Feature article

Versatility of photoalignment techniques: From nematics to a wide range of functional materials

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ABSTRACT

Alignment methods of nematic liquid crystals (LCs) by surface photoreactions on substrate surfaces were initially proposed around 1990, and the photoalignment technology of nematic LCs has recently been integrated into the LC device fabrication industry due to its profitable features. Accumulated efforts in this field have revealed that applications of photoalignment processes are not limited to conventional nematic LCs but that a variety of functional materials can also be manipulated according to this principle. Target materials have now been extended to thermotropic smectic LCs, discotic LCs, LC polymers, block copolymers, gel networks, conjugated polymers, and organic semiconductors and lyotropic systems including chromonic LCs and inorganic–organic mesostructured hybrids. Through these photochemical approaches, many types of photopatterning for both topographical and orientational modulations have become feasible. This article reviews photoalignment processes applied to a wide range of materials, surveying relatively recent work. Some important related alignment and patterning processes are also introduced to clarify the significance of these photoalignment techniques.

1. Introduction

Strong orientational cooperativity and its long range correlation in liquid crystals (LCs) have attracted great attention from physicists and chemists. The cooperative nature magnifies a local orientation preference to larger macroscopic regions. Typically, the molecular or topological orientation on the substrate surface is reflected in a large volume of contacting LC materials. Even though the surface is not homogeneous, the contacting LC smooths out the inhomogeneity and provides uniform domains over large areas and volumes. In the last two and half decades, photoalignment techniques have been recognized as new and significant tools for molecular and material processing. These techniques in general do not require expensive instruments, and the light manipulations possess spatial accuracies with high resolutions. Therefore, they have potential widespread applicability. In this review, we will introduce the widespread applicability and utilities of photoalignment processes.

The first demonstration of LC alignment control by surface photochemistry was provided by Ichimura et al. [1] in 1988. They found that the E/Z (trans/cis) photoisomerization of an azobenzene monolayer on a substrate could switch the alignment of nematic LC molecules between homeotropic and planar modes (Fig. 1). This active functional surface is called a "command surface" or "command layer." Shortly after this finding, Gibbons et al. [2], Dyadyusha et al. [3], and Schadt et al. [4] showed that angular selective excitation by linearly polarized light (LPL) onto an azo dye-doped polyimide or a photocrosslinkable polymer film led to in-plane alignment control. At the same time, Kawanishi et al. reported the same effect for an azobenzene self-assembled monolayer (SAM) [5]. The dawn of research on the induction of optical (structural) anisotropy in polymer films tracks back to the work of Weigert in the beginning of the 1920s [6]. Todorov et al. first observed LPL-induced birefringence in amorphous polymer films [7] in 1984. Regarding LC polymer systems, Eich, Wendorff et al. first demonstrated holographic recording based on the LC molecular orientation change of polymers [8,9] in 1987. In addition to LPL irradiation, oblique (slantwise) irradiation of non-polarized light can also create obvious effects such as angular selective anisotropic excitation (Fig. 2).

Through the accumulated efforts of researchers and engineers over the years, the surface photoalignment phenomena of nematic LCs on polymer films have become areas of significant industrial interest. In 2009, Sharp Corporation initiated a mass production of LC TV panels via a photoalignment process (UV^{2}A) in lieu of the rubbing process [10]. This revolutionary event facilitated the

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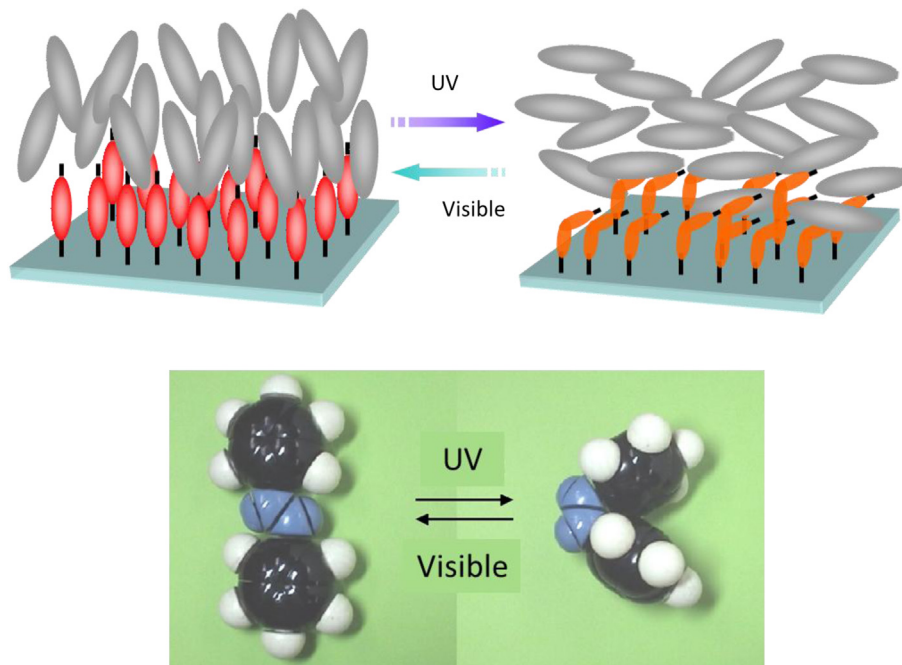 *E-mail address:* tseki@apchem.nagoya-u.ac.jp (T. Seki).

Fig. 1. Schematic illustration of reversible photoalignment by a "command surface" composed of an azobenzene monolayer [1,29].

development and adoption of photoalignment processes in the industry. As has long been discussed, photoalignment technology characterized by non-contact and high resolution processes has great advantages when compared with rubbing processes [11].

Details of nematic LC systems will not be discussed here, but the reader is referred to the well-documented literature [11–17]. Summary tables and a short description of new trends will be presented as background. This article will discuss relatively recent literature, mostly after 2000. The major purpose of this review is to introduce new trends and directions in photoalignment phenomena and processes, including some related peripheral topics that may be extended to future polymer thin film technologies. Emphases are placed on the photoalignment and patterning processes of other types of nematic LCs, including both thermotropic (smectic LCs, discotic LCs, polymer films with various architectures, gel networks, etc.), conjugated polymers/organic semiconductors and lyotropic systems (chromonic and inorganic–organic hybrids, etc.). Photoalignment at the molecular level can be transformed to larger
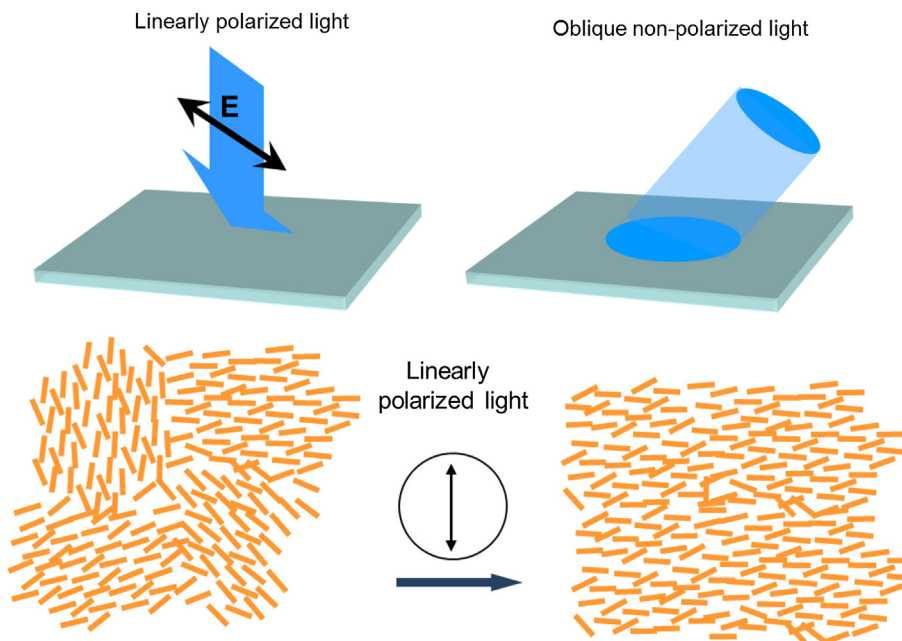

Fig. 2. Schematic drawings of irradiation with linearly polarized light (LPL) and oblique non-polarized light (upper). The lower drawing shows a model of aligned monodomain formation of LCs by irradiation with LPL.

mesoscopic systems such as microphase separation patterns of block copolymers and lyotropic organic–inorganic sol–gel systems. We will describe mesoscopic (mesostructured) systems in more detail in anticipation that they will find new and unknown applications in the future.

This article reviews for the first time the wide applicability and scope of photoalignment techniques. The contents of this review are as follows. In Section 2, recent trends in surface photoalignment studies are surveyed together with other related surface aligning techniques. Section 3 focuses on the results of other types of thermotropic LCs, including chiral LCs, discotic LCs and LC networks. Section 4 briefly reviews the photoalignment studies of polymers of various architectures such as linear, dendritic, surface-grafted, block copolymers, and organic semiconductors. In Section 5, the systems are further extended to lyotropic ones ranging from chromonic LCs to inorganic mesostructures templated by organic surfactants and chromonics. This section also briefly introduces some new trends in the biomineralization process exerted on engineered surfaces.

2. Surface photoalignment of nematic LCs

2.1. Surface alignment techniques

The physics and mechanisms of the surface alignment of nematic LCs have been systematically reviewed by Jerome [18,19]. From a technological viewpoint, fabrications of LC display (LCD) panels are, of course, the most important applications. A number of surface alignment methods have been developed as shown in Table 1. Note that this table does not cover the totality of reports on surface alignment of nematic LCs. Only selected examples are listed.

Mechanical methods have mostly been applied to align nematic LCs. These methods include rubbing, air-buffing [20], friction transfer of polymer materials [21], and stretching and peeling of a substrate [22–24]. As widely known, the rubbing of a polymer film (mostly polyimides) on a substrate has been adopted for the production of LCD devices.

The second category in Table 1 indicates photoalignment processes for various types of film forms. They include self-assembled monolayers (SAMs) [1,25–28], Langmuir–Blodgett (LB)

films [29–33], alternatively adsorbed layer-by-layer (LbL) films [34], spincast polymer films, photo-rubbing [35], surface polymer brushes [36], topographical surface relief gratings (SRGs) generated by patterned photoirradiation [37–39], and photochemical surface modification to introduce photoreactive units [40]. SAM and LB films are most suitable to communicate the effect of molecular and surface design for the photoalignment behavior. However, their utility may be limited to laboratory explorations. Spincast polymer films can readily be applied to industrial fabrication processes, and a vast amount of results have been reported. Thus, they are summarized in a separate table (Table 2) sorted by the photoreactions and polymer types employed, which will be explained later.

Turning to methods of scientific interest, the surface alignment system of nematic LCs provides a fascinating system in which the surface information is greatly magnified via orientational change of LC molecules. Very subtle orientational preferences on the substrate surface can be reflected by the LC orientation in the correlation length. These are the most attractive properties with which to conduct investigations on LC alignment. This situation provides unique systems in which dynamic molecular communication between the surface and LC molecules can be detected at high sensitivities. The contact of rodlike LC molecules on an azobenzene monolayer surface prepared by the Langmuir–Blodgett method induces upright orientation of the azobenzene unit on the substrate [29]. This observation clearly suggests that the obtained orientation is the result of cooperative interaction (molecular recognition) between the flexible azobenzene side units and LC molecules. Abbott et al. [41–46] have conducted systematic investigations on LC alignment changes which demonstrate that a variety of surfaces, including molecular/polymer and biological macromolecules, can be applied to sensitive chemical and biological sensors.

