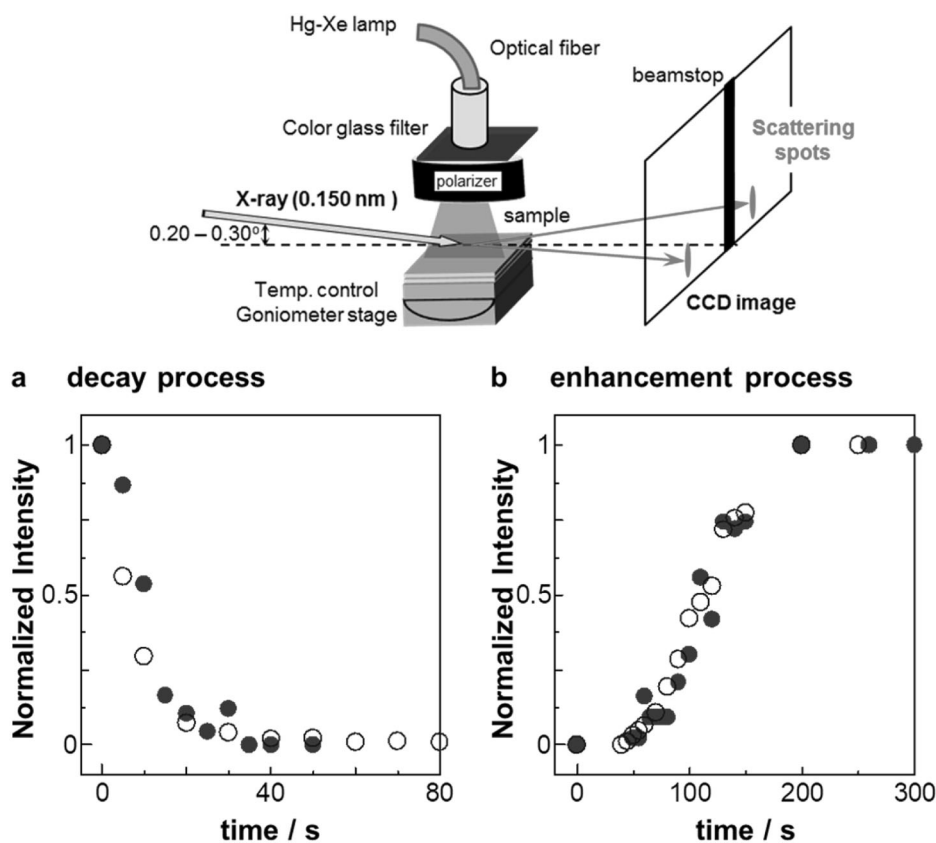
in-plane photoalignment of the MPS structure of an Az SCLC block copolymer was first demonstrated by two independent groups, Yu et al [80], and our group [81], almost simultaneously. Subsequently, our group reported rewritable in-plane and out-of-plane photoalignment controls (three-dimensional photoalignment) for MPS cylinder structures in an Az SCLC block copolymer with a polystyrene (PS) block [82]. As the block copolymer exhibits a homeotropically oriented SCLC block and vertically oriented cylinder structure by self-assembly, these photoalignment systems require monoaxial growth of the LC phase to an energetically unstable direction from the isotropic phase or as-cast state for in-plane alignment.

To realize a thermodynamically stable planar orientation, we induced a surface segregation structure in the block copolymer films (Fig. 2b) [83, 84]. Polymer molecules or polymer blocks with relatively low-surface free energy migrate and segregate at the free surface in the polymer and block copolymer thin films (surface segregation) [85–90]. In block copolymer films, in particular, the low free-surface energy blocks cover the film surface. The low-energy topmost surface layer, as the starting point, determines the arrangement and orientation of the MPS structure in many situations [89, 90]. In the case of SCLC-coil block copolymers with an amorphous coil block with a low-surface free energy, the coil block preferentially covers the film surface side and forms a surface-segregated layer. A MPS interface is formed parallel to the surface-segregated layer (the film surface). As mesogens orient parallel to the MPS

interface (Fig. 4a), a random planar orientation is inevitably induced due to surface segregation of the amorphous coil block layer. We previously proposed an Az SCLC block copolymer system with an amorphous PBMA block with low-surface free energy and low  $T_g$  (PBMA-*b*-PAz, Fig. 2b) [83, 84]. As expected, in thin films, PBMA-*b*-PAz always exhibits a random planar orientated LC phase and MPS cylinders by self-assembly due to surface segregation of the PBMA block layer at the topmost surface (Fig. 4b). The Az SCLC block copolymer system exhibits the active in-plane photoswitching for the reorientation of the MPS structure under a smectic A phase of the LC block (“active” photoalignment, Fig. 4c). The active photoalignment can switch the in-plane orientation of the MPS cylinders a desired number of times in any azimuthal direction in a few minutes by LPL irradiation. The planar orientation of the SCLC block copolymer films can produce highly efficient in-plane photoswitching in the MPS structure.

