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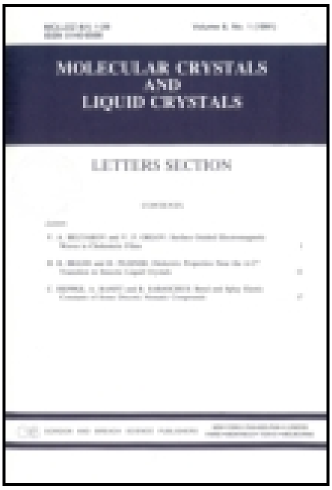

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# Free Surface-Induced Planar Orientation in Liquid Crystalline Block Copolymer Films: On the Design of Additive Surface Active Polymer Layer

Kei Fukuhara[a], Mitsuo Hara[a], Shusaku Nagano[b] & Takahiro Seki[a]
[a] Department of Molecular Design & Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya, Japan
[b] Nagoya University Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa, Nagoya, Japan

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# Free Surface-Induced Planar Orientation in Liquid Crystalline Block Copolymer Films: On the Design of Additive Surface Active Polymer Layer

KEI FUKUHARA,[1] MITSUO HARA,[1] SHUSAKU NAGANO,[2]
AND TAKAHIRO SEKI[1,*]

[1]Department of Molecular Design & Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya, Japan
[2]Nagoya University Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa, Nagoya, Japan

*We recently demonstrated that addition of a surface active polymer (SAP) that segregates on the free (air) surface in liquid crystalline (LC) block copolymer films crucially alters the orientation of the mesogens and microphase separation domains. A block copolymer of poly(butyl methacrylate) (PBMA) combined with an azobenzene LC polymer has been blended as SAP in a polystyrene-based LC block copolymer films possessing similar structure. The present work reveals that the polymer design, the blend ratio, and molecular weight of the surface active polymer significantly affect the orientational alternation for the block copolymer film. The orientational alternation effect by the free surface segregation becomes significantly efficient when SAPs with higher molecular weight is employed.*

**Keywords:** Diblock copolymer; microphase-separation; azobenzene; liquid crystal; orientational control; surface segregation

## 1. Introduction

Recently, numerous studies have been carried out to control the orientation of micro phase-separation (MPS) structures of block copolymer films due to the practical interests for nanolithography, fabrication of high density media and photonic crystals.[1, 2] Among many aligning techniques, photoalignment methods [3, 4] has been becoming increasingly important to achieve on-demand orientation controls of MPS domains [5–8].

The photoalignment technique leads to static uniform orientational inductions of MPS structures [5–8] and further to dynamic rewritable functions [9]. We have demonstrated such dynamic rewritable photoalignment controls by using a block copolymer of poly(butyl methacrylate) (PBMA) connected with an azobenzene (Az)-containing liquid crystalline (LC) polymer (PBMA-*b*-P5Az10MA, see Scheme 2). In this polymer film, the Az mesogens and PBMA cylinder domains are always directed in the in-plane directions, and the out-of-plane induction is not observed. This tendency can be interpreted as a consequence of surface coverage of PBMA possessing a lower surface tension. The importance of the

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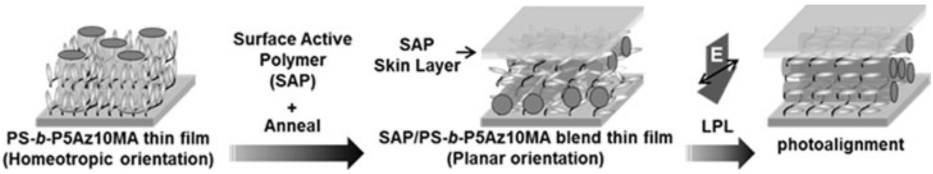
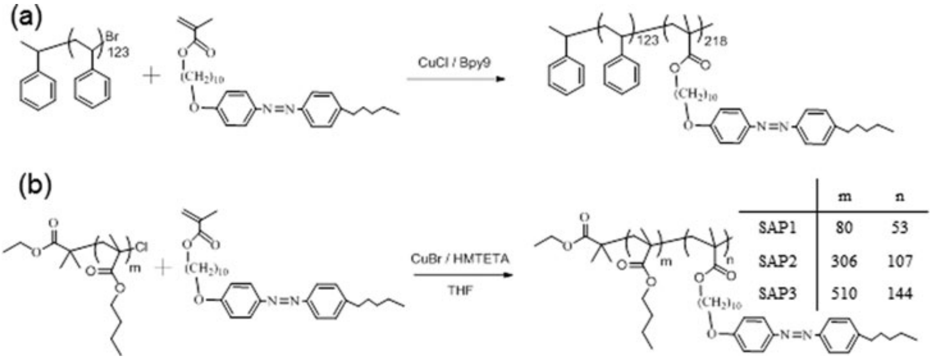
[*] Address correspondence to Takahiro Seki, Department of Molecular Design & Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan. E-mail: tseki@apchem.nagoya-u.ac.jp