Apart from the photoalignment in SAM systems, a topical study has been reported by Hoogboom, Nolte et al. [47]. They found that a supramolecular aggregate of the SAM component forms robust nanogrooves for nematic LC alignment. The robustness, when compared to a relevant cinnamate derivative, is due to intermolecular hydrogen bonding and π-stacking of the

Table 1
Surface aligning methods for nematic LCs (references mostly after 2000).

		References
Mechanical method	Rubbing	Standard technique
	Air-buffing	[20]
	Friction transfer	[21]
	Stretch	[22,23]
	Peeling	[24]
Photoalignment	Self-assembled monolayer	[1,25–28]
	Langmuir–Blodgett film	[29–33]
	Layer-by-layer	[34,135]
	Spincast polymer films	See Table 2
	Photo-rubbing	[35]
	Surface polymer brush	[36]
	Surface relief grating (SRG)	[37–39]
	Surface modification	[40]
Topographical patterning	Nanoimprint	[49–53]
	Wrinkle	[54–56]
	Pillar array	[57]
	Ink-jet printing	[58]
Beam technology	Ion beam	[59,60]
	Plasma beam	[61]
	Electron beam	[52,62,63]

Table 2
Photoreactions and selected photoaligning polymers for LC alignment (references mostly after 2005).

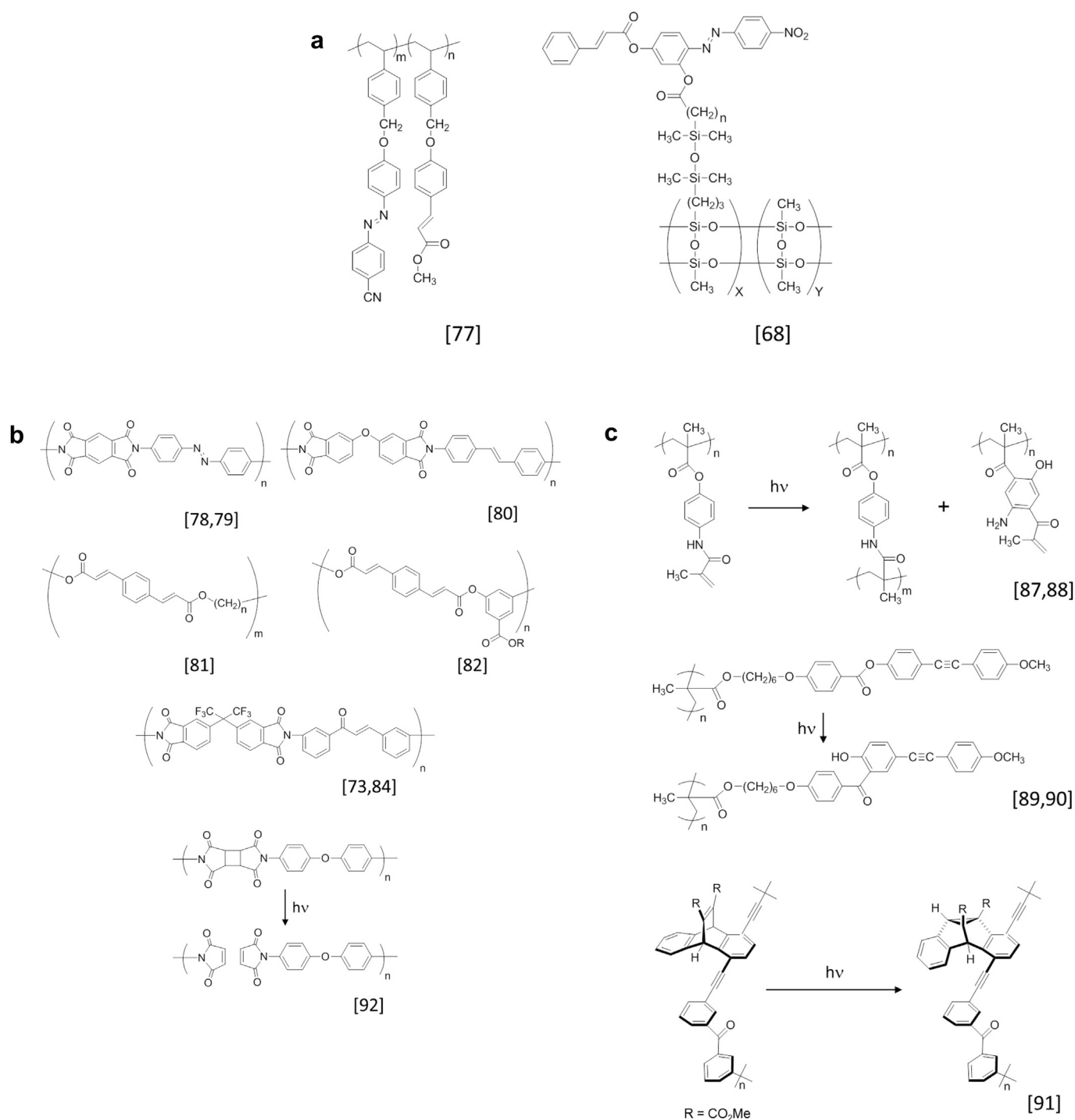|		Polymer type	References
E/Z (trans/cis) isomerization	Azobenzene	Side chain	[11–13,15,64,65]
		Main chain	[78,79]
	Stilbene	Main chain	[80]
	Styrylpyridine	Side chain	See below for [2 + 2] cycloaddition
	Cinnamate	Side chain	See below for [2 + 2] cycloaddition
[2 + 2] Cycloaddition	Cinnamate	Side chain	[64,69–71]
	Cinnamate-type	Main chain	[81–83]
	Coumarin	Side chain	[66] [67]
	Chalcone	Side chain	[72,73]
		Main chain	[73,84]
	styrylpyridine	Side chain	[74,75]
[4 + 4] Cycloaddition	Anthracene	Side chain	[76]
E/Z + cycloaddition		Side chain	[68,77]
Photo-rearrangement	Photo-Fries	Side chain	[87–90]
	Di-π-methane	Main chain	[91]
Photodecomposition	Cyclobutane polyimide, polystyrene, etc.	Main chain	[92]
	Polysilane	Main chain	[93,94]

Fig. 3. a. Dual functional polymers for photoalignment of nematic LCs. The numbers in parenthesis indicate the references. b. Main chain type polymers for photoalignment of nematic LCs. The numbers in parenthesis indicate the references. c. Photo-rearrangement reactions for photoalignment of LCs. The numbers in parenthesis indicate the references.

larger aromatic moiety. The direction of the grooves appears to be governed by the existence of seeds of nanogrooves on the indium tin oxide surface. Based on this knowledge, they further constructed tunable command layers for LC alignment by the aggregations of Zn phthalocyanines attached on a pyridine-functionalized oligosiloxane [48].

The third category in Table 1 utilizes topographical patterns on the substrate surface. The most popular way to produce topographical patterns is to employ photolithography processes. This method is not included in the table because most examples are found in patents. In recent years, the significance of the nano-imprint process has been increasing [49–53]. This versatile method can provide topographical patterning down to some tens of nano-meters. For larger undulation patterns, surface wrinkle formation via compression of an elastomeric substrate is also an attractive process [54–56]. In this facile procedure, the surface topographical structure and directions can be changed or tuned simply by changing the mechanical compression conditions. Pillar array

formation [57] and ink-jet printing [58] are recent advances in LC alignment technology.

Beam technologies in the fourth category are important issues in LC alignment technology for fabrications of precise surface structures. Ion beams [59,60], plasma beams [61], and electron beams [62,63] have been utilized.

2.2. Photoalignment of nematic LCs on spincast films

From the practical viewpoint, spincast film systems are the most important. Table 2 summarizes photoalignment systems using spincast polymer films utilizing various types of photoreactions. Polymer structures of selected examples are shown in Fig. 3. Introduction of photoreactive units as side groups of a backbone is the major strategy for polymer design [11–13,15,64,65]. In Fig. 3, only the more unconventional types are displayed, i.e., dual functional polymers (a), main chain type polymers (b), and photo-rearrangement types. The photoisomerization of azobenzene and [2 + 2] cycloaddition of cinnamate and coumarin are the most frequently employed. Coumarin undergoes only photodimerization [66–68]. However, in the case of cinnamate [64,69–71] and chalcone [72,73], both photoisomerization and photocrosslinking occur, and the alignment behavior becomes rather complicated. For the side chain polymers, the alignment behavior often depends on the irradiation energy dose [11,64]. The alignment of nematic LCs can be changed from perpendicular to parallel or the inverse. In the case of styrylpyridine, three types of photoreactions, photo-isomerization, cyclization and crosslinking, can occur. This process was extensively studied by Yamaki, Ichimura et al. [74,75]. In addition to [2 + 2] type, [4 + 4] cycloaddition of anthracene side groups was explored by Kawatsuki et al. [76]. In attempts to combine the functionality of the photoisomerization of azobenzene and photocrosslinking of cinnamate in one polymer chain, Kang et al. [77] and Gu et al. [68] studied random copolymers and dual chromophore groups, respectively (Fig. 3a).

Main chain polymers have superior stability and durability. The molecular design of main chain polymers also has many options. Azobenzene [78,79], stilbene [80], cinnamate-type [81–83] and chalcone [73,84] have been introduced to polyester and polyimide main chain structures (Fig. 3b). Hahm et al. demonstrated that orientation inversion also occurs with light energy for a main chain stilbene polymer [80].

With regard to cinnamate polymers, direct excitation of this unit suffers from its need for wavelengths typically below 320 nm and large amounts of light energy. In this context, Furumi and Ichimura [85,86] proposed an intriguing procedure in which the triplet photosensitization from a phosphorescent donor leads to highly sensitive photoalignment by irradiation at 365 nm. This finding of axis-selective triplet energy transfer is of great significance not only from a practical viewpoint but also from an academic viewpoint. The triplet energy transfer occurs via the exchanging electron mechanism by collisions between molecules, yet interestingly, this collisional dynamic process retains the directional information of the angular selective excitation by LPL or oblique irradiation.

Other types of photoreactions are also available. Utilization of photo-rearrangement reactions is a recent topic of investigation. Typical photo-rearrangement reactions are shown in Fig. 3c. Yar-oshchuk et al. reported the axis-selective photo-Fries rearrangement in a photopolymer containing a methacrylamidoaryl side group [87,88]. More recently, side chain polymers with phenyl benzoate side groups have been explored by Kawatsuki et al. [89,90] for photoorientation via photo-Fries rearrangement. Cox, Swager et al. recently showed that a di-π-methane arrangement (formation of cyclopropane) leads to homogeneous LC alignment via triplet sensitization by a benzophenone moiety introduced in the polymer backbone [91]. An angular selective excitation by LPL for the benzophenone, leading to rapid intersystem crossing followed by fast energy transfer to an adjacent di-π-methane unit, induces the homogeneous LC alignment. As a secondary effect, benzophenone diradicals can crosslink the film to yield a robust alignment layer.

Photodecomposition reactions in the polymer main chain have been investigated from the earliest stages of development. The most important reaction is probably the retro [2 + 2] cyclization reaction by shorter wavelength UV of polyimides possessing cyclobutane units in the main chain [92]. The σ-conjugated main chains of polysilanes are readily photodecomposed, a process which can be utilized for the photoalignment layer [93,94].