The MPS structure of block copolymers is classified as lyotropic LC in the field of liquid crystals. SCLC block copolymers can be recognized as hierarchical molecular structures possessing thermotropic LC phases in a lyotropic LC MPS system. Therefore, MPS photoalignment processes involve hierarchical motions of the two LC phase systems [83, 84, 91–93]. Interestingly, the Az SCLC block copolymer system with planar orientation can elucidate the photoalignment and photoswitching mechanisms in the hierarchical LC molecular system. In situ observations of photoswitching of the LC phase and MPS cylinders were

**Fig. 5** Time-course profiles of the scattering intensity from real-time in situ GI-SAXS measurements. **a** Decay processes assigned to the fluctuation of both the smectic LC phase (open circle) and the PBMA cylinders (full circle) upon LPL irradiation. **b** Enhancement processes ascribed to the ordering and growth of the periodicity of the two hierarchical structures. Adapted with permission [83]. Copyright 2012, John Wiley & Sons

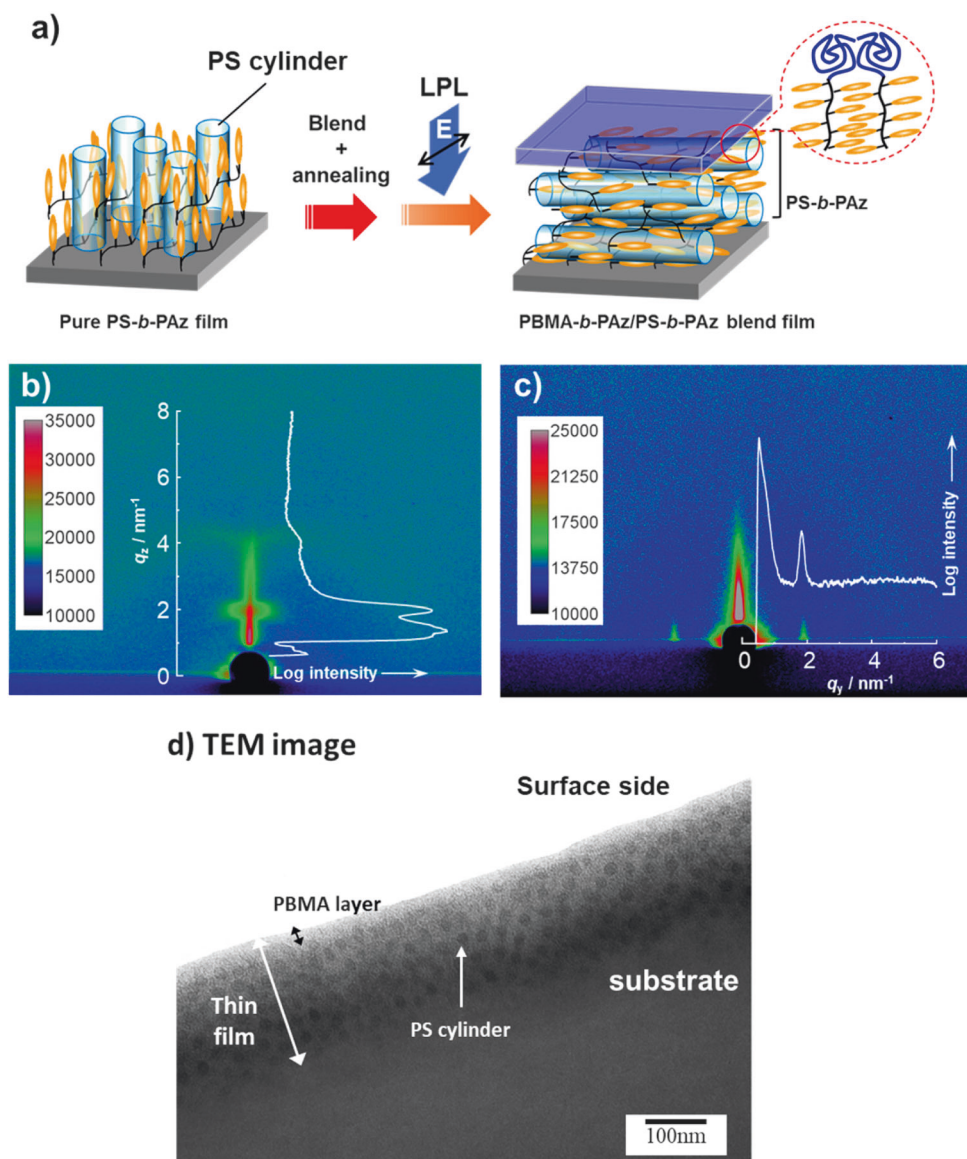


realized by GI-SAXS measurements using a synchrotron radiation source [84, 91]. In real time, changes in the scattering intensity due to the PAz SCLC phase and MPS cylinder structure were observed under LPL irradiation (Fig. 5). The scattering due to both the smectic phase and the cylinders decayed quickly, within approximately 40 s (Fig. 5a). After this, the growth of the orthogonally oriented hierarchical structure was relatively slow, taking approximately 300 s (Fig. 5b). The scattering intensity transitions for the LC phase and MPS cylinders synchronized entirely in the photoalignment and photorealignment processes. In fact, the motions of the two different hierarchies of the LC phase (molecular scale) and MPS domains (mesoscopic scale) were strongly cooperatively coupled and synchronized in the active