Macroscopic Regulation of Hierarchical Nanostructures in Liquid-crystalline Block Copolymers towards Functional Materials

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Abstract  The great potential of liquid-crystalline block copolymers (LCBCs) containing photosresponsive mesogens toward novel applications in photonics and nanotechnology has been attracting increasing attention, due to the combination of the inherent property of microphase separation of block copolymers and the hierarchically-assembled structures of liquid-crystalline polymers (LCPs). The periodically ordered nanostructures in bulk film of LCBCs can be acquired by supramolecular cooperative motion, derived from the interaction between liquid-crystalline elastic deformation and microphase separation, which are able to improve physical properties of polymer film toward advanced functional applications. Moreover, various micro/nano-patterned structures have been fabricated via light manipulation of photosensitive LCBCs with good reproducibility and mass production. Thanks to recent developments in synthesis and polymerization techniques, diverse azobenzene-containing LCBCs have been designed, resulting in the creation of a wide variety of novel functions. This review illustrates recent progresses in macroscopic regulation of hierarchical nanostructures in LCBCs towards functional materials. The existing challenges are also discussed, showing perspectives for future studies.

Keywords  Liquid-crystalline block copolymers; Microphase separation; Hierarchical nanostructures; Functional materials

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1. INTRODUCTION

Generally, block copolymers (BCs) consist of two or more polymer modules named “blocks” linked together by covalent or supramolecular bonding. The interaction among the incompatible blocks enables BCs to assemble into various microphase-separated (MPS) nanostructures such as spheres, cylinders, and lamellae with a size range of 10–100 nm. In the past decades, BCs have attracted extensive attention due to their capability of forming multifarious self-assembled nanostructures towards various advanced applications. However, it currently faces many challenges, e.g., how to prepare ordered nanostructures in a large area, rapidly regulate and pattern the MPS nanostructures, obtain stabilized and functionalized the nanostructures, and further explore their practical applications. To solve these problems, liquid-crystalline (LC) ordering has been elegantly incorporated into BC systems, providing the designed LC block copolymers (LCBCs) with unique feature of supramolecular cooperative motion which offers one effective way to control MPS nanostructures via modulation of mesogenic alignment under different external conditions such as thermal or solvent, rubbing and light. Among them, light possesses fascinating advantages since it can be remotely, instantly, and...
Fig. 1  (a) Scheme of liquid-crystalline block copolymers (LCBCs). (b) The obtained nanostructures prepared by MPS of LCBCs. (c) Fabrication of periodic array of Ag nanoparticles. (Reproduced with permission from Ref. [46]; Copyright (2007) WILEY-VCH). (d) Preparation of anisotropic ionic conduction in nanochannels. (Reproduced with permission from Ref. [47]; Copyright (2007) American Chemical Society). (e) Fabrication of patterning with CaCO₃ using nanotemplates of LCBC MPS nanostructures with and without photo-regulation. (f) Selective absorption of Au nanoparticles (Reproduced with permission from Ref. [48]; Copyright (2007) WILEY-VCH).

precisely controlled in a noncontact way. Through optimizing these conditions, LCBCs undergo MPS processes to form the primary structure, as shown in Fig. 1(b).

As is known, azobenzene is one of the most favorite chromophores due to its photochemical trans-cis isomerization. The azobenzene compound usually exists in the form of trans conformation because of the low energy level at this state. Its cis isomer can be produced upon irradiation with UV light and the trans isomer can be regenerated on exposure to visible light or heat treatment. When it serves as a functional group, photoisomerization can occur, followed by some amusing properties including molecular cooperative motion, volume change, photoalignment and photoinduced phase transition. The excellent properties render azobenzene group with applicabilities in some specific areas. The azobenzene-containing molecules or polymers have been used for preparation of bilayer photomechanical films based on volume change. By depositing one layer of azobenzene-containing molecule or polymer on flexible polymer substrate, precise control of photoinduced curling of bilayer film can be achieved upon UV irradiation. In addition, photoinduced crystal-to-melt transition in azobenzene-containing materials has been observed. Therefore, azobenzene-containing materials can serve as solar thermal fuels which store and release energy by photoinduction.