3. Photoalignment of various types of thermotropic LCs

As described above, surface photoalignment is mostly targeted to nematic LCs because of the potential for LC display fabrication. However, it has been demonstrated that various types of LC materials can be photoaligned both in thermotropic and lyotropic systems. Photoalignment of other types of thermotropic systems is introduced in this section and research examples are summarized in Table 3 together with related methods. Lyotropic LCs will be introduced later in Section 5.

3.1. Chiral calamitic LCs

Alignment control of chiral nematic (cholesteric) LCs has been achieved by Ruslim and Ichimura [95]. They illuminated oblique light on an azobenzene polymer film, and found that the helix axis aligned perpendicular to the propagation direction of the incident non-polarized light.

Ferroelectric LCs (FLCs) produced with a chiral smectic C phase in the surface stabilized mode are expected to be applied to rapid response LC displays. In 2000, Fünfschiling, Schadt et al. demonstrated the photoalignment of an FLC using a thin (12 nm) photocrosslinkable polymer for the first time [96]. Ishitani et al.

Table 3
Photoalignment of low-molecular-mass thermotropic LC materials other than conventional nematics (some other related processes included, references mostly after 2000).

	Aligning method[a]	Alignment layer, remark	Reference
Chiral nematic LC	SPA	Azobenzene side chain	[95]
Ferroelectric LC	SPA	Cinnamate polymer, azo dye	[96–98]
Discotic LC	SPA	Azobenzene or cinnamate polymer	[86,99–101]
	SA	Chemically patterned SAM	[102]
	PA	Alignment by IR laser	[106,107]
	Friction transfer	Transferred PTFE	[103]
Columnar ionic liquid	Shear or SA	SAM	[104,105]
Ion complex LC	PA	Anionic Az-dialkyl ammonium complex	[108]
LC gel network	PA	Crosslinked LC azobenzene polymers	[109–111]
	Rubbing	Crosslinked LC film on polyimide	[112–115]
		LC + gelator on polyimide surface	[116–118]

[a] SPA: surface photoalignment; SA: surface alignment; PA: photoalignment.

discussed, by comparison with a rubbed layer, the advantage of the photoalignment technique in the electrooptical responses of an FLC cell [97]. Pozhidaev et al. produced a high quality photoaligned FLC cell by using an LPL irradiated azo dye layer instead of a polymer layer [98]. The optimal contrast was obtained with a very thin film (3–5 nm) of the alignment dye layer.

3.2. Discotic LCs

Not only calamitic LCs but also discotic ones can be targets for surface photoalignment. Ichimura, Furumi et al. initiated this approach in 2000 [99]. They demonstrated that a triphenylene-type discotic LC can be photoaligned on a thermally stable azobenzene polymer thin film (Fig. 4). Robustness of the alignment layer is required because the viscosity of this type of LC is high. In the case of azobenzene polymer as the photoalignment layer, LPL irradiation leads to a homeotropic orientation with the director perpendicular to the surface. In contrast, oblique irradiation gives rise to a tilted discotic LC orientation with well-ordered optical birefringence at a discotic nematic phase. The discotic molecules are aligned in a hybrid manner where the tilt gradually changes along the film thickness direction [99,100]. Photocrosslinkable polymer films containing cinnamoyl units are also available for discotic LC alignment [101]. Oblique irradiation onto polymer films containing cinnamoyl moieties also leads to aligned discotic LC molecules in a hybrid manner. Interestingly, the alignment behavior strongly depends on the chemical structure of the alignment polymer. It has also been shown that, like calamitic LCs, discotic LCs can be aligned via triplet energy transfer from a phosphorescent donor embedded in the alignment film [86].

Surface alignment of discotic LCs and related columnar ionic liquids is of high significance in optical applications such as production of optical compensation films and anisotropic carrier conducting and ion conducting functions. Therefore, other related

alignment methods such as chemically patterned surface of SAM [102], friction transfer [103], shear [104,105] and irradiation with IR laser [106,107] are also listed in Table 3 for reference.

3.3. Ionic LCs and gel networks

A remarkably high photoinduced optical anisotropy has been obtained in an ion-complex LC material between an anionic azo dye and a dialkyl complex as revealed by Zakrevsky, Stumpe et al. [108]. As predicted, the orienting motion of the ionic material is not very sensitive to LPL irradiation, however, prolonged irradiation of some hundreds of J cm^{-2} leads to a surprisingly high dichroic ratio, as high as 50, which almost corresponds to the level of crystalline materials.

Zhao and Chenard reported anisotropic LC gels prepared by optical alignment. A mixture of LC molecules and azobenzene-containing diacrylate was prepared and thermal polymerization was carried out in the isotropic phase while the mixture was exposed to LPL [109,110]. By continuing the LPL irradiation during the cooling process, optically anisotropic gels with aligned polymer networks were obtained. The LC orientation was preserved even when heating above the isotropization temperatures.

With regard to FLC systems, Priimagi, Shishido et al. prepared an aligned crosslinked sheet of FLC containing an azobenzene unit [111]. They observed a high contrast second order non-linear optical switching of the noncentrosymmetric aligned LC polymer sheet.

In Table 3, LC gel materials aligned on rubbed polyimide films are also included as related systems. Ikeda et al. prepared uniformly aligned LC elastomer films, which have been applied to a large variety of photomechanical film devices [112–115]. They showed that light irradiation on the aligned azobenzene-containing elastomer films displayed bending motions along the rubbing direction. Uniformly oriented gelation of LC materials has been
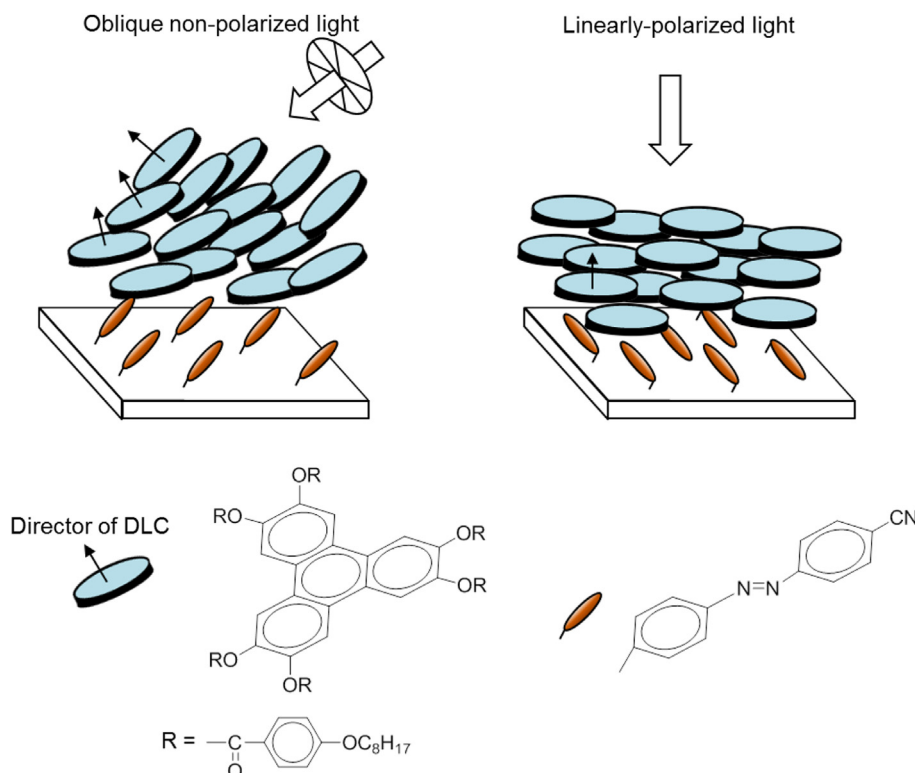

Fig. 4. Photoalignment of discotic LCs by an angular selective surface photoreaction. Redrawn from Ref. [99].

Table 4
Photoalignment of LC polymers (related processes included, mostly after 2000).

Method	Systems and remarks	References
Photoalignment	Azobenzene side chain polymer	[119–123]
	Azobenzene supramolecular side chain	[133,134]
	Stilbene side chain polymer	[124]
	Donor-acceptor substituted ethene	[129], Fig. 5
	Azobenzene main chain polymer	[125,126]
	Cinnamate main chain polymer	[127,128]
	Dendrimer/star-like molecule	[137–140], Fig. 6
	Surface-grafted polymer	[36,141,142,144]
	Block copolymer	[151–159]
Rubbing	Block copolymer	[161]
Surface photoalignment	LC polymer on azobenzene side chain polymer	[130,131]

performed by Kato et al. [116–118]. They prepared supramolecular anisotropic LC gels showing various optical and electric functions.

4. Photoalignment of polymer films

In this section, photoalignment of polymeric and oligomeric film materials is reviewed. Table 4 lists later examples in this category. The table contains examples of photoresponsive LC polymer films possessing self-photoalignable ability and non-photoresponsive ones that require the aid of separate photoalignment layers.

4.1. Self-photoalignable LC polymer films

Conventional polymerizations and condensations provide linear backbone polymers, therefore linear polymers have been most extensively studied. However, recent investigations involve various types of polymers covering dendrimer or star-like architectures, surface grafted polymers and block copolymers.

4.1.1. Linear polymers

A comprehensive review in this area was recently published by Kawatsuki [64] and will not be duplicated here. Table 4 summarizes recent examples. To induce optical anisotropy by LPL in photoresponsive polymer films, side chain type LC polymer films have mostly been investigated [119–124], but some research has involved main chain type polymers [125–128].

In addition to widely applied familiar chromophores, Rosenhauer, Stumpe et al. [129] developed a new photoorienting unit consisting of a central donor–acceptor substituted photosensitive ethene which was elongated by cyclohexane ring systems for forming rod-like liquid crystals (Fig. 5). Linearly polarized UV light irradiation led to optical anisotropy which was further amplified by annealing above the glass transition temperature. This unit does not absorb light in the visible region, therefore, fabrication of colorless anisotropic optical films was possible. The advantage here is that the anisotropy cannot be erased or changed by visible light.

LC polymers are also aligned by the surface effect. Ichimura et al. [130] showed that LC side chain polymer films can be photoaligned on a thermally stable photoalignment azobenzene layer. Huang et al. [131] prepared an aligned LC polymer film via surface-assisted alignment and characterized the film by sum frequency vibrational spectroscopy.

4.1.2. Supramolecular polymers

To introduce photoresponsive units into polymers, the supramolecular approach via hydrogen bonding or ionic interaction is appealing to avoid exhaustive procedures in polymer synthesis. Photoalignment in supramolecular polymer material systems is systematically summarized by Stumpe et al. [132]. Here, only some typical examples are introduced.

With regard to the hydrogen bonding approach, Medvedev et al. prepared a polymer in which a cyanobiphenyl mesogenic group and a benzoic acid group were copolymerized. Pyridine containing azobenzene mesogens was introduced via hydrogen bonding to the polymer. The extent of photoinduced optical anisotropy was found to be dependent on the dopant concentration [133]. Zhao et al. synthesized a polymer containing azopyridine side chain LC polymers attached to various carboxylic acid derivatives via hydrogen bonding [134]. The behavior of photoinduced optical anisotropy becomes highly modified by the structure of the carboxylic acid derivatives employed.

Supramolecular LbL assembly via ionic interaction is also an important strategy to obtain photoaligned films. Advincula et al. used an anionic azo dye to form LbL films with a cationic polymer, which provided a relatively high dichroic ratio of 2.3 by irradiation with LPL [135]. Ziegler et al. investigated a number of LbL films by changing the structure of ionens and bolaamphiphilic azobenzene derivatives [136]. The photoaligning behavior strongly depended on the combination of the ionic complexes.