photoalignment systems [84, 91, 92]. The detailed mechanisms involved in the active in-plane photoalignment system were elucidated by capturing the orientational transition structures [84, 91]. The observations by polarized optical microscopy (POM) and transmission electron microscopy (TEM) revealed that the orientational domains possess smectic order and MPS cylinder structures in the transition state, even in the highly fluctuating state, under LPL irradiation, which proves that photoreorientation of the LC phase and MPS cylinders involves LC domain rotation [84, 91, 92].

### Free-surface command system

The PBMA block possesses alkyl chains and has a low  $T_g$ , which can impart a relatively low-surface free energy compared with that of other SCLC polymers. Accordingly, the induced planar orientation triggered by surface segregation of the PBMA block in an Az SCLC block copolymer can be applied to other SCLC polymer systems [94, 95]. When a small amount of PBMA-*b*-PAz was added to homeotropically oriented SCLC polymers and block copolymers in thin film form, the PBMA block was preferentially segregated at the topmost film surface. The surface segregation structure induced a planar orientation in the LC phase and MPS structures after annealing treatment of PAz at an isotropic temperature (Fig. 6a) [94]. The PAz homopolymer (Fig. 3a) and PS-based Az SCLC block copolymer (PS-*b*-PAz, Fig. 6b) normally adopt a homeotropic orientation. The addition of PBMA-*b*-PAz led to a random planar orientation in thin films of the PAz homopolymer and PS-*b*-PAz (Fig. 6c) [94]. These added films with planar orientation can exhibit highly efficient in-plane photoreorientation. The cross-sectional TEM profiles of the PS-*b*-PAz film with the addition of PBMA-*b*-PAz clearly demonstrated that the topmost PBMA block layer (ca. 20 nm) of PBMA-*b*-PAz segregated to the free surface (Fig. 6d).

