

## Role of the Free Surface for Orientations in Liquid Crystalline Polymer Films

There is a strong tendency for side chain liquid crystalline (LC) polymers to exhibit homeotropic orientation in thin films. We have shown the control of homeotropic-to-planar LC alignment in a side chain LC polymer, P5Az10MA, thin film by “free surface” modification. Adding a small amount of surface-active block copolymer composed of poly(butyl methacrylate) and P5Az10MA blocks, PBMA-*b*-P5Az10MA, to a LC homopolymer thin film induced orientational alternations of the LC phase from homeotropic to planar alignment effected by surface segregation and coverage of PBMA at the free surface. The present result demonstrates that the free surface and surface segregation are important for controlling the inner structure of the polymer LC film.

The molecular orientation of liquid crystals (LCs) depends strongly on the surface characters [1]. LC alignment techniques include surface molecular orientations and topographical grooves and undulations of the substrate. Controlling the LC alignment layers is an important technique in applications for LC optical devices. LC surface alignment by mechanically rubbing the polymer surface on a substrate is the most widespread and popular industrial process for LC devices [2]. Recently, LC alignment was carried out on photoreactive polymer films by anisotropic irradiation [3]. Currently, the photoalignment method has begun to be used in the industrial production of liquid crystal televisions. Most LC devices are made of fluid low molecular LCs; the LC active layer in these devices is sandwiched between the alignment layers on substrates. On the other hand, polymer LCs can form robust thin films on substrates by themselves, and so there are expectations that polymer LCs could form free-standing films with a free surface for applications. At a free surface (an air surface), calamitic LC molecules strongly prefer the homeotropic (vertical) molecular alignment; this has been shown experimentally [4] and has also been verified by theoretical simulations

[5]. Actually, homeotropic alignment dominated by the free surface is generally preferable in side chain LC polymer films. Furthermore, the low birefringence character of the homeotropic alignment narrows down the application of LC polymers to display devices.

Recently, we reported the LC orientational alternation of a polymer LC induced by free surface modification in polymer thin films through polymer surface segregation [6]. Surface segregation is one of the interfacial phenomena in polymer thin films, involving enrichment of a specific polymer component at the surface by self-assembly in polymer blend films [7]. Polymer components with low free energy, relatively low surface tension [8] and high mobility [9] are easily concentrated at the surface. To modify the free surface of the LC polymer film, we apply the surface segregation of a small amount of a free-surface-active polymer. Coverage of the film surface with the free-surface-active polymer leads to homeotropic-to-parallel orientational alternations of LC mesogens, which further enable efficient in-plane photoalignment of LC and microphase separation (MPS) domains of a relevant LC polymer and block copolymer by linearly polarized light (LPL).

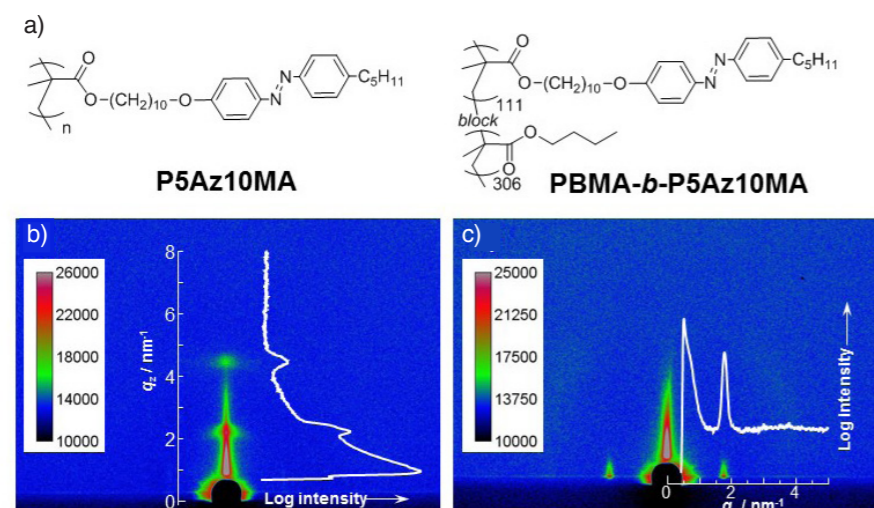


Figure 1: Chemical structures for P5Az10MA and PBMA-*b*-P5Az10MA (a). 2D GI-SAXS images of a pure P5Az10MA thin film (b) and PBMA-*b*-P5Az10MA (10%)/P5Az10MA blend thin film (c) after annealing at 130°C. In the SAXS patterns, 1D intensity profiles are indicated as curves in white.