4.1.3. Dendrimers and star-like polymers

Dendritic and star-shaped compounds have also been the target of photoalignment [137–139]. Tomczyk, Stumpe et al. [137] recently explored the photoinduction of optical anisotropy and morphology by LPL (an example is displayed in Fig. 6). UV light treatment prior to irradiation with LPL leads to induction of very high values of anisotropy. By subsequent thermal treatment,
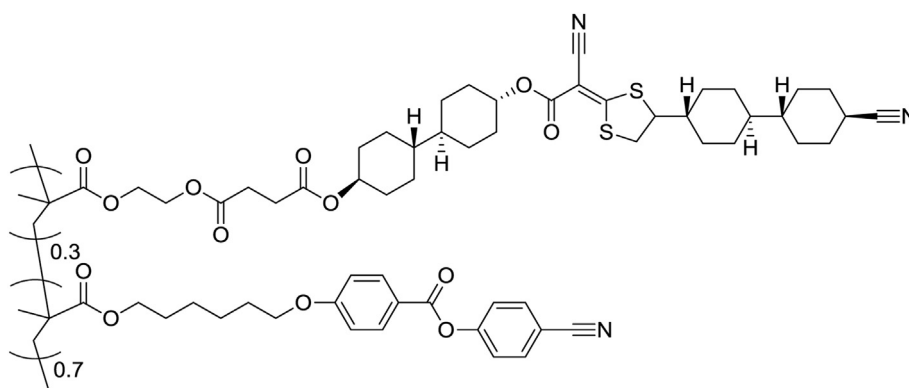

Fig. 5. Photoalignable LC polymer consisting of donor–acceptor ethane that is transparent in the visible light region [129].
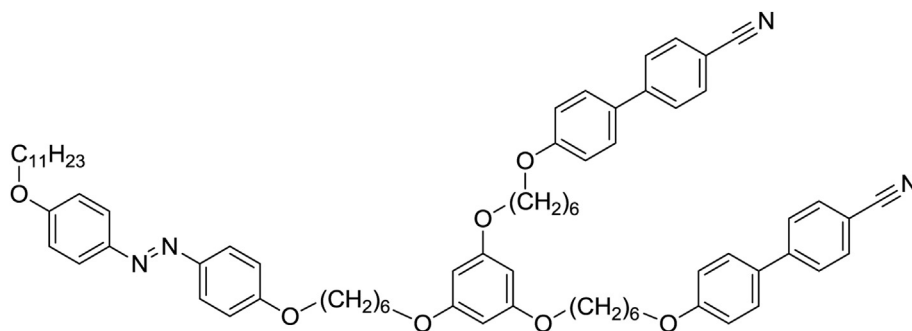
Fig. 6. Star-shaped LC compound that exhibits high photoalignment anisotropy [137].

dewetting and the formation of 3D macroscopic anisotropic stripe- and dome-like structures occur. Li, Seki et al. [140] showed the UV-induced dewetting for a dendritic LC azobenzene compound. For this system, an anisotropic morphology was not formed by LPL. In combination with mass migration, hierarchical morphologies where dome structures are embedded into the relief structure can be formed.

4.2. Surface-grafted LC polymers

In ordinary spincast films of side chain LC polymers, the mesogens are oriented normal to the substrate surface. Uekusa et al. found that when one end of the polymer chains is anchored via surface initiated atom transfer radical polymerization on the substrate, they orient parallel to it [141] (Fig. 7). This unique
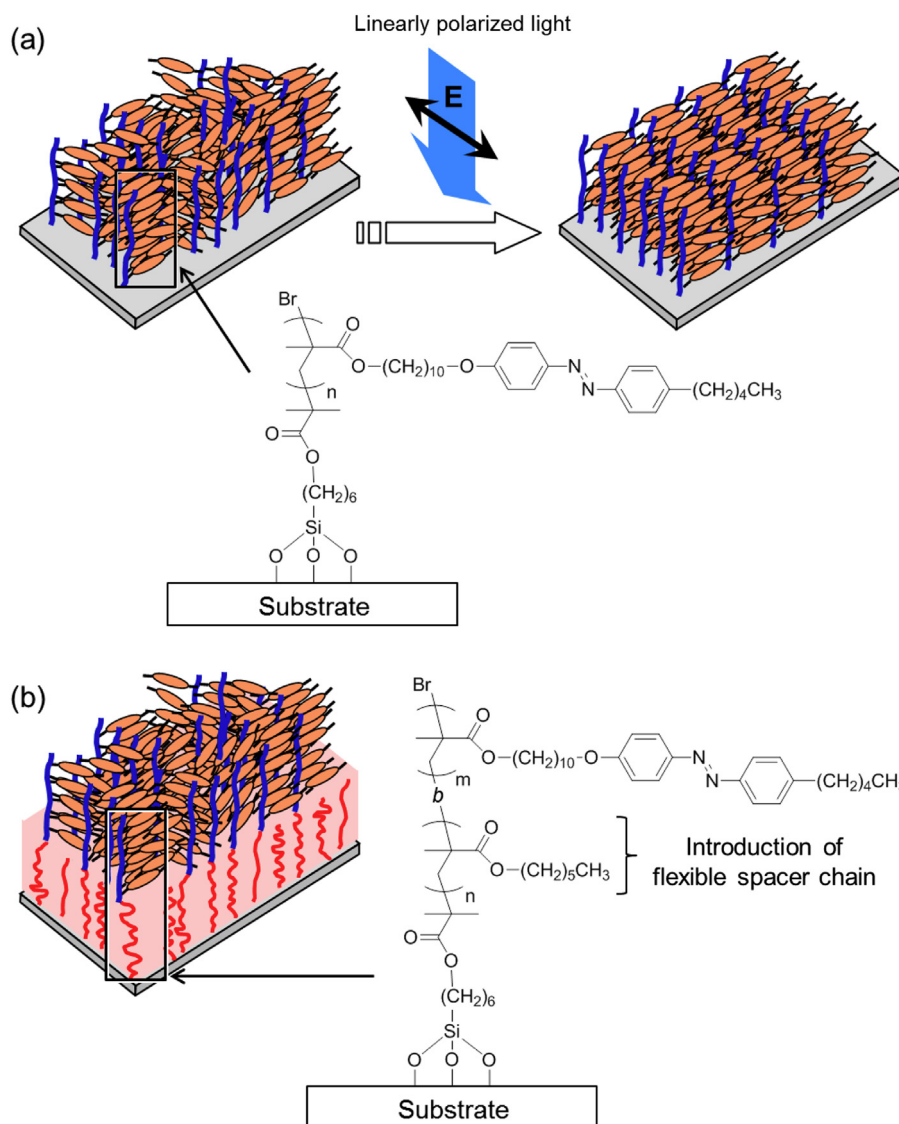

Fig. 7. Surface-grafted side chain azobenzene LC polymer film that shows strong optical anisotropy due to parallel mesogenic orientation with the substrate (a). Introduction of low T_g flexible spacer polymer between the LC layer and substrate leads to more effective photoalignment (b). Adapted from Refs. [141,142,144] with the permission of ACS.

orientation is confirmed by UV–visible absorption spectroscopy and grazing angle incidence X-ray diffraction measurements. Such surface grafted LC azobenzene chains are beneficial for efficient light absorption and in-plane photoalignment. Highly ordered in-plane orientation is attained by this geometry [142,143]. The photoalignment behavior is dependent on the chain length. Hafiz et al. conducted a two-step atom transfer radical polymerization to introduce flexible amorphous polymer chains underneath the LC azobenzene polymer [144]. The flexible amorphous chain of poly(hexyl methacrylate) (glass transition temperature = −20 °C) facilitates the efficient in-plane photoorientation and reorienting motions, and thus this buffer chain works as a lubricant layer in the grafting architecture film. Related to these systems, Camorani et al. prepared a similar surface-grafted LC azobenzene polymer as a command layer for nematic LCs [36] as mentioned in Section 2.

4.3. Block copolymer films

4.3.1. Alignment control of microphase separated structures

Block copolymers spontaneously form ordered mesoscopic patterned morphologies, e.g., spheres, cylinders, and lamellar phases [microphase separation (MPS) structures]. The length of the ordered structure depends on the radius of gyration of the polymer coils. The size of the phase separations typically ranges from 10 to 100 nm. The MPS structures are promising candidates for next generation nanolithographic applications. Therefore, the development of alignment techniques for MPS structures shapes current nanoscience and technology research areas. The alignment of MPS structures has been performed by application of external fields such as shear, electric and magnetic fields, solvent evaporation flows, and surface alignment such as topographical and surface wetting nanopatterns [145–147].
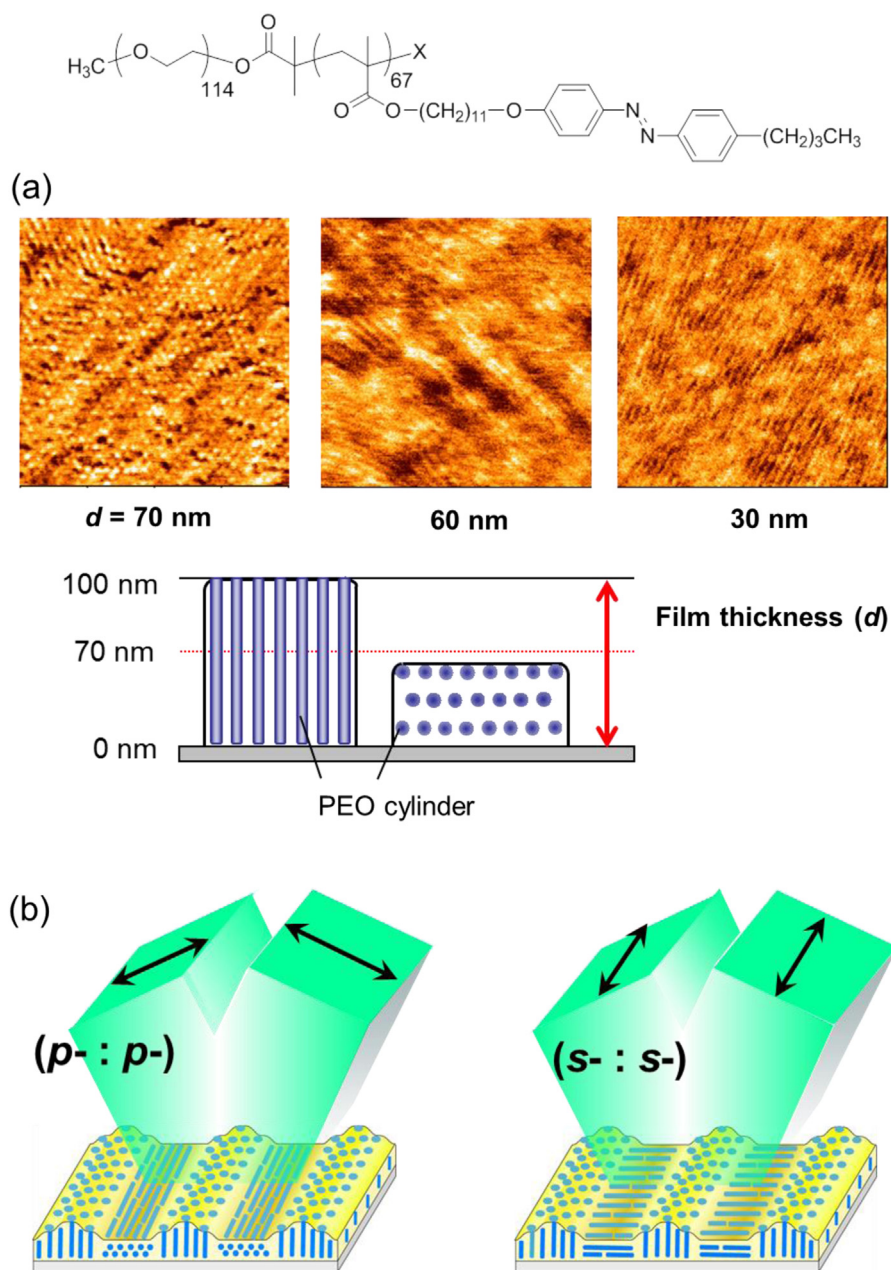

Fig. 8. Thickness-dependent orientation of MPS cylinder domains of polyethylene oxide (PEO) in the azobenzene-containing LC block copolymer. Irradiation of an interference argon ion laser beam provides both out-of-plane and in-plane orientation controls in the resulting surface relief structure (see text for details). Adapted from Ref. [152] and redrawn with the permission of John Wiley and Sons.