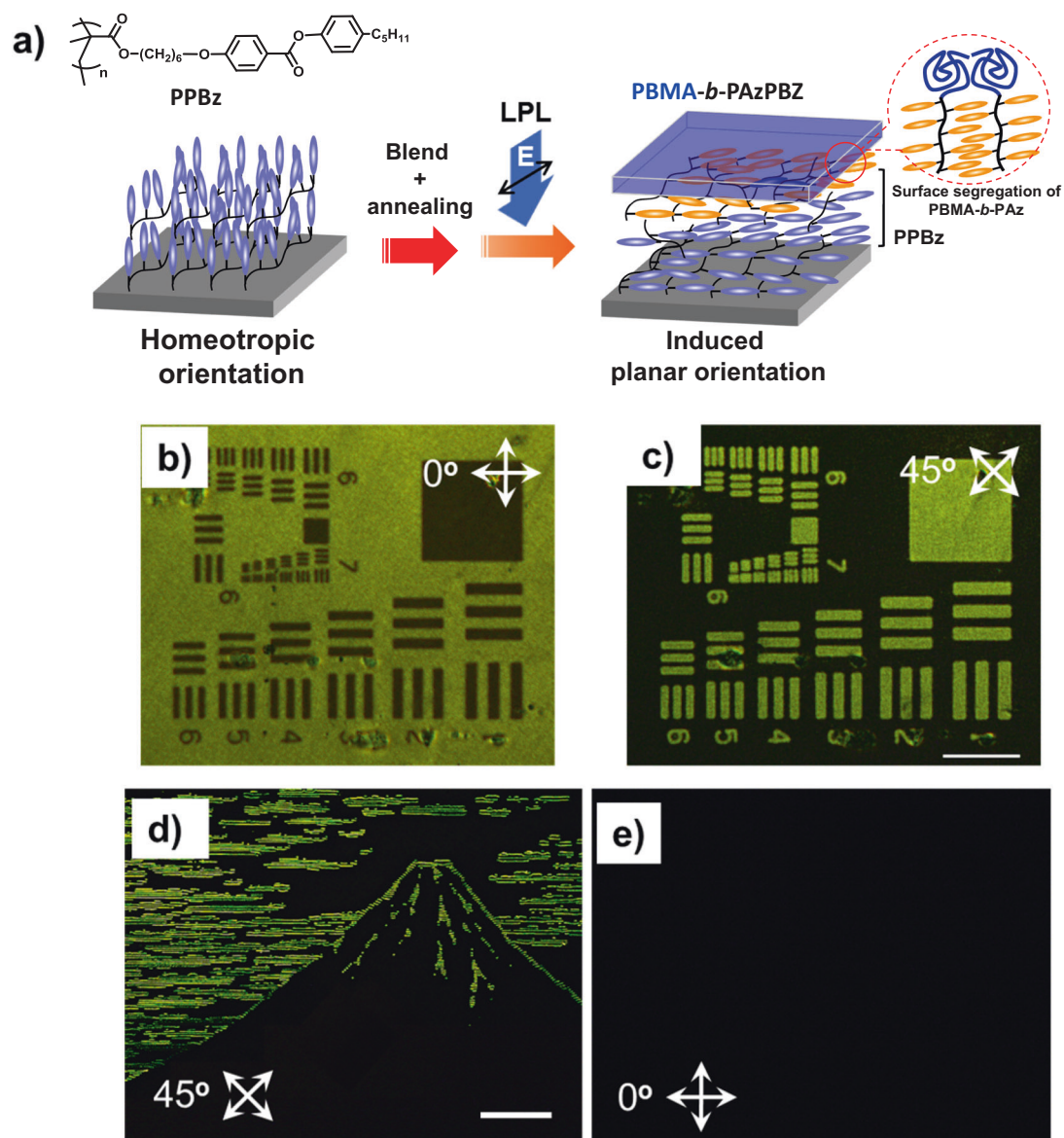
**Fig. 6** **a** Schematic illustrations of the induced planar orientation and photoalignment processes for a *PS-*b*-PAz* film with a surface-segregated *PBMA-*b*-PAz* layer in a mixed film. The 2D GI-SAXS images of **b** pure *PS-*b*-PAz* film and **c** *PBMA-*b*-PAz/PS-*b*-PAz* mixed film after annealing at the same conditions. In the images, the 1D intensity profiles are indicated as white lines. **d** A cross-sectional TEM image of the *PBMA-*b*-PAz/PS-*b*-PAz* mixed film. The sample was sliced in the direction parallel to the actinic LPL light. Adapted with permission [94]. Copyrights 2013, John & Wiley Sons



Moreover, this surface segregation approach could be applied to the photoalignment of nonphotoresponsive SCLC polymer films (PPBz, Fig. 7a) [95, 96]. In this case, the topmost *PBMA-*b*-PAz* layer has the role of a free-surface LC photoalignment layer in SCLC polymer films with a phenyl benzoate mesogen. A pure PPBz film normally adopts a homeotropic orientation (Fig. 7a (left)), exhibiting scattering corresponding to the smectic phase in the out-of-plane direction by GI-SAXS measurements [95]. On the other hand, a PPBz film with the addition of 3% by weight *PBMA-*b*-PAz* exhibited scattering only in the in-plane direction after thermal annealing of both LC components at an isotropic temperature [95]. The in-plane scattering demonstrates the random planar alignment of the PPBz smectic phase induced by the surface-segregated *PBMA-*b*-PAz* layer (Fig. 7a (right)). As expected, the

photoresponsive PAz layer in the surface-segregated block layer can control the in-plane alignment of the underlying PPBz film (command effect [20]). Patterned LPL irradiation at the LC temperature of PAz can achieve the photo-patterning of the in-plane alignment of the PPBz film. The crossed Nicols POM observation demonstrated birefringence patterns (Fig. 7b, c), suggesting that the in-plane photoalignment of the PPBz mesogens was attained by the photoresponsive PAz blocks underneath the surface-segregated *PBMA* blocks.