**Scheme 1.** Illustration of the orientation change of mesogens and MPS domains by the surface segregation layer of SAP and photoalignment process for the PS-*b*-P5Az10MA film described in this study.



| | m | n |
|---|---|---|
| SAP1 | 80 | 53 |
| SAP2 | 306 | 107 |
| SAP3 | 510 | 144 |

**Scheme 2.** Synthetic routes of PS-*b*-P5Az10MA (a) and PBMA-*b*-P5Az10MA(b).

surface coverage in the orientation control of MPS structures have been also pointed out for other block copolymers [10, 11].

The above facts inspired us to investigate blend film systems in which a polystyrene-based Az LC block copolymer (PS-*b*-P5Az10MA, see Scheme 2) exhibiting the homeotropic orientation and the in-plane orienting PBMA-*b*-P5Az10MA are mixed. In such system, it was expected that the addition of a minor amount of PBMA-*b*-P5Az10MA in the PS-*b*-P5Az10MA film crucially changes the molecular and domain orientations from a homeotropic direction to a planar one. Upon annealing, the blended PBMA-*b*-P5Az10MA segregates to the free (air) surface in the blend film due to the lower surface tension, and acts as a surface active polymer (SAP) [12]. The planaly oriented MPS cylinder domains are then readily aligned homogeneously by irradiation with linearly polarized light (LPL) (Scheme 1) [12]. Surface segregation at the surface and interface is of practical importance [13–15]. The present work is achieved to gain further understandings on the design of the SAP (PBMA-*b*-P5Az10MA). Factors such as i) polymer architecture, namely, block copolymer or homopolymer of PBMA, ii) blending amount, and iii) molecular weight of SAP are explored in this work.

## 2. Experimental Section

### 2.1 Materials

Styrene (99.5%, Kishida) and butyl methacrylate (BMA) (98.0%, Wako) were passed through a column filled with neutral alumina to remove polymerization inhibitor, dried over calcium hydride, and distilled under reduced pressure. CuBr (95.0%, Kanto Chem.) and CuCl (99.9%, Wako) were washed with acetic acid containing a drop of HCl solution and diethyl ether for several times, and dried in vacuum. The initiators of ethyl 2-bromoisobutyrate (EBB) (98.0%, Tokyo Chem. Ind.) and 1-phenylethyl bromide (1-PEBr) (95.0%, Tokyo Chem. Ind.) and the ligands of 4,4′-dinonyl-2,2′-dipyridyl (Bpy9) (97.0%, Aldrich) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97.0%, Aldrich) were used as received. Tetrahydrofuran (THF) of dehydrated stabilizer free grade (Kanto Chem.) was used for polymerization. 90% active neutral aluminum oxide (Merck, active stage 1, particle size: 63-200 $\mu$m) was used for column chromatography.

### 2.2 Synthesis of Diblock Copolymers

*2.2.1 PS-b-P5Az10MA via ATRP.* Synthesis of 4-(10-methacryloyloxydecyloxy)-4’-pentylazobenzene (5Az10MA) was described previously [16]. Polystyrene-Br macroinitiator was polymerized by ATRP. Scheme 2a. shows the synthetic route of PS-*b*-P5Az10MA. PS-Br, CuCl, Bpy9, and 5Az10MA were add into a 15 ml pressure glass tube. The mixture was dissolved in THF in glove box. The sealed mixture solution was removed from the glove box and placed for 24 h in a ChemStation at 70 °C. The polymerization was stopped by exposing the catalyst to air. The reaction solution was dissolved in chloroform and passed through an activated neutral alumina column to remove the Cu catalyst. After being concentrated, the solution was poured to methanol to remove polystyrene-Br macroinitiator and 5Az10MA monomer. The averaged numbers of repeating unit of S and 5Az10MA were 123 and 218, respectively ($PS_{123}$-*b*-$P5Az10MA_{218}$). $M_n$ ($^1$H-NMR) = $1.2 \times 10^5$, $M_w/M_n$ (GPC) = 1.29. In this paper, this polymer will be denoted as PS-*b*-P5Az10MA.