Thermotropic LC polymers incorporated into the microphase separation structure can offer hierarchically orientational molecular order in different ways than phase separation structures. Particularly, in the case of side chain liquid crystalline block polymers, the divided interfaces between blocks are usually formed parallel to the oriented side chain mesogens [148]. Therefore, the orientation of MPS structures in the LC block copolymers strongly depends on the manner of LC block orientation [148,149]. Tian, Iyoda et al. have demonstrated the formation of highly ordered vertical cylindrical structures with homeotropic orientation of a smectic LC azobenzene polymer matrix by self-assembly in thin films of the amphiphilic LC block copolymer [150]. Zhao et al. showed the orientational cooperative effect in an LC azobenzene block connected with a non-photoresponsive LC block [151]. These polymers are good design examples with which to exert cooperative alignment in LC block copolymer thin films.

4.3.2. Photoalignment of block copolymer films

Attempts to perform the photoalignment of MPS structures in azobenzene LC block copolymer films started in 2006. Morikawa et al. demonstrated the first example of the photoalignment of MPS cylinder morphologies in amphiphilic azobenzene block copolymer films by LPL irradiation [152]. The LC block copolymer essentially exhibits a homeotropic LC phase and vertically aligned MPS cylinders are formed. In this case, the direction of the transition moment of the azobenzene chromosphere is almost perpendicular to the LPL light. Therefore, the LC block copolymer films are less responsive to the reorientation reaction by LPL irradiation. However, when the LC block copolymer film becomes thinner than 60 nm, it adopts a random planar orientation for both LC azobenzene and MPS cylinders, which is favorable for photoalignment by LPL (Fig. 8a). By performing mass migration by an interference polarized beam, an undulated film is obtained. In the thicker and thinner parts, vertical and planar orientations of MPS cylinders are obtained, respectively. In the lower planar area, cylinders are aligned monoaxially in-plane following the orientation of azobenzene by the LPL irradiation (Fig. 8b).

The photoalignment process can provide oriented MPS morphologies over a large area without using particular devices in non-contact and addressable manners. These features lead to new methods to rewrite and drive oriented MPS morphology by the photoirradiation procedure. Morikawa et al. demonstrated a *rewritable* 3D photoalignment process in the polystyrene MPS cylinder morphology in LC azobenzene block copolymer films (Fig. 9) [153]. As a result, the polystyrene cylinders were aligned in the anisotropic LC matrix. The key process is the anisotropic self-
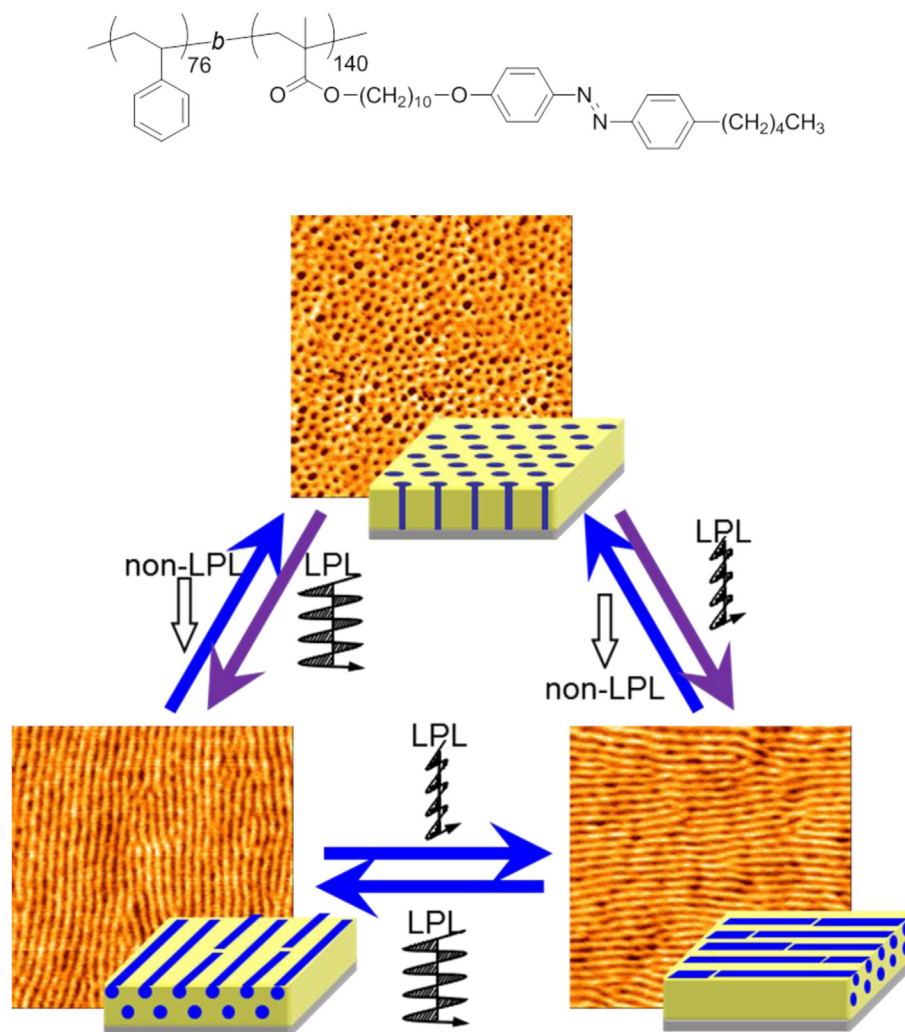

Fig. 9. On-demand 3D rewritable MPS cylinder domain alignment of polystyrene in the azobenzene-containing LC block copolymer. In each rewriting process, heating and cooling procedures are required. Adapted from Ref. [153] with layout modifications with the permission of ACS.

assembly of MPS domains in the block copolymer following the alignment of LC mesogens. The alignment can be initialized and formatted by the angular selective photoreaction via the isotropic and disordered phase. This rewritable system is unique in that one material can encode three types of orthogonal independent information (x, y, and z directions), while in most other cases information switching is performed between two states.

Recently, Nagano et al. succeeded in monitoring the orientational switching of the MPS cylinder morphology under LC temperature in an LC azobenzene block copolymer thin film (Fig. 10) [154]. In this case, the LC azobenzene block copolymer with poly(butyl methacrylate) (PBMA) has a lower surface tension and glass transition temperature. Unlike the polystyrene case, this block copolymer characteristically exhibits random planar orientation of the LC azobenzene mesogens and cylinders by self-assembly. The PBMA block of lower surface tension segregates to cover the "free (air) surface" of the film. Thus, divided interfaces between blocks are selectively formed parallel to the free surface. This situation leads to a random planar orientation of the side chain mesogens with favorable orientation in the photoalignment process. Highly efficient photo-orientation and reorientation of the LC phase and MPS cylinders are attained at an LC temperature of ca. 95 °C. The mono-axially aligned LC azobenzene block copolymer film can switch and drive in any in-plane direction. The reorientation process can be stopped after several minutes. The grazing incidence angle X-ray scattering measurements using a synchrotron X-ray source provide real time transient structural data of the reorientation process. It is found that the motions of smectic LC domains and MPS cylinders are reoriented in a synchronized manner. The strong cooperative motions in the
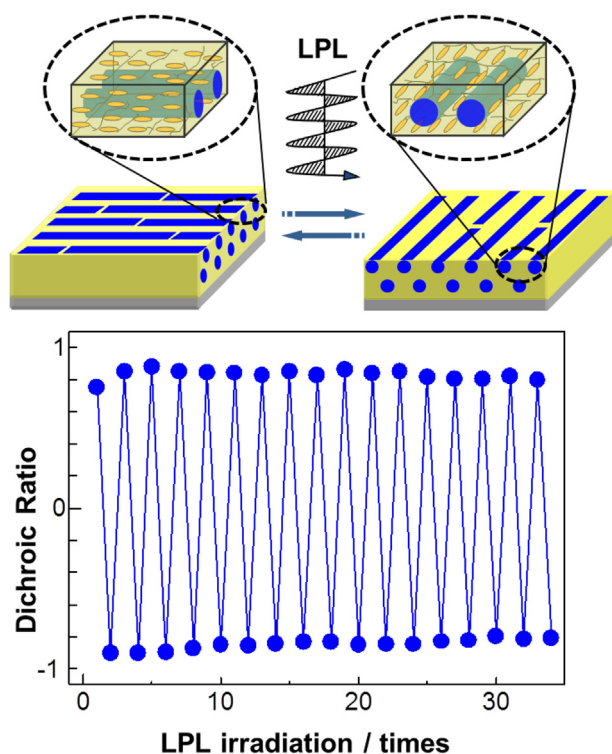

Fig. 10. Direct (isothermal) in-plane photoswitching of MPS cylinder domain alignment of PBMA in the azobenzene-containing LC block copolymer. Real time GI-SAXS measurements of domain reorientation by use of synchrotron X-ray revealed the strong cooperativity involved in the reorientation process between the LC structure and polymer domain. The lower figure illustrates the full repeatability of this photoalignment process. Adapted from Ref. [154] with the permission of John Wiley and Sons.

structure reorientation between the LC phase and MPS morphologies are clearly demonstrated.

Based on this knowledge, the polystyrene MPS cylinders in the block copolymer can be oriented in the planar direction by mixing a small amount of PBMA-based block copolymer as demonstrated by Fukuhara et al. [155]. Coverage of segregated PBMA blocks of the blended polymer at the free surface leads to this effect. This allows for a facile photoreorientation of polystyrene-based LC block copolymer films by LPL irradiation. A significant role of the free surface on the LC and MPS domain orientation is proposed.

Yu, Ikeda et al. also demonstrated highly structured photoaligned MPS cylinders by exposure to a polarized laser beam using a relevant block copolymer [156–159] (Fig. 11). They demonstrated that not only a smectic LC block as usually used but also a nematic phase of LC block can be employed for the photoalignment of MPS domains [158]. Han, Zhao et al. attempted to align poly(3-hexyl thiophene) (P3HT) domains of a block copolymer consisting of P3HT and LC azobenzene polymer (Fig. 11) by irradiation with LPL [160]. Due to limited alignment conditions, the domain alignment is not efficient, since the amorphous polymer domains are flexible as described above, but photoalignment is achieved to some extent.

The rubbing procedure is the standard method to align LC materials, which is also found to be very effective for LC block copolymers. Yu et al. demonstrated that the smectic LC phase and cylindrical structure of the LC Az block copolymer can be aligned by using a rubbed polyimide surface [161]. Tong, Zhao et al. very recently showed that the P3HT-containing block copolymer (Fig. 11) forms nanofibrils via self-assembly in nematic solvents [162]. Highly aligned unidirectional nanofibrils are obtained by rubbing the polyimide surface. The chain direction of P3HT is parallel to the LC mesogenic groups, namely to the rubbing direction, because the π–π stacking of P3HT chains cannot grow laterally by the orientation effect of the surrounding LC polymer.