To demonstrate the orientational change in PPBz from the free surface, *PBMA-*b*-PAz* was overcoated onto a homeotropically oriented PPBz film using an inkjet printing method. Thermal annealing and LPL irradiation at the LC temperature induced monoaxial photoalignment only at the printed area. Under crossed Nicols, birefringence patterns



**Fig. 7** **a** Schematic illustrations of the induced planar orientation and photoalignment processes for a nonphotoresponsive SCLC polymer (PPBz) film with a surface-segregated PBMA-*b*-PAz layer. **b**, **c** POM images of an in-plane photoalignment-patterned film of PPBz/PBMA-*b*-PAz under crossed polarizers that were rotated from each other

(scale bar = 100 μm). **d**, **e** POM images of the in-plane and out-of-plane patterned film overcoated by inkjet printing under crossed polarizers that were rotated 45° from one another (scale bar = 200 μm). Note that the positive and negative patterns of the images were fully switched

were observed only in the printed area (Fig. 7d). They appeared and disappeared with every 45° rotation of the cross polarizers (Fig. 7d, e). On the other hand, the uncoated areas remained dark and were unchanged by rotation of the crossed polarizers. This indicates that homeotropic and homogeneous planar patterns were created in the noncoated and overcoated areas, respectively. The appearance and disappearance of the printed image were observed by the rotation of the polarizers in the oblique direction because the PPBz mesogens were in-plane photoaligned in the printed area. By using various printing methods, we can draw any desired pattern or figure (Fig. 7d, e). Thus, the

surface-segregated SCLC block copolymer system can be regarded as a “command surface ink.”

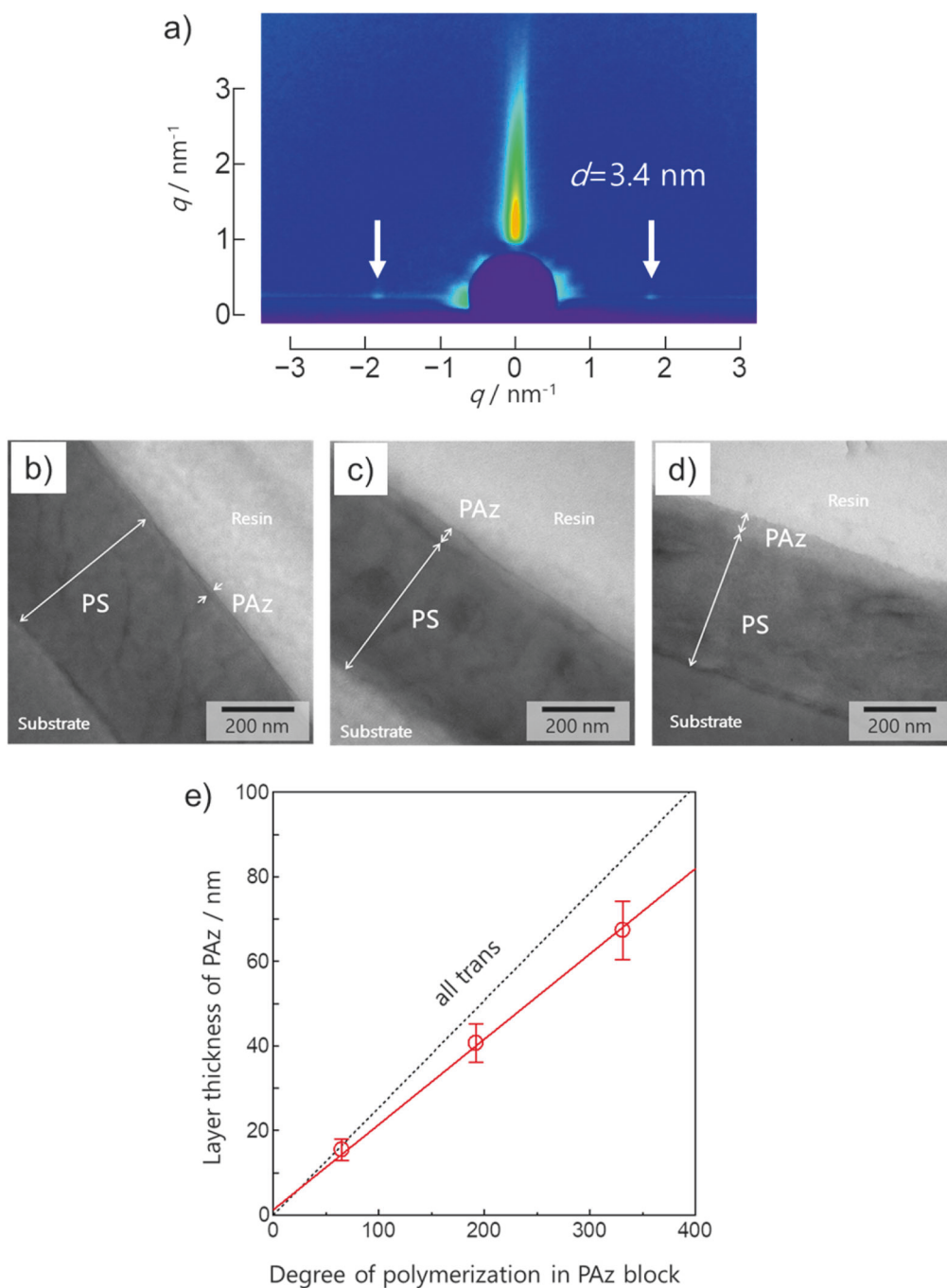
Surface segregation phenomena in polymer thin films have been mostly used for changing the wettability of a polymer film surface. On the other hand, surface segregation of the SCLC block copolymer changes the internal molecular orientation at the topmost film surface. Recently, molecular orientation was carried out at the film surface of free-standing films of various materials, such as LC polymers [97], semi-conducting polymers [98], discotic LCs [99], and MPS structures [100]. In the present case, nonphotoresponsive mesogens up to 10 μm thick can be oriented by a