*2.2.2 PBMA-b-P5Az10MA (SAP) via ATRP.* PBMA-Cl macroinitiator was polymerized by ATRP. The polymers were synthesized in similar procedures as described for PS-*b*-P5Az10MA. Scheme 2b shows the synthetic route of PBMA-*b*-P5Az10MA. For this polymer, three block copolymers possessing different molecular weight were synthesized. The block copolymers will be denoted as SAP1, SAP2, and SAP3, the molecular weight being larger in this order, for simplicity (See Scheme 2). $M_n$ ($^1$H-NMR) = $3.7 \times 10^4$, $M_w/M_n$ (GPC) = 1.27 for SAP1, $M_n$ ($^1$H-NMR) = $9.6 \times 10^4$, $M_w/M_n$ (GPC) = 1.22 for SAP2, and $M_n$ ($^1$H-NMR) = $1.4 \times 10^5$, $M_w/M_n$ (GPC) = 1.17 for SAP3. The averaged number of repeating unit of BMA and 5Az10MA were 80 and 53, respectively, for SAP1, 306 and 111, respectively, for SAP2 and 510 and 144, respectively, for SAP3. These data on the numbers of repeating unit are also listed in Scheme 2.

### 2.3 Preparation of Thin Films and Photoirradiation

Thin films of PS-*b*-P5Az10MA and PBMA-*b*-P5Az10MA/PS-*b*-P5Az10MA were prepared by spincoating. In the blended thin films, the PBMA-*b*-P5Az10MA of SAP1, SAP2, and SAP3 were blended at different mixing ratios. After spincoating, thin films were successively annealed at 130 °C for 10 min followed by gradual cooling to room temperature. The thin films were irradiated with LPL (436 nm visible light) at 1000 mJ cm$^{-2}$ through an optical polarizer. Photoirradiation was performed with a REX-250 (ASAHI SPECTRA Co.). LPL at 436 nm was irradiated at 110 °C to the blended PBMA-*b*-P5Az10MA/PS-*b*-P5Az10MA thin film. The in-plane anisotropy of the Az chromophore in the resulting films was evaluated by polarized UV-Visible absorption spectroscopy.

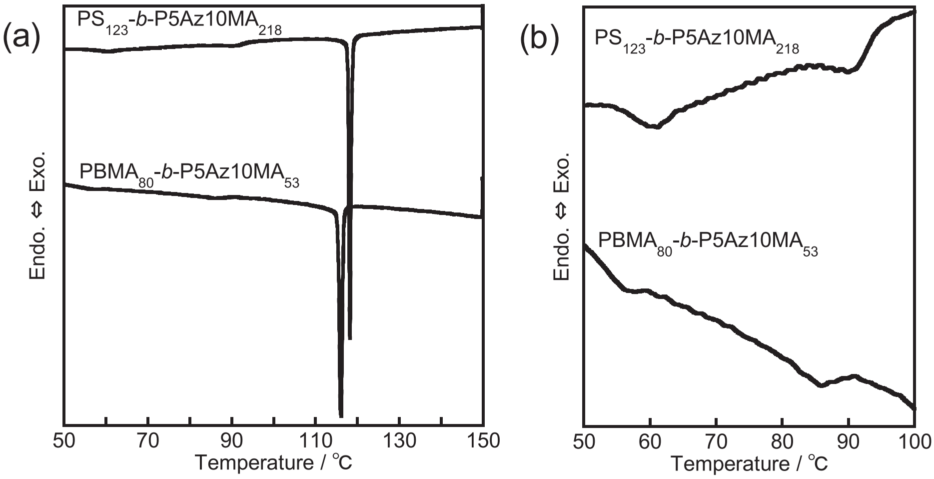


**Figure 1.** DSC curves of the block copolymers on the second heating in ranges from 50 to 150 °C (a) and 50 to 100 °C (b). The heating rate is 2.0 °C/min. Curves for $PS_{123}$-*b*-$P5Az10MA_{218}$ and SAP1 are indicated.