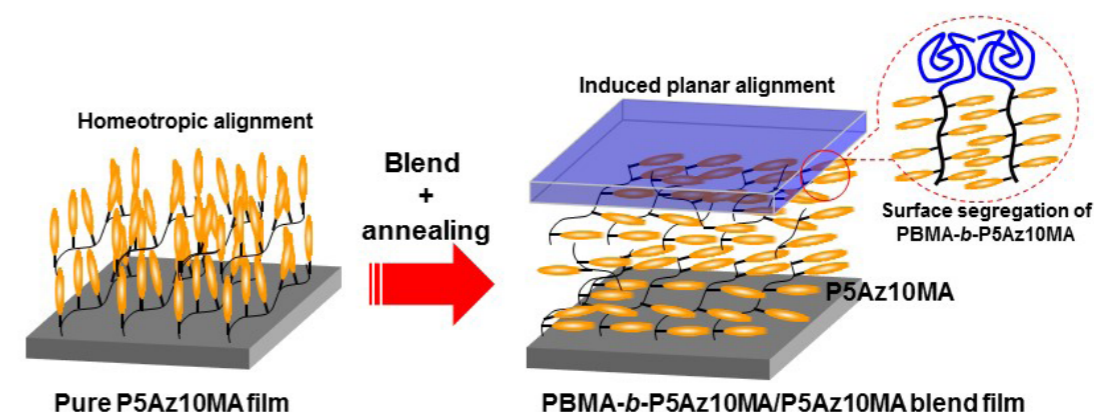


Figure 2: Schematic illustrations of the orientational alternation and alignment process for the P5Az10MA homopolymer.

The smectic liquid crystalline azobenzene polymer P5Az10MA [Fig. 1(a)] exhibits homeotropic alignment in a thin film. In grazing incidence small angle X-ray scattering (GI-SAXS) measurements, scattering corresponding to the smectic lamella structure was observed in the out-of-plane direction [Fig. 1(b)]. On the other hand, adding 10 weight% (%) of PBMA-*b*-P5Az10MA [Fig. 1(a)] induced the opposite LC orientation in the film. In the PBMA-*b*-P5Az10MA (10%)/P5Az10MA film, scattering spots due to the smectic layer were observed in the in-plane position by GI-SAXS 2D imaging [Fig. 1(c)], suggesting that the smectic LC layer aligned normal to the substrate with planar aligned azobenzene side chains. Contact angle measurements demonstrate that the PBMA component is segregated and enriched at the film surface in the PBMA-*b*-P5Az10MA (10%)/P5Az10MA film. The surface segregated top layer of the PBMA block provides a microphase separated interface parallel to the surface plane. As a result, a random planar aligned smectic LC layer is induced with perpendicularly oriented rigid rod LC polymer backbone from the surface segregated layer. The present approach through the surface-active layer can be also applied to in-plane alignment for the microphase separated cylinder structure for a P5Az10MA block copolymer. The homeotropic alignment has a disadvantage for efficient photoalignment by LPL irradiation because the transition moment for azobenzene side chains is normal to the actinic LPL electric field. In the normal aligned smectic layer, LPL irradiation can lead to efficient angular selective photoisomerization of the azobenzene LC.

The orientation and photoalignment behaviors proposed in the present processes are illustrated in Fig. 2. In the pure P5Az10MA film, the normal anchoring from the free surface of azobenzene side chain mesogens induces the homeotropic LC orientation. Adding the surface-active PBMA-*b*-P5Az10MA and subsequent annealing leads to the formation of a skin layer on the surface and provides planar orientation of mesogens. Owing to the preformed parallel orientation, LPL irradiation

efficiently leads to homogeneous in-plane alignment orthogonal to the electric field of the LPL. The proposed alignment process via surface segregation is very simple and therefore provides new possibilities for orientation control of various types of LC materials. Selective surface segregation of a surface-active polymer component offers promising applications for imposing surface functions such as adhesive and frictional properties and for improving biocompatibility. In addition to such functions accessing the exterior phase, the present work indicates that the free surface and surface segregation are also important for controlling the inner structure of the polymer LC film.

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### BEAMLINE

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