photoresponsive topmost surface layer with a thickness of approximately 20 nm. The photoresponsive block layer can direct the orientation of a nonphotoresponsive mesogen layer that is approximately 500 times thicker. The effects at the free surface are very powerful for LC orientational control in SCLC polymer films.

### Spontaneous formation of a SCLC polymer brush in the surface-segregated block copolymer layer

Surface segregation of the amorphous block with low-surface free energy in the SCLC-coil block copolymer induces a



**Fig. 8** **a** GI-SAXS 2D image of the surface-segregated PS-*b*-PAz onto a PS film. Cross-sectional TEM images of **b** PS<sub>96</sub>-*b*-PAz<sub>65</sub>/PS, **c** PS<sub>96</sub>-*b*-PAz<sub>192</sub>/PS, and **d** PS<sub>96</sub>-*b*-PAz<sub>331</sub>/PS mixed films (all polymer films were stained by RuO<sub>4</sub> vapor). **e** The variation in thickness of the surface-segregated PAz block as a function of degree of

polymerization of the PAz block unit. The red line and black dotted line show the layer thickness observed in cross-sectional TEM and all-*trans* chain length calculated from the PMMA backbones, respectively. Adapted with permission [97]. Copyrights 2016, John & Wiley Sons

planar orientation in the SCLC polymer film [94–96]. What is the molecular orientation of the surface-segregated SCLC block? In a block copolymer containing PS and PAz, PAz exhibits a relatively lower free energy. Therefore, the PAz block preferentially segregates at the film surface in mixed films of PS homopolymer and PS-*b*-PAz (Fig. 2c) [101]. In that case, the surface-segregated SCLC block builds the high-density polymer brush structure by self-assembly. Pure PS-*b*-PAz exhibits homeotropic LC and vertical cylinder phases in thin film form (Fig. 6a (left)) [82]. In contrast, scattering due to the smectic phase of the PAz block in the surface-segregated layer was observed at the in-plane position (Fig. 8a), indicating that the surface-segregated SCLC block adopted a random planar orientation (Fig. 2c) [101]. The cross-sectional TEM observations revealed the magnitude of the chain extension of the polymer brushes. The thickness of the PAz layer is proportional to the degree of polymerization ( $N$ ) of the PAz chains in PS-*b*-PAz (Fig. 8b–d). The slope of the fitted line between the segregated PAz layer and the  $N$  of the PAz chains was 0.202 N/nm (Fig. 8e). The estimated slope for the length of PMMA in the trans-zigzag conformation is calculated to be 0.254 N/nm (dotted line in Fig. 8e). From these values, the length of the PAz chains reaches approximately 80 % of the ideal trans-zigzag conformation of PMMA, suggesting that the surface-segregated PAz SCLC chains exhibit a highly extended polymer brush structure (high-density polymer brush) at the topmost surface of the film. The dry state of the amorphous polymer brushes reaches only 40 % of the fully extended chain length [40, 41]. In comparison, the value of the surface-segregated SCLC polymer brush indicates extremely high extension in dry conditions. The formation of the highly stretched polymer brush is likely due to three spontaneous factors: (i) the lower surface tension of the PAz block, (ii) the PS block anchoring to the base PS, and (iii) the self-assembly LC nature of the SCLC block to form a smectic A phase.