4.4. Conjugated polymers and organic semiconductors

There have been great demands for alignment of conjugated polymer and oligomer systems due to their potential utilities for organic semiconducting and light emitting devices. Molecular alignment of these materials is of particular importance for carrier transport and polarized emission properties. In general, functional conjugated materials cannot be mass produced and thus are often very expensive. Therefore, the development of orienting processes of these materials on photoalignment layers is crucial. Reports along these lines are summarized in Table 5. Structures of selected materials in this category are shown in Fig. 12. In earlier research, Seki, Fukuda et al. showed the aligned crystallization of a poly(di-n-hexylsilane) (PDHS) film on an azobenzene monolayer irradiated with LPL [163–165]. Poly(diacetylene) LB films are also aligned to some extent in this approach [166,167]. Recent efforts have been devoted to organic semiconductors of pentacene, thiophene oligomers, thiophene–fluorene oligomers, and fluorene oligomers for their practical use in opto and electrical devices.

Surface photoalignment of pentacene film, a widely studied typical organic semiconductor, was reported by Jin et al. using a maleimide-based polymer with a photoreactive pendant group [168]. Improved properties of field effect mobility and on/off current ratio were exhibited by the photoaligned film compared to those from a SiO$_2$ gate dielectric insulator. Fujiwara, Bao et al. showed the photoalignment of an LC semiconductor polymer containing thiophene and fluorene units (F8T2) on a azobenzene polymer with a solution process [169]. Dröge, O'Neill et al. conducted the photoalignment of a related material on a photodecomposing polyimide [170]. To achieve these results, photocrosslinkable units of coumarin were employed by Chen et al.
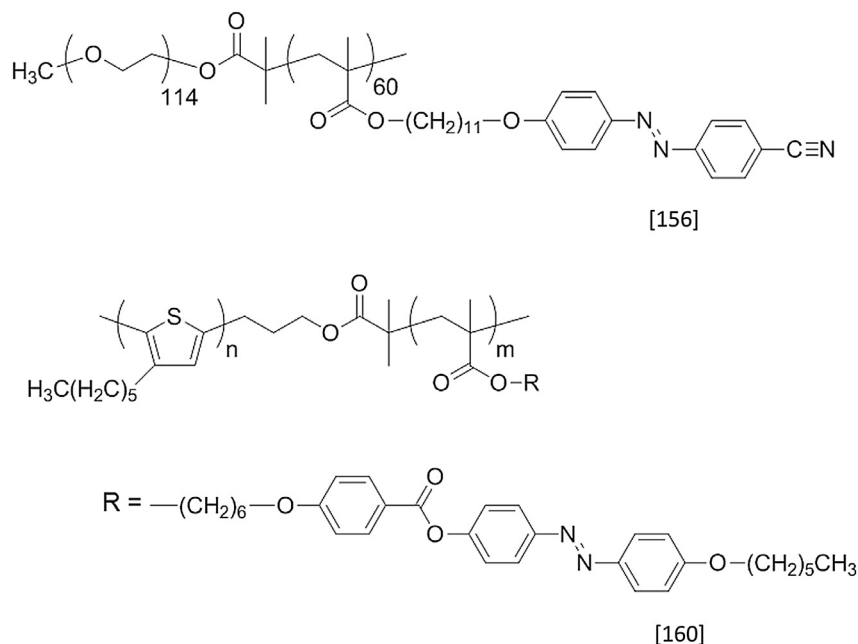
[156]

[160]

Fig. 11. Block copolymers used in the works of Yu et al. [156] and Zhao et al. [160].

[171,172]. Further, Sakamoto et al. demonstrated an anisotropic carrier transport property using a polyimide containing azobenzene in the main chain as the photoalignment layer [173]. Polarized emission of fluorene derivatives was demonstrated by Kawatsuki et al. [174] using a cinnamate side chain polymer. The alignment patterning with a photomask provided a clear emissive image. They further extended this to supramolecular systems in which fluorene derivatives were embedded by sandwiching hydrogen bonds between cinnamic acid in the side of a polymer [175]. Interestingly, the strength of the hydrogen bonding modified the emission wavelength. Kinashi, Ueda et al. synthesized a series of fluorene–azobenzene main chain polymers, which were then used to prepare anisotropic light emissive films of a pure fluorene polymer [176].

5. Photoalignment of lyotropic LCs and related systems

Lyotropic LC systems are another important class of LC materials where the existence of solvent (mostly water for practical use) provides fluidity and long range orientation. Needless to say, the great significance of lyotropic LCs can be recognized in biological systems (biomembranes, etc.) and in the surfactant industries. In addition to ordinary surfactant aggregates forming LC rodlike micelles and lamellae, Lydon pointed out the importance and generality of columnar aggregates of pharmacological agents and dyes with LC natures, and named these "chromonic" [177,178]. These molecules consist of a disk or plank-like core in the center with hydrophilic or charged moieties scattered in the periphery. In these systems, columnar aggregates are formed via π–π interaction of the planar molecules rather than the hydrophobic effect that drives ordinary surfactant systems. In-plane alignment of chromonic lyotropic LCs has been mostly achieved by application of shear and flow. Tam-Chang's group and others have extensively promoted this method [179–184]. The literature is summarized in Table 6 together with the photoalignment systems mentioned below.

5.1. Chromonic LCs

In 1995, Ichimura et al. [185] demonstrated the surface-assisted photoalignment of a lyotropic chromonic LC on an azobenzene polymer. A chromonic LC of an azo dye [C. I. Direct blue 67 (B67)] [186] can be aligned on an azobenzene film irradiated with LPL, and after drying the system, a uniformly aligned or patterned dye film is obtained. The photoaligned state is already formed before the

Table 5
Photoalignment of conjugated and organic semiconducting materials.

	Method[a]	Photoalignment layer, material	References
Poly(di-*n*-hexylsilane)	SPA	Azobenzene LB monolayer	[163–165]
Poly(diacetylene)	polymerization control and SPA	Azobenzene LB monolayer	[166,167]
Pentacene	SPA	Cinnamate side chain polymer	[168]
F8T2 oligomer	SPA	Photodecomposing polyimide	[170]
F8T2 polymer	SPA	Azobenzene side chain polymer	[169]
F8T2 polymer	SPA	F8T2 on azobenzene main chain polymer	[173]
F8T2 oligomer/polymer and fluorene derivative	SPA	Coumarin side chain polymer	[172]
Oligofluorene	SPA	Coumarin side chain polymer	[171]
Fluorene derivative	SPA	Cinnamate side chain polymer	[174]
Fluorene polymer	PA	Fluorene-Az main chain polymer	[176]
Fluorene derivative	PA	Cinnamic acid side chain polymer via H-bonding	[175]

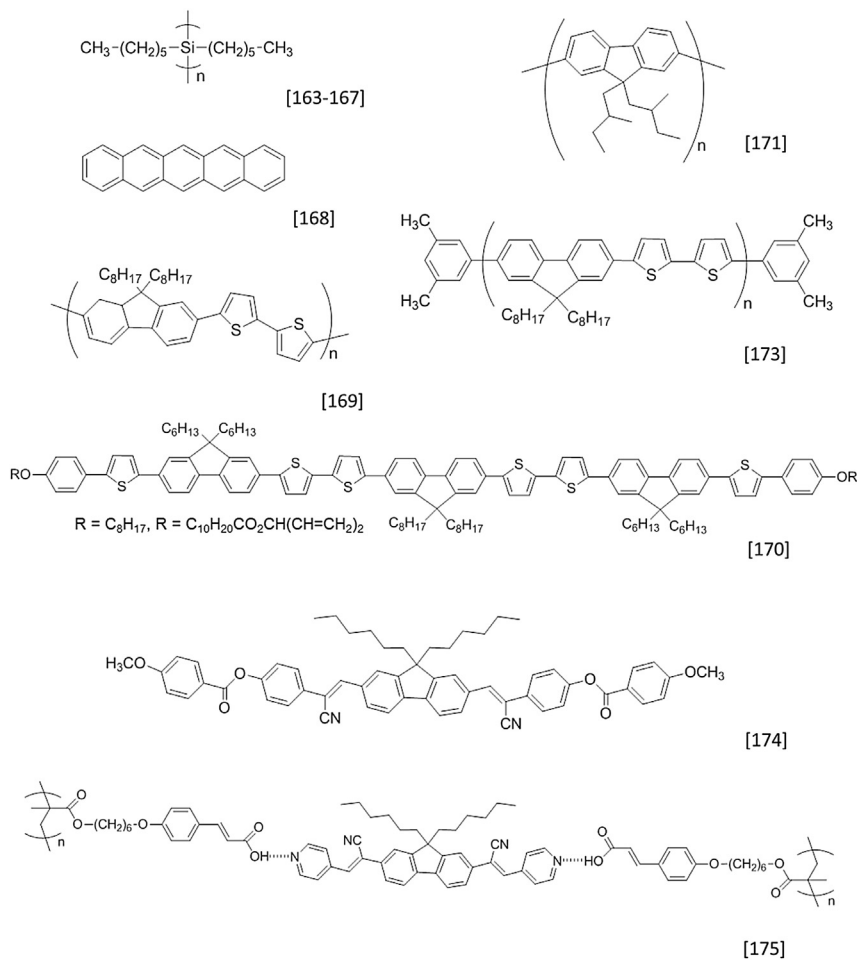[a] SPA: surface photoalignment; PA: photoalignment.

Fig. 12. Conjugated polymers and organic semiconductors used in the photoalignment processes. The numbers in parenthesis indicate the references.

solvent (water) evaporates [187]. A typical chromonic drug, disodium chromoglycate, is also photoaligned in the lyotropic LC state [188].

For a B67 chromonic LC system, very high optical anisotropy has been achieved in a dry film by using a polyamide with a dimethylaminoazobenzene side chain as the alignment layer (Fig. 13). The

order parameter reached ca. 0.85. By using patterned LPL, optical patterns with a very high contrast have been obtained [189,190].

Nastishin et al. observed a photoinduced reorientation of a chromonic lyotropic LC system composed of indanthrone-stacked aggregates by irradiation with a polarized laser beam [191]. Interestingly, this effect is also observed in a non-light absorbing system

Table 6
Photoalignment of lyotropic LCs and organic–inorganic mesostructured hybrids (including other related processes, references mostly after 2000).