### 2.4 Characterizations

Differential scanning calorimetry (DSC) measurements were achieved with a TA DSC Q200. DSC scans were performed in the temperature range of 30∼150 °C at a heating rate of 2 °C $min^{-1}$ under nitrogen. About 5.0 mg of a polymer sample was used for DSC measurements. An empty aluminum pan was used as a reference. The glass transition temperature ($T_g$) for amorphous polymer chains and phase transition temperatures of LC phase to isotropic phase for the LC block were evaluated by the DSC scans.

Polarized UV-visible absorption spectra were taken on an Agilent 8453 spectrometer (Agilent Technologies) with a polarizer in front of the samples. A $D_2$-W lamp was used as the light source. Quartz plates were used as the substrate for the spectroscopic measurements.

Atomic force microscope (AFM) has been used scanning probe microscope (SPA400) and probe station (SPI3800N) (Seiko Instruments Inc.). Scanner table and silicon-based cantilever (SI-DF20) used to measuring at DFM mode of non-contact. AFM image size of annealed thin films at 130 °C for 10 min was 2.0 × 2.0 $\mu$m of phase mode for checking cylinder structures.

Grazing incidence small angle X-ray scattering (GI-SAXS) measurement was performed on voltage 45 kV, current 60 mA and camera length was 960 mm with a detected by the imaging plate. (NANO-Viewer X-ray diffractometer) (Rigaku Co.). GI-SAXS measurements were carried on the incident angles of X-ray beam to the films were set at 0.18-0.22° by using pulse controllers (ATS-C316-EM/ALV-300-HM) (CHUO PRECISION INDUSTRIAL CO., LTD.). The diffraction patterns of the in-plane direction were informed about microphase-separated structures of diblock copolymers by GI-SAXS. Samples were stained by $RuO_4$ vapor for ca. 20 min.

## 3. Results and Discussion

Thermal properties of the block copolymers were investigated by DSC. Figure 1 shows the DSC curves of the $PS_{123}$-*b*-$P5Az10MA_{218}$, $PBMA_{80}$-*b*-$P5Az10MA_{53}$ (SAP1) on their

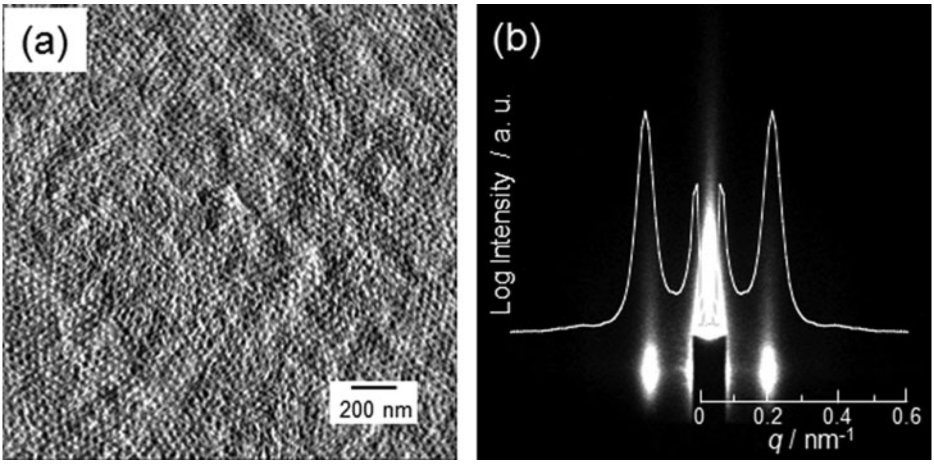


**Figure 2.** (a) 2.0 × 2.0 $\mu$m AFM images (phase mode) of annealed $PS_{123}$-*b*-$P5Az10MA_{218}$ film after annealing at 130 °C. (taken from reference 12). (b) GI-SAXS patterns for the MPS cylindrical domain detection. In the GI-SAXS patterns, 1D intensity profiles are indicated as white lines.