As shown above, a similar random planar orientation to SCLC is obtained in the PAz polymer brush prepared by SI-ATRP on a solid substrate [55–60]. The segregated brush on the PS film also exhibits high in-plane anisotropy by irradiation with LPL at 436 nm, comparable to the high-density brushes formed by SI-ATRP. The segregated polymer brush, as a new approach, has the following advantages. First, the new approach can produce a high-density polymer brush by simply mixing PS-*b*-PAz into a base polymer (PS) film by self-assembly, without the need for complex synthetic routes. The thickness of the brush is precisely controlled using simple well-characterized diblock copolymers. Second, the segregated polymer brush can be applied on various flexible polymer substrates. Yokoyama et al. demonstrated the self-assembled polymer brush structure of amphiphilic diblock copolymers with a poly (ethylene oxide) block by studying the surface segregation

and solvation dynamics in water [90, 102]. A segregated SCLC brush was formed and was stable in air due to the surface free energy and LC characteristics.

## Summary

Owing to the excluded volume effect, mesogens in SCLC polymers tend to adopt homeotropic orientation at a free interface, which propagates through the entire film from the surface. In the case of Az mesogens, a homeotropic orientation is disadvantageous to realize an effective photoresponse because the actinic light  $E$  is usually irradiated at a normal incidence to the substrate plane. For in-plane photoalignment in particular, the random planar orientation of the Az mesogenic groups is required. This review introduced various molecular designs at interfaces and surfaces to induce the random planar orientation of Az mesogens in SCLC polymer films for photoalignment processes. The surface-grafted SCLC polymer brush and the surface-segregated SCLC block brush form a random planar orientation with vertically oriented main chains. Surface segregation of the low-surface free-energy block also induces a planar LC orientation due to the formation of an MPS interface parallel to the surface plane. These planar orientations realize efficient in-plane photoalignment and orientational photoswitching of hierarchical LC mesostructures, such as smectic LC and MPS structures. Moreover, the surface-segregated photoresponsive SCLC block layer acts as a free-surface command layer and can switch the in-plane homogeneous photoalignment in SCLC polymer systems. It should be emphasized that these induced random planar orientations were self-assembled (thermodynamically stable) through surface and interface molecular designs. The results demonstrate that the interface and surface of films have an essential role in the orientation of LC polymer systems. We hope that the new surface and interface molecular designs shown here open the door to new LC polymer devices.

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## Compliance with ethical standards

**Conflict of interest** The author declares that he has no conflict of interest.

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Shusaku Nagano is an associate professor at Nagoya University Venture Business Laboratory. He received his B.S. (1995) and M.S.(1997) degrees in chemistry from Gakushuin University, and Ph.D.(2001) degree from Tokyo Institute of Technology under the supervision of Professor Takahiro Seki. From 1998 to 1999, he worked in the Central Research Laboratories at Nihon Parkerizing Co., Ltd. as a researcher. In 2001, he joined the central research center at Ricoh Company, Ltd. as a researcher. In 2002, he worked as an assistant professor of Graduate School of Engineering, Nagoya University. Since 2011, he has been an associate professor of the Nagoya University Venture Business Laboratory. He has been working on interdisciplinary research in polymer chemistry, polymer physics focusing on liquid crystalline polymers, photoresponsive polymers, polymer semiconductor devices, polymer surfaces, and polymer ultrathin films.