System	Method	Alignment layer, material	References
Chromonic LCs	SPA	Azo dye and disodium chromoglycate on azobenzene side chain polymer	[185,187–190]
	SPA	Reorientation by chromonic adsorption	[191]
	Topographical mold	PDMS mold	[179]
	Shear		[180–184]
Inorganic–surfactant LC hybrids	Rubbing	Surfactant/silica or titania, on polyimide	[213]
	Dip-orienting on LB film	Surfactant/silica, polyimide	[214]
	SPA	Surfactant/silica on Az	[219,220]
	SPA	Surfactant/silica on PPLC	[222–224]
Inorganic–chromonic LC hybrid	Dip-flow	Chromonic/silica	[225]
	SPA	Chromonic/silica on PPLC	[226]
Inorganic–discotic LC hybrid	SA	π–π Interaction with graphite	[235]
Biomineralization of CaCO$_3$	Immersion	On stretched LC chitin	[236]
		On PVA–SbQ	[237]

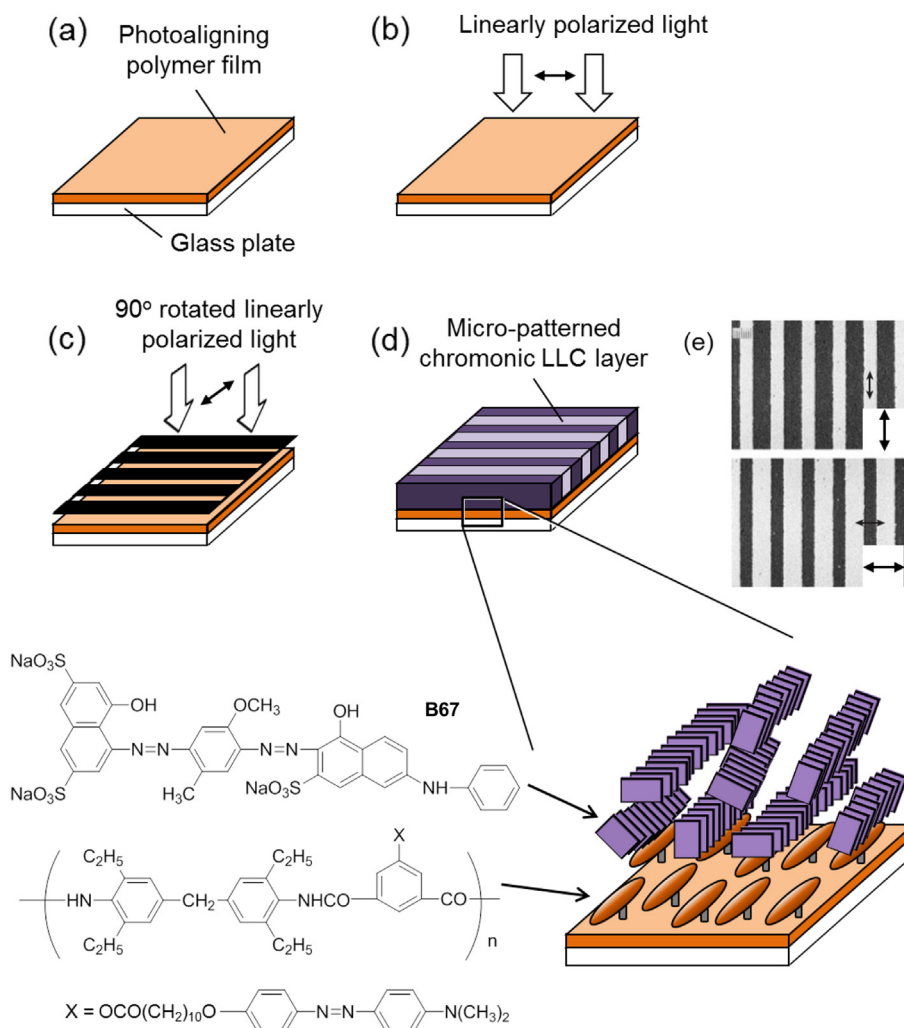SPA: surface photoalignment; SA: surface alignment; PA: photoalignment.

Fig. 13. Photoaligned lyotropic chromonic LC of an azo dye (B67) that leads to a photopatterned dry film exhibiting strong dichroic properties. Images in (e) indicate the stripe-patterned film observed with the polarizer shown in the images. Note that the contrast is fully reversed. Adapted from Ref. [189] and redrawn with the permission of Wiley-VCH.

which contains a small amount of chromonic (light absorbing) molecules.

5.2. Inorganic mesostructure template by lyotropic LCs

In inorganic materials chemistry, mesostructured organic/inorganic hybrid films and their calcinated porous (mesoporous) films are prepared by a sol–gel process via templating of various lyotropic LC phases as the structure-directing agents [192–194]. This approach is particularly important in fabrication of nano- and mesomaterials, therefore some background on related systems is mentioned here. Both low-molecular-mass surfactants and polymeric ones (amphiphilic polymer) can serve as templates. Film formations are mainly achieved by hydrothermal synthesis at various substrate surfaces [195–197], vapor-phase synthesis [198,199], and a solvent-evaporation technique by spin-coating [200,201] or dip-coating methods [202,203]. The macroscopically aligned mesochannels are anticipated to find many attractive applications in optics, electronics, separation technologies, etc. Due to the lyotropic liquid crystallinity of the template aggregate, the structures are potentially aligned over large areas. However, in general, mesochannels form randomly oriented polydomains on a macroscopic level. This section introduces some attempts to orient

mesostructured thin films, in particular, surface-directed alignment techniques.

5.2.1. Homogeneous alignment

Homogeneous alignments of mesochannels are available by application of various flow or shear fields, such as synthesis in a continuous-flow reactor [204], a dip-coating method [202], hot air flow [205,206] and a rubbing method [207–209]. Very recently, synthesis of a homogeneous aligned mesoporous silica film has also been achieved by a flow-injection approach within glass microfluidic channels [210]. Since the precursor lyotropic LC phase and its cast film before drying are viscous liquids, flow and shear techniques are effective for facile alignment of the LC phase.

5.2.2. Surface-directed homogeneous alignment

The first demonstration of surface-induced homogeneous alignment of mesostructures was achieved by Miyata et al. in 1999 [211]. The mesoporous silica films with in-plane alignment were prepared by a hydrothermal deposition process onto an anisotropic substrate surface such as a silicon (110) surface [211], a rubbed polyimide film surface [212,213] and a polyimide Langmuir–Blodgett (LB) film surface [214]. They further showed the preparation of a homogeneously aligned mesoporous silica onto a rubbed
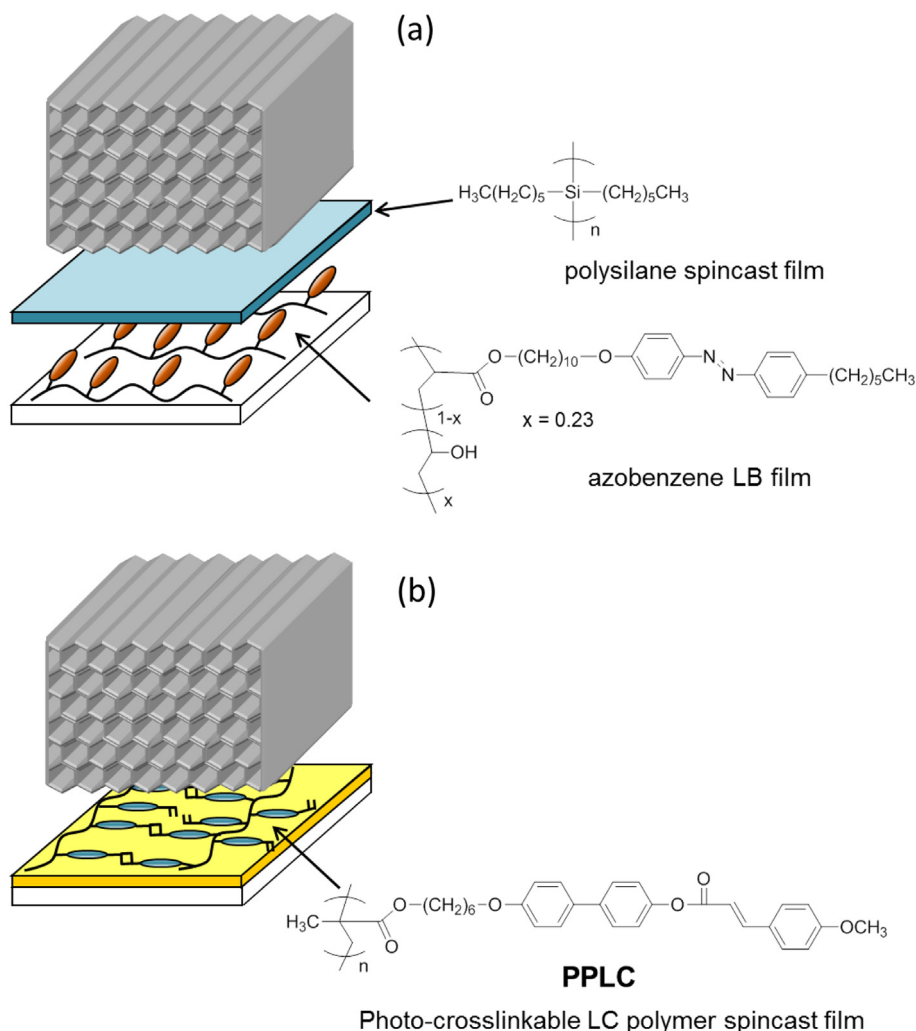
Fig. 14. Schematic illustrations of photoaligned surfactant-templated silica mesostructures (and mesoporous film) formed on an azobenzene monolayer-polysilane film (upper) [219,220] and a cinnamoyl LC polymer (PPLC) film (lower) [222–224].

polyimide film surface by the dip-coating method [215]. In this film, the alignment direction is not governed by the dip-coating direction but by the rubbing direction.

Several recent reports demonstrate that ordered mesochannels can be arranged on a freshly cleaved mica surface [216], a polyimide film surface with laser-induced periodic microgrooves [217] and a patterned silicon surface with submicrometer scale trenches [218].

Photoaligned polymer surfaces can align such mesostructures (Fig. 14). Kawashima et al. proposed a photoalignment approach for the surface-induced homogeneous alignment of mesochannels. In this procedure, mesoporous silica films are prepared on an aligned polysilane film formed on an azobenzene LB monolayer irradiated with LPL [219,220]. Later, Fukumoto et al. employed a cinnamate-containing photocrosslinkable polymer with LC nature (PPLC) developed by Kawatsuki [221–224]. Fig. 15 shows micropatterning of the silica mesostructures on the photoaligned PPLC layer that was irradiated with LPL through a photomask and subsequently annealed [223]. In the irradiated areas, linear cracks evolve, whose direction runs perpendicular to the direction of LPL.

Hara et al. demonstrated that the chromonic LC of B67 is also applicable as a fascinating mesoscopic template if suitable conditions are fulfilled [225]. The photoalignment of mesostructures of the chromonic dye aggregates can be photoaligned on the cinnamate-containing PPLC [226]. The chromonic LC/silica hybrid

film possessed optical anisotropy, which could be readily discerned when observed with a polarizing film (Fig. 16). Such optical features strongly suggest the existence of photoaligned mesostructured columns templated by the chromonic LC phase.

5.2.3. Vertical alignment

Vertical alignment of mesochannels is of great demand in applications, therefore a brief survey is given here even though they are not photoaligned systems.

In block copolymer films, tuning interfacial interactions at air/film or film/substrate interfaces is very effective for morphology control of MPS structures. When both blocks are neutral for the surface, there is no preferential segregation of the components at the interfaces. This means that both blocks can appear at a neutral surface. Lin et al. developed a method of confining a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer/silica hybrid between a bilayer membrane vesicle [227,228]. The platelets adopted perpendicular cylinders in order to minimize unfavorable interactions between unlike species. Rankin et al. showed that modifying an initial substrate with PEO–PPO copolymer as a chemically neutral surface for the PEO–PPO triblock copolymer can induce copolymer-templated ceramic films with orthogonally tilted hexagonal closed packed pores [229,230]. When the film thickness is less than a critical thickness (between
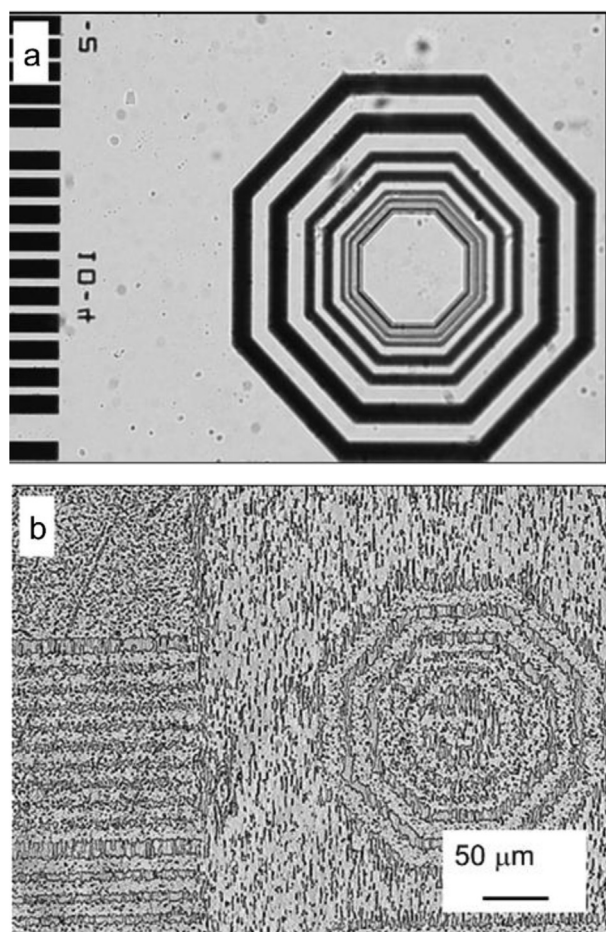
Fig. 15. Photopatterned orientation control of surfactant-silica mesostructured film. Photomask (a) and photopatterned mesostructured film (b). Reprinted from Ref. [223] with the permission of ACS.

70 and 100 nm in this case), spontaneous vertical alignment of the mesochannels is induced in air. Kim et al. reported that tuning interfacial energy at both air/film and film/substrate interfaces of a polystyrene-*block*-poly(ethylene oxide)/silsesquioxane hybrid film allows the control of cylindrical pore and lamella orientations normal to the supported film surfaces [231,232].

Specific interactions between template molecules and substrate surfaces also lead to vertically aligned mesochannels in films. Richman, Tolbert et al. showed nanometer-scale epitaxial growth of mesochannels on a patterned substrate [233]. For construction of such a patterned sublayer under the mesochannels, they used a surface of cubic mesoporous film. A precise lattice match between the vertically aligned mesochannels and the cubic sublayer is needed for vertical alignment. Wang, Ozin et al. reported a single-layer graphene oxide-periodic mesoporous silica sandwich nano-composite in which vertically aligned mesochannels were grown on both sides of the graphene oxide sheets [234].

Hara et al. proposed another strategy to attain the surface-mediated vertical alignment of mesochannels by utilizing the π-π interaction between a π-conjugated discotic molecule and a 2D π-plane of graphite (highly oriented pyrolytic graphite; HOPG) [235]. Here, the π−π stacking interaction at the HOPG surface promotes the columnar orientation of stacked disc molecules directed verti-cally. Fig. 17 shows a transmission electron microscopy image of the hybrid film of the π-conjugated molecules and silica prepared on the HOPG substrate. The film exhibited a highly oriented stripe morphology directed perpendicular to the substrate plane. In the vertically aligned system, calcination does not lead to contraction of the structure, which is often observed in parallel aligned mesostructures.

5.3. Surface aligned and photopatterned biomineralization

Crystal formations on substrates are important issues with re-gard to biomineralization. Nishimura, Kato et al. indicated that a crystal of $CaCO_3$ grew on a unidirectionally aligned chitin film, which was aligned via stretching in a lyotropic LC state of a
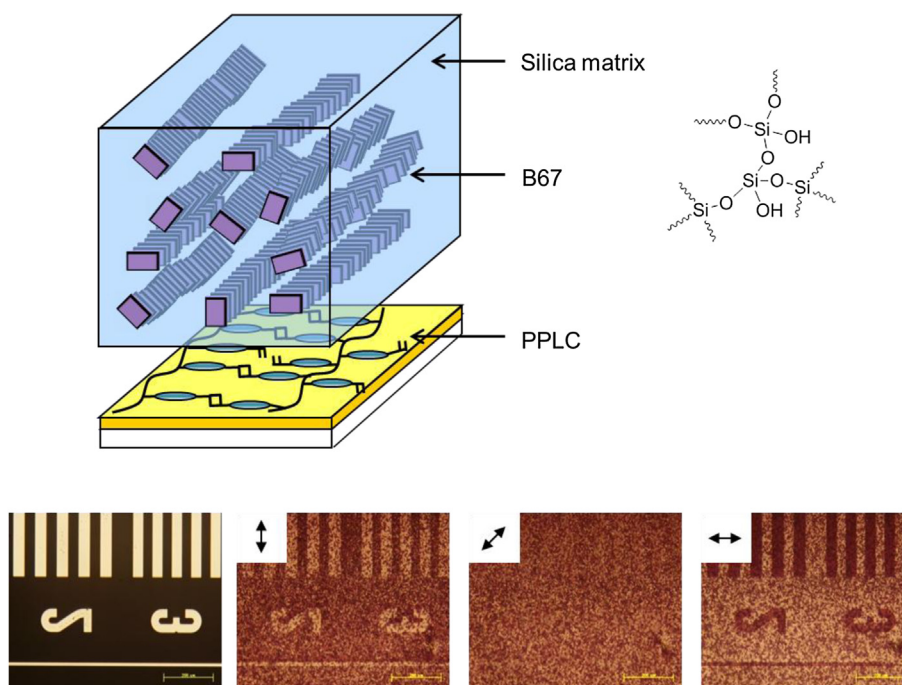

Fig. 16. Photoalignment of chromonic B67-silica hybrid film on the PPLC film. The lower images indicate the dichroic patterned images. The arrows indicate the direction of the observing polarizer. The top left shows the photomask. Adapted from Ref. [226] and redrawn with the permission of Royal Chemical Society.
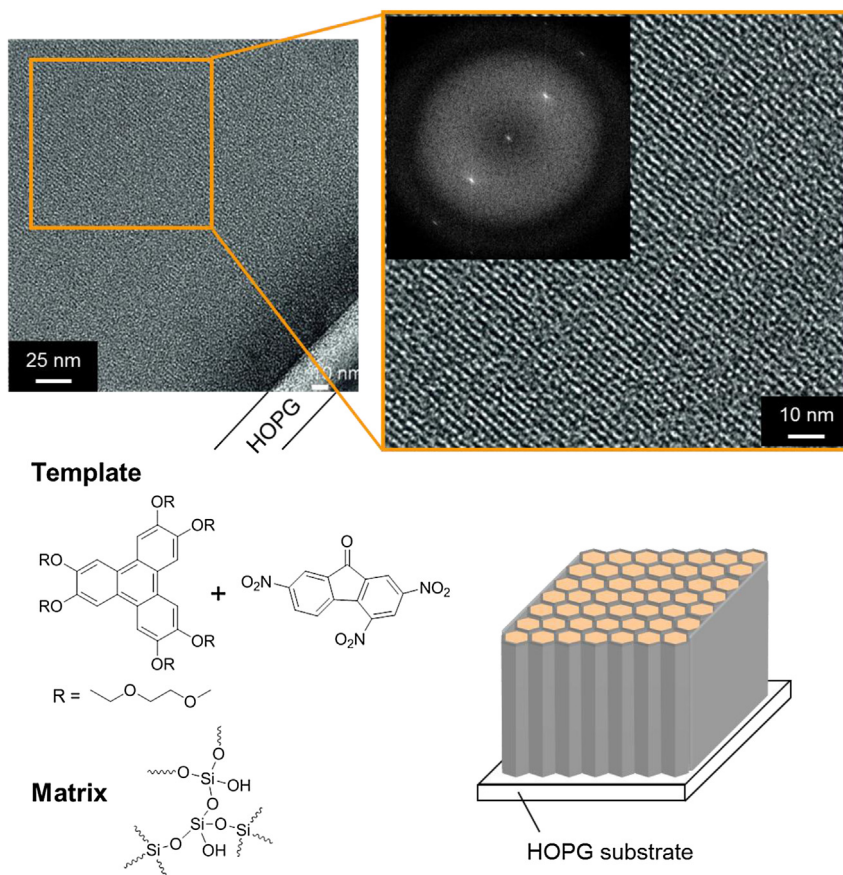
Fig. 17. Vertical alignment of discotic column–silica nanohybrid film attained by π–π interaction with a surface of HOPG. Adapted from Ref. [235] with the permission of ACS.

precursor formed of chitin phenylcarbamate [236]. Both crystal morphology and crystallographic orientation are achieved in this process. The same group reported an interesting photoimaging process in a relevant system [237]. They employed a poly(vinyl alcohol) bearing a 4-styrylpyridinium moiety (PVA–SbQ [238], Fig. 18) as a substrate in the CaCO$_3$ crystallization process. In the photopatterned film, CaCO$_3$ crystals are formed as flat and undulated morphologies on UV-irradiated (photocrosslinked) and nonirradiated areas, respectively. Examples of patterning of the CaCO$_3$ morphologies are shown in Fig. 18. The crosslinking suppresses the ion diffusion in the hydrogel matrix, and this may be the origin of the differences in the resulting morphology induction. The demonstration of photopatterned hierarchical morphologies of the crystals should open up a new area in materials technology.

6. Summary

This article provides an overview of photoalignment and related processes for various functional materials. As mentioned here, photoalignment technology has profound potential for processing of a very wide range of materials from soft LCs to hard materials. Photoalignment procedures have been developed over the last 25 years to align mostly nematic LCs of industrial significance for LC displays. However, as this article emphasizes, photoalignment procedures are not limited to this particular system, and wide ranges of materials can be targeted. With the exception of nematic LC photoaligning systems, applications for most of the systems are still in the beginning stages of research and development. Regarding photoreactive units, photochromic materials, typically
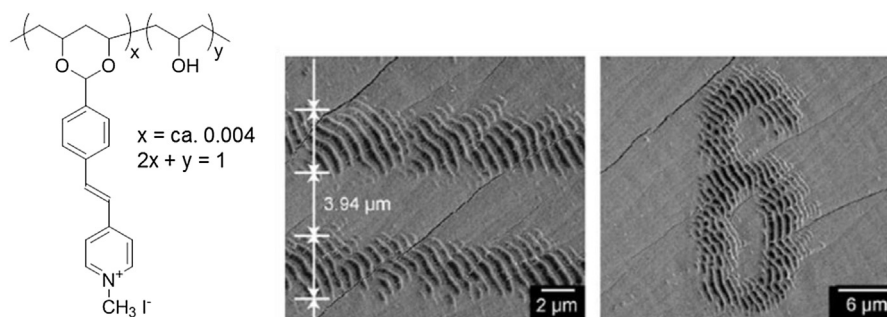

Fig. 18. Photopatterned biomineralization of CaCO$_3$ crystal formed on a PVA–SbQ film. Adapted from Ref. [237] and redrawn with the permission of John Wiley and Sons.

azobenzene-containing ones, allow erasures and rewriting of photoaligned states. The actual applications and outlook of such reversible processes are still in their infancy, but these phenomena are expected to find new technological directions soon.

The surface alignment of nematic LCs was recognized by Mauguin [239] and the rubbing effect was clearly demonstrated by Chatelain [240] in the early 20th century; however, it was only applied to the actual output of LC display devices about 40 years ago [241]. It may also take this long to find applications for other types of materials, but we expect that accumulation of knowledge in this respect will open unknown possibilities and breakthroughs for material processing and device fabrication. We hope that this article provides useful information on the relevant research fields including polymer materials, material processing, thin film technologies and information technologies.

Acknowledgment

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