second heating processes. In the case of the $PS_{123}$-*b*-$P5Az10MA_{218}$ on heating, well-defined sharp endothermic transitions was observed at 118 °C, and minor transition were observed at 59 and 89 °C. These transitions were repeatedly observed on the cooling process at a few degrees lower temperatures due to supercooling. These transitions can be assigned as glass-59 °C -SmC-89 °C-SmA-118 °C-iso, $T_g$ of PS = ca. 104 °C). Similarly, SAP1, SAP2, and SAP3 gave endothermic peaks at 116, 118, and 118 °C, respectively. The three PBMA-based block copolymers differ in molecular weight, however, the minor transition temperatures around 60 and 90 °C did not change, therefore only the DSC profile of SAP1 is displayed in Figure 1b. The transition behavior are assigned as follows. SAP1: glass-60 °C-SmC-91 °C-SmA-116 °C-iso, SAP2: glass-61 °C-SmC-91 °C-SmA-118 °C-iso, and SAP3 glass-60 °C-SmC-90 °C-SmA-118 °C-iso: $T_g$ of PBMA was ca. 20 °C.

A spincast film of $PS_{123}$-*b*-$P5Az10MA_{218}$ prepared from 1 and 2 weight% chloroform solution exhibits cylindrical MPS domains of polystyrene (thickness: 100 – 200 nm. After annealing at 130 °C (above the isotropization temperature of the LC Az block and above $T_g$ of polystyrene) for 10 min followed by gradual cooling via the smectic LC phase to room temperature, this film spontaneously formed a homeotropic orientation of 5Az10MA side mesogens. The surface morphology evaluated by AFM revealed that the vertically oriented cylindrical domains of PS are exposed to the surface in the $PS_{123}$-*b*-$P5Az10MA_{218}$ film (Figure 2a). The AFM image in the phase mode showed a dot array structure (average dot-to-dot distance; 46 ± 0.7 nm). The structure of the MPS cylinders of the $PS_{123}$-*b*-$P5Az10MA_{218}$ film was evaluated by GI-SAXS measurements (Figure 2b). The scattering spots in the GI-SAXS were observed at ($q = 0.21$ nm$^{-1}$ ($d = 42$ nm, white arrows), which corresponds to the MPS cylindrical domains.

The annealed $PS_{123}$-*b*-$P5Az10MA_{218}$ film exhibited a significant reduction of the $\pi-\pi^*$ absorption band of Az unit around 320 nm (Figure 3, 0%). By adding 5, 10 and 20 weight% of SAP1 to $PS_{123}$-*b*-$P5Az10MA_{218}$, the same procedure led to marked spectral changes compare to $PS_{123}$-*b*-$P5Az10MA_{218}$ -thin film, showing systematic and considerable increases in the $\pi-\pi^*$ absorption band. These results indicate that the Az mesogenic groups

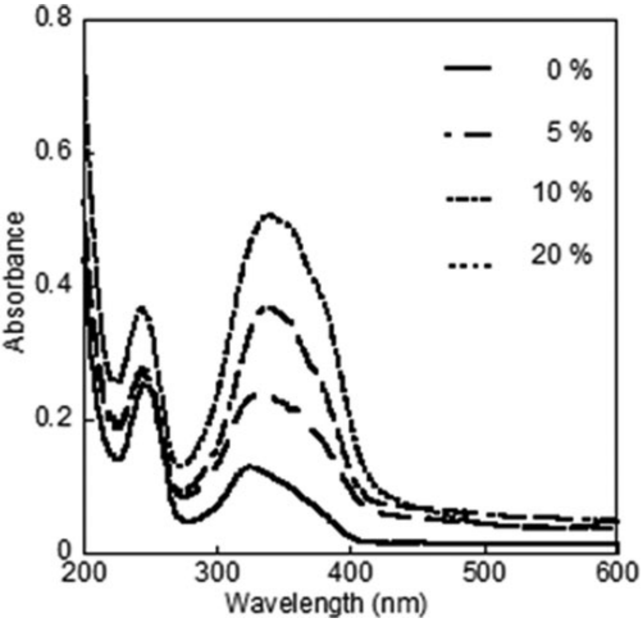


**Figure 3.** UV-visible absorption spectra of the $PS_{123}$-*b*-$P5Az10MA_{218}$ film adding 0, 5, 10, and 20 weight% of SAP1 after annealing at 130 °C.

of the $PS_{123}$-*b*-$P5Az10MA_{218}$ thin film tends to be oriented in more planar directions to the substrate with increasing the amount of blended SAP1.