When azobenzene is introduced into macromolecule or polymer system as one photoresponsive mesogen, the obtained azobenzene-containing LC polymer (LCP) has hierarchically assembled structures, which may render macromolecules with some fascinating properties and novel functionalities. More interestingly, the primary structure (often in nanoscale) formed via MPS of azobenzene-containing LCBC changes the orientation direction after illumination, forming novel nanostructures or their patterning according to the irradiation conditions, which is called the secondary structure. Regardless of whether it is primary or secondary structures, the resulting micro-morphology is the basic structure of LCBCs. Thus, they are collectively named as intrinsic structures, which have been widely used in photonics and nanotechnology as shown in Fig. 1.

However, the various microstructures and orientations formed in LCBCs are still relatively limited, which restricts their further applications. Recently, the microstructure of BCs was modified through chemical and physical methods to acquire desirable nanostructures. The chemical method is mainly to introduce new functional groups into LCBCs, so that the obtained polymer has novel nanostructures with additional functionalities. The physical method is often through doping various nanoparticles with a specific oriented structure into LCBCs, and the corresponding interaction between the nanoparticles and one of phases of BCs, such as hydrogen bonding (HB), may result in a supramolecular system with a desirable nanostructure.
but formed by post-regulation, so they are the extrinsic structure of LCBCs. These extrinsic structures increase the vitality of LCBCs, making its application range wider.

On the one hand, to meet the requirements of practical applications, MPS of LCBCs can be adjusted by means of light, chemical functionalization and physical addition for obtaining various nanostructures. On the other hand, how to make the nanostructure in LCBCs stably exist in a specific structure and not be affected by external effects such as light, heat and solvent is a challenge that researchers need to face urgently. Therefore, this review discusses recent progresses in the use of self-assembled LCBC nanostructures as functional materials for photonics and nanotechnology applications, considering how the performance of the functional materials can be more effectively influenced by adopting LCBC self-assembly. A new fabrication strategy combined with the LCBC self-assembly process will provide a novel outlook on the further development of these functional materials.

2. BLOCK COPOLYMERS (BCS) AND LC BLOCK COPOLYMERS (LCBCS)

2.1 BCS

BC self-assembly has been captivating researchers for decades, allowing convenient generation of periodic nanostructures with uniform feature sizes in the condensed state.[1] Driven by MPS processes due to their chemically-linked distinct building blocks, BCS can self-assemble into various nano morphologies including lamellae, cylinders, spheres, and double gyroids, by simply adjusting the volume fraction of the blocks (Fig. 2).[2,3] In fact, most modern theories of MPS use “Flory-Huggins interaction parameter”, χ, as the description of the driving force for MPS. The equation of χAB for AB-type BCS can be described as following:

$$\chi_{AB} = \left( \frac{Z}{k_B T} \right) \left[ \varepsilon_{AB} - \frac{1}{2} (\varepsilon_{AA} + \varepsilon_{BB}) \right]$$

which describes the free-energy cost per monomer (in units of the thermal energy $k_B T$) of contacts between A and B monomers. Z is the degree of polymerization of monomers and $\varepsilon_{AB}$ is the interaction energy per monomer between A and B. When $\chi_{AB}$ is negative, a free-energy drive will take place towards mixing. While $\chi_{AB}$ is positive, the repulsion is formed between blocks A and B.[2] Most of the desirable properties of BCS can be acquired by molecular design of each block. This multi-phase structure improves the film-forming, processability and stability of polymer, while achieving homo-dispersity of multi-component system. Being typical BCS, polystyrene-b-polybutadiene-b-polystyrene (SBS) and polystyrene-b-polyisoprene-b-polystyrene (SIS) have been extensively studied as adhesives and thermoplastic elastomers.[6,63]