Addition of the same amount of PBMA homopolymer up to 20 weight% blend did not lead to this effect. This fact strongly suggests the important role of P5Az10MA block in the SAP to cause the orientation change of $PS_{123}$-*b*-$P5Az10MA_{218}$. The PBMA homopolymer did not cover the surface homogeneously but exhibited heterogeneous dewetting on the base $PS_{123}$-*b*-$P5Az10MA_{218}$ film.

Based on these UV-Visible absorption spectra, the in-plane photoalignment control by irradiation with linearly polarized light (LPL) at 436 nm was examined for the surface-segregated films. The extent of planar orientation of Az mesogenic groups should influence the effectiveness for the photoalignment in the in-plane directions. The resultant polarized UV-Visible absorption spectra are shown in Figure 4 for films containing 5 weight% (a), 10 weight% (b), and 20 weight% (c) of SAP1 in the $PS_{123}$-*b*-$P5Az10MA_{218}$ thin film. The degree of in-plane anisotropy was estimated by the order parameter $S\ [=(A_{\perp}-A_{\parallel})/(A_{\perp}+2A_{\parallel})]$, where $A_{\perp}$ and $A_{\parallel}$ denote absorbance at the $\lambda_{max}$ of the $\pi-\pi^*$ absorption band of the Az unit (ca. 320 and 350 nm for 10% and 20% samples, respectively) obtained by measurements using LPL with $E$ perpendicular and parallel to that of actinic polarized light. When the blend amount was 5 weight%, the photoinduced in-plane anisotropy was of minor (a). Blending 10 and 20 weight% of SAP1 led to clear in-plane anisotropic nature. The pronounced anisotropy was observed for the film containing 20 weight% of SAP1 (c). $S$ values were 0.02, 0.18, and 0.76, for 5, 10 and 20% blend films, respectively. Thus, in case of SAP1, sufficient in-plane orientation is performed in the 20% blend film.

The induction of planar orientation of Az mesogenic group by the SAP was found to be strongly dependent on its molecular weight. Figure 5 indicates polarized UV-visible

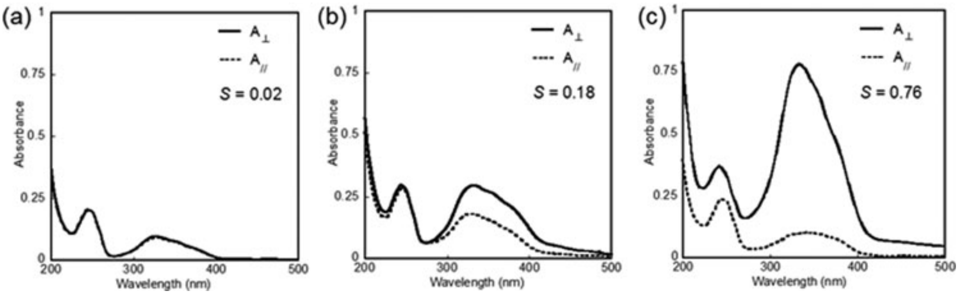


**Figure 4.** Polarized UV-visible absorption spectra of $PS_{123}$-*b*-$P5Az10MA_{218}$ films adding 5 (a), 10 (b), and 20 (c) weight% of SAP1 after annealing at 130 °C and irradiation with 436 nm LPL at 1000 mJ $cm^{-2}$. For procedures see SCHEME 1. The spectra are taken with the probing beam parallel (dotted line) and orthogonal (solid line) to the actuating light.

absorption spectra obtained for SAP2 and SAP3 after LPL irradiation and annealing under the same conditions for SAP1 as mentioned above. With these SAP with larger molecular weight, the blend amount of SAP required to attain the sufficient in-plane orientation became significantly smaller. As shown in Figure 5, the blending ratios of 5 and 3 weight% were sufficient for SAP2 and SAP3, respectively, to provide large in-plane anisotropy, in contrast with the fact that 20 weight% is needed for SAP1. *S* values calculated for SAP2 and SAP3 form the data in Figure 5 were 0.48, and 0.56. The chemical composition of these surface active polymers is essentially the same, however interestigly, SAP2 and SAP3 having molecular weight 2.6 times and 3.8 times larger, respectively, than SAP1 bring about the clear orientation alternation of Az mesogens from the homeotropic to planar mode with substantially smaller amounts of SAP. Such molecular weight effect is interesting but the reasons for this behavior is still unclear. At the moment, we assume that the surface skin layer of SAP with smaller melecular weight is mechanically unstable supposedly showing

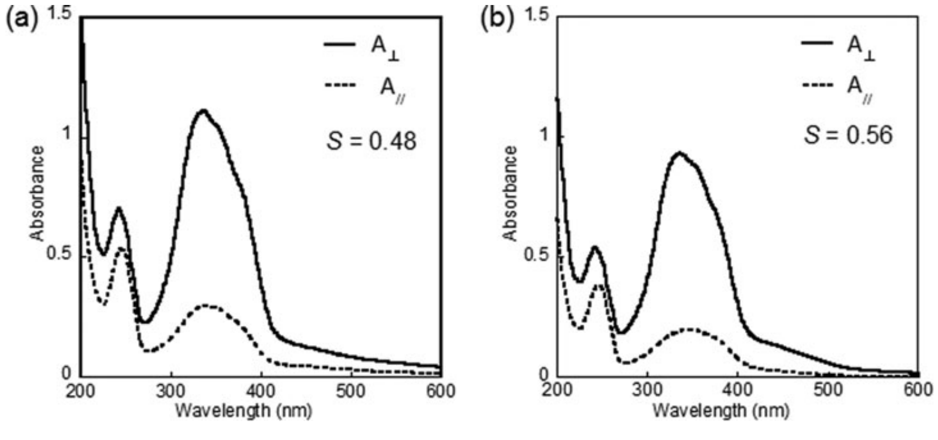


**Figure 5.** Polarized UV-visible absorption spectra of SAP2 (5%)/$PS_{123}$-*b*-$P5Az10MA_{218}$ (a) and SAP3 (3%)/$PS_{123}$-*b*-$P5Az10MA_{218}$ (b) blend thin films after irradiation with 436 nm LPL at 1000 mJ $cm^{-2}$. The spectra were taken with the probing beam parallel (dotted line) and orthogonal (solid line) to the actuating light.

surface dewetting, therefore, more amount of SAP is required to form homogeneous and stable surface layer.

In this paper, discussions are based only on the characterizations of the molecular orientation of Az units obtained by polarized UV-visible absorption spectroscopic data. However, it is already confirmed that the information at the molecular level obtained by spectroscopic evaluation can be directly related to the orientation of cylinder MPS cylinder domains at the mesoscopic level. It is well established by X-ray measurements and atomic force microscopy that the mesogenic orientation and the MPS domain orientations are parallel with each other to minimize the elastic energy of the system [5–9, 12]. Therefore, the total hierarchical structures including Az mesogens and polystyrene cylinder domains should be controlled in the film as displayed in Scheme 1.

## 4. Conclusion

LC block copolymers possessing polystyrene (PS-*b*-P5Az10MA) and poly(butyl methacrylate) PBMA-*b*-P5Az10MA with three different molecular weight are synthesized in the range of narrow dispersions from 1.17–1.29 by the ATRP method. Blending a small amount of PBMA-*b*-P5Az10MA (surface active polymer, SAP) possessing lower surface tension with PS-*b*-P5Az10MA film and successive annealing give rise to the segregation of SAP to the free surface. The segregation causes the homeotropic to planar orientation of the Az mesogen of PS-*b*-P5Az10MA and MPS cylinder of polystyrene. In terms of polymer design and conditions of SAP, the factors influencing the free surface-induced orientational alternation found in this work are summarized as follows. (i) Block copolymers containing the mesogens should be used. The homopolymer of PBMA is not favorable due to the low compatibility with the base block copolymer, exhibiting dewetting on the surface. (ii) The blend ratio of SAP should be large enough to cover the base polymer surface. (iii) The molecular weight significantly influences the surface coverage, and the smaller amount will be sufficient for the larger molecular weight SAP. The procedure of blending of surface active block copolymer is very simple to place a polymer skin layer on the free surface, but leads to marked effects on the molecular and domain orientations in the base films. Such approach should have potential significances in the inductrial applications in terms of versatility and low-cost processing.

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