2.2 LCBCs

The MPS process enables BCS to form well-defined nanostructures with featured morphologies and tunable periodicity, offering driving force for sustaining interests in this field. When one block of BCS is designed as one LCP containing azobenzene moieties, the photoresponsive feature and mesogenic ordering are correspondingly brought about (Fig. 3). As for MPS, the intrinsic driving force for BCS is suitable for azobenzene-containing LCBCs. Therefore, researchers can choose the optimum $\chi_{AB}$ in order to form the expected microphase-separated nanostructures of azobenzene-containing LCBCs. Usually, the LC self-assembly plays an important role in formation of unique nanostructures upon MPS processes, and the interaction between the orderliness of LCs and the MPS of BCS is called supramolecular cooperative motion. This enables the MPS nanostructures of LCBCs to be controlled by light or external stimuli when the photosensitive mesogenic block forms as the continuous phase. Thus, the photoresponsive LCBCs combine the merits of the advanced performance of LCPs with the self-assembly of BCS, which results in the scope of possible applications rapidly expanding, involving the fields of chemistry, physics, materials science, as well as optics.[39–41]

In the past few years, various azobenzene-containing LCBCs have been intensively investigated. In order to obtain well-organized MPS nanostructures, LCBCs should have well-defined molecular structures, a large enough molecular weight and a narrow polydispersity.[56,62] So far, several controlled polymerization methods such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), ring-opening metathesis polymerization (ROMP) and nitroxide-mediated polymerization (NMP) have been utilized for synthesizing well-defined azobenzene-containing LCBCs.

3. INTRINSIC STRUCTURES OF LCBCS

3.1 Thermal Annealing

It is meaningful to fabricate periodic nanostructures in a large area by using supramolecular self-organization due to the simplicity and the low-cost process.[64] Although macroscopic regularly-ordered MPS nanostructures have been successfully obtained with amorphous BCS, both mass production and high reproducibility of these ordered nanostructures through self-assembling nanofabrication processes still remain challengeable. Therefore, specially designed azobenzene-containing
Photoresponsive LCBCs
Supramolecular cooperative motions
LC ordering helps regulation of nanostructures

Photoresponsive LCBCs
Supramolecular cooperative motions

Fig. 3 Schematic representation of an AB LCBC and supramolecular cooperative motion of LCBC.

LCBCs with supramolecular cooperative motion are promising candidates to prepare the cost-effective materials with hierarchically self-assembled nanostructures.

Thermal annealing is one of the most popular methods for preparing ordered MPS nanostructures in BCs, and is also appropriate for azobenzene-containing LCBCs. Fig. 4 shows MPS nanostructures of one poly(ethylene oxide) (PEO)-based LCBC film upon thermal annealing at its isotropic phase, in which hexagonal packing PEO nanocylinder arrays were obtained vertical to the substrate. Moreover, the TEM cross-sectional image indicates formation of regularly periodic arrangements of PEO nanocylinder arrays. Here, the substrate materials can be hard silicon wafers, mica, glass, or soft poly(ethylene terephthalate) (PET) films.

Through thermally annealing the same LCBC, the randomly-arranged nanocylinders can be uniformly oriented perpendicular to the substrate, as shown in Fig. 5. In the UV-VIS absorption spectra of the LCBC film, the characteristic band was observed at 337 nm, which is attributed to n-n’ transition of azobenzene chromophores. After thermal annealing, the maximum absorption band has a distinct decrease in the absorbance, and an obvious widening trend and blue shift were also observed simultaneously, which might be attributed to H-aggregation of chromophores. This suggests that the out-of-plane arrangement of the smectic mesogens occurs upon thermally annealing due to the existence of lamellar structures of the smectic LC phase.

3.2 Solvent Annealing

Generally, the synthesis of BCs should undergo hard chemical steps, and the process is obviously cumbersome. Therefore, small functional molecules are added to adjust the microscopic morphology via formation of BC supramolecules. A typical BC supramolecular system is polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) with 3-n-pentadecylyphenol (PDP) due to HB formation. Like the BC system, the BC supramolecule still achieves the control and construction of MPS nanostructures through thermal annealing or solvent annealing. However, thermal annealing sometimes causes small molecules to crystallize and changes the MPS morphology of BC supramolecules. It has been reported that suitable annealing conditions such as solvent annealing at room temperature can avoid macroscopic phase separation.

Therefore, Wu et al. used azobenzene compounds substituted with carboxylic or phenolic groups as photosensitive molecules which can form hydrogen-bonds (HBs) with the P4VP block of PS-b-P4VP, as shown in Fig. 6. The obtained BC supramolecules can undergo macro- or microphase separation according to the doping amount of azobenzene molecules. Macroscopic phase separation was observed in PS-b-P4VP with carboxyl-containing azobenzene molecules even when the molar ratio of azobenzene molecules to pyridine

Fig. 4 Perpendicular array of PEO nanocylinders and azobenzene mesogens in PEO-based LCBC films by thermal annealing. (Reproduced with permission from Ref. [65]; Copyright (2007) American Chemical Society).
groups was as small as 0.1. Contrary to carboxyl-containing azobenzene molecules, phenol-containing azobenzene molecules can be incorporated homogeneously into P4VP phases at a molar ratio up to 0.5. The following conclusions can be drawn through the experimental results: (1) a phenol group as a HB donor instead of using carboxyl groups can effectively inhibit macroscopic phase separation since carboxylic groups self-associate more strongly than phenol group; (2) reducing n-n stacking of small molecules can also suppress the macroscopic phase separation.

Depending on the compatibility and solubility of different polymer segments in solvents, both BCs and LCBCs can self-assemble in solvent vapor to form various microscopic morphologies. For BC supramolecules, the construction of nanopatterns can be achieved by selecting different solvents to change the interaction between small molecules and BCs. Therefore, solvent annealing can not only suppress the precipitation, migration and crystallization of small molecules, but also avoid the irreversible impact of long-term high-temperature annealing on polymer structure and performance. Regardless of whether it is high-temperature annealing or solvent annealing, it uses the untangling mechanism of the entangled polymer segments under external stimulation. For BC systems, solvents such as tetrahydrofuran, chloroform, toluene and other highly volatile solvents are used in most cases. It is believed that with the continuous research and development of LCBCs, more mature and sophisticated solvent annealing processes will be developed.

### 3.3 Surface Modification of Substrate

#### 3.3.1 Rubbing lines up mesogens

In diverse areas of nanotechnology, perpendicular arrays of nanostructures and parallel processes for patterning densely-packed nanostructures are often required. A mechanical rubbing process on polyimide (PI) layers has been widely used to produce microgrooves for mesogenic alignment in commercial production of LC displays (LCDs), and such a mechanical method is highly effective to control the MPS nanostructures in azobenzene-containing LCBCs. As shown in Fig. 7, regular patterning of parallel alignment of nanocylinders in bulk film of one PEO-based LCBC was achieved on rubbed polyimide film along the rubbing direction.\(^6\) The LCBC film shows a large anisotropy upon the mechanical treatment, suggesting that mesogens in the LCP block have been homogeneously aligned. Further characterization showed the 3D patterning of nanostructures was obtained by the mechanical rubbing method, as observed in the cross-sectional FESEM and AFM images.

In general, the intermediate state of matter, LC molecule, gives rise to intrinsic anisotropy on the micrometer scale and allows for long-range alignment along the rubbing direction on the surfaces of rubbed polyimide films due to the lower energy level along the mechanically-induced microgrooves.\(^6\) Then the periodic ordering of aligned LC molecules can be transferred to MPS nanocylinders by supramolecular cooperative motion. With the development of soft materials, this mechanical rubbing method has become an important subject of interest and is a core technological requirement for aligning low-molecular-weight compounds, linear or branched LCPs, crosslinked LC network and LC elastomers.
3.3.2 Surface-grafted diblock copolymer

Compared with the spin-coated polymer films, attaching polymer chains to a solid surface often affords different mechanical and thermal properties. As shown in Fig. 8(a), surface-initiated ATRP has been widely used for the formation of surface-grafted polymers. With regard to design of polymer chain, further questions arise as to what extent and how the photoinduced orientation behavior can be affected by connecting the azobenzene-
containing LCP chains to the substrate surfaces. Accordingly, surface-grafted LCPs exhibited surprisingly different properties from those of spin-coated films. The azobenzene chromophores were orientated parallel to the substrate, while they were aligned perpendicularly for spin-coated films.[76] Moreover, one highly ordered in-plane anisotropy was obtained in the surface-grafted LCP film.[76] More interestingly, when a flexible amorphous polymer chain was introduced to link the azobenzene-containing LCP chains with the substrate, a completely different phenomenon occurred.[77] As shown in Fig. 8(b), the surface-grafted LCBCs were synthesized by a two-step surface-initiated ATRP where the upper block contains azobenzene groups, which exhibited a significant improvement of the in-plane anisotropy compared to the surface-grafted LC homopolymer upon linearly polarized light (LPL) irradiation (Fig. 8c). The effect of the flexible block chains could be summarized as three aspects.[78] (1) Much higher optical anisotropy is obtained for the surface-grafted LCBCs due to the more efficient cooperative photoinduced orientation. (2) Compared with the surface-grafted LC homopolymer restricted by the substrate, the surface-grafted LCBCs are more conducive to in-plane orientation of azobenzene groups. (3) The rate of the photoinduced reorientation with orthogonal LPL increases with the help of underlying flexible polymer blocks between the LCP block and the solid substrate.

Seki’s group also introduced the moderately flexible and rigid block chains to the substrate surface and investigated the role of the chain rigidity in the photoinduced orientation of the azobenzene-containing LCP blocks, as shown in Fig. 8(b).[79] As the glass transition temperature ($T_g$) of the polymer blocks connected to the substrate decreases, the photoinduced orientation ordering for the azobenzene LCP blocks becomes higher. This may be attributed to the fact that the more flexible amorphous polymer chains could facilitate ordering motion of the azobenzene chromophore upon LPL irradiation.[80] Since this surface-grafted diblock copolymer method can significantly enhance the optical anisotropy of LCP blocks, it is very promising for surface functional modification.

3.4 Photo-regulation

3.4.1 Photoalignment method

Although the rubbing method is effective for fabricating MPS nanostructures in LCBCs, the mechanical process has certain disadvantages, such as possible accumulation of electrostatic charge, debris and local defects caused by the line pair. These often cause defect for mesogenic alignment. To solve these problems, non-contact methods, such as photoalignment, have been introduced into LCBC systems. It is well known that photoalignment of azobenzene mesogens provides a convenient non-contact approach for control over LC alignment. The mesogenic orientation can be controlled by adjusting the polarization direction of the actinic light, which also has a crucial influence on the orientation of MPS nanostructures in LCBCs, where the mesogenic block should serve as the continuous phase. Seki and coworkers also studied the photoalignment of nanocylinders in azobenzene-containing LCBC films upon surface-relief grating formation, and they revealed that the photoalignment of the mesogens along with the nanocylinders orient in-plane or out-of-plane depended on the film thickness, as shown in Fig. 9.[81]

In a spin-coated film with uniform thickness, one photoalignment method was proposed to control a homogeneous in-plane orientation of PEO nanocylinders in PEO-based amphiphilic LCBCs on exposure to LPL.[18] Firstly, PEO nanocylinders perpendicular to the substrate were prepared upon thermal annealing and then the mesogenic alignment was easily converted into homogeneously in-plane orientation, perpendicular to the polarized direction of the actinic LPL. This method has advantages of clean, simple and convenient, providing a novel approach to obtain regular surface patterns even on curved surface, as shown Fig. 10.

3.4.2 Photoinduced phase transition

For practical applications, a rapid, reversible and precise tuning method of MPS nanostructures of LCBCs at room temperature is still remaining challengeable. More recently, we reported that regularly patterned cylindrical nanostructures in azobenzene-containing PEO-based LCBCs could be quickly photo-directed from in-plane orientation to out-of-plane arrangement at room temperature.[82] On the one hand, the trans–cis isomerization of azobenzene mesogens led to the phase transformation and photoswitching of $T_g$ of the LCP block. On the other hand, the azobenzene-containing blocks with the lower free surface energy migrate to the free surface. Common function in above both sides would cause the PEO segments to reorganize into another ordered orientation state (Fig. 11). Upon annealing the photo-irradiated LCBC sample at 145 °C, the initial state of in-plane orientation can be recovered, indicating the good reversibility of light-directed manipulation process. Moreover, Schenning et al. prepared a series of photoresponsive hybrid oligo(dimethylsiloxane) LCPs that form periodic cylindrical nanostructures with periodicities between 3.8 and 5.1 nm.[83] The azo-
benzene mesogens here can be oriented in-plane on exposure to LPL and out-of-plane on exposure to unpolarized light.

3.4.3 Photoinduced reorientation

Covalent bond. Numerous researches have been conducted to control the photoinduced orientation of mesogens in photo-responsive LCPs upon LPL irradiation. However, whether the reorientation of MPS nanostructures can be achieved is a problem that we need to consider. Since BCs have been widely investigated as useful nanotemplates to prepare the patterning and alignment of various functional materials, the photoinduced reorientation of MPS nanostructures in multiple times instead of once appears very essential. Moreover, the preparation of all kinds of patterned nanotemplates is very cumbersome and expensive. Seki et al. comprehensively investigated the switching behaviors in azobenzene-containing LCBC films by the photo-induced reorientation method. As shown in Fig. 12(a), they synthesized a novel azobenzene-containing LCBC with poly(butyl methacrylate) as the non-LCBC blocks. The MPS nanostructure was firstly uniformly photoaligned by initial LPL irradiation, and then was irradiated by LPL in the orthogonal direction at the temperature within the range of smectic A phase of the LCP block (Fig. 12b). They proposed that photoinduced reorientation follows the subdomain rotation mechanism and the reorientation process by LPL occurs at three stages: (1) the smectic layer becomes fluctuated and subdomains are formed;

![Diagram](https://doi.org/10.1007/s10118-021-2531-1)
(2) azobenzene mesogens, smectic layers and the MPS cylinder nanostructures are retained, but the film domains break up to the submicrometer scale; (3) fusion and growth of the successive domain structures occur. Most importantly, the pattern formed by such photoinduced reorientation could be erased and reoriented to any desired directions controlled with LPL irradiation. Therefore, this method not only has a very important scientific significance, but also functions as a very essential strategy for preparing advanced functional materials.

Supramolecular interaction. As mentioned above, the researchers have realized the processes of photoinduced orientation and reorientation of the MPS nanostructures of LCBCs by changing the polarization direction of LPL. Since the orientation and reorientation of the nanostructures can be achieved within a covalent bond system, one would naturally ask whether this effect can also be achieved in a non-covalently bonded LCBC supramolecular system. The answer is absolutely yes. An efficient photoalignment and photoreorientation of MPS nanostructures was successfully obtained by manipulating photoirradiation of LPL for the one halogen bond (XB)-involved LCBC. Above all, the hexagonal-close-packed nanocylinder array orientated perpendicular to the substrate was directed by XB-driven LCBC supramolecule self-assembly, as shown in Fig. 13.\[85\] Whereafter, a parallel nanocylinder array was directed perpendicular to the LPL polarization direction. When changing the direction of LPL, the degree of order parameter (S) became negative. The alternating negative and positive S values demonstrate that the photoreorientation was successfully achieved by manipulating the LPL polarization direction. Moreover, the process of photo-induced alignment and reorientation was carried out at 75 °C, and the S value was maintained at 0.58. There is no decrease in S value during elastic deformation of the polymer segments and the micromorphology has good thermal stability. Therefore, this simple method provides scientific research foundation and application possibilities for the development of a new generation of intelligent responsive supramolecular LC materials.

4. EXTRINSIC STRUCTURES OF LCBCs
4.1 Hydrogen Bonds (HB)
Whether it is through thermal and solvent annealing, physical friction, surface grafting, or photoalignment and reorientation, the final MPS nanostructures formed in LCBCs are all intrinsic structures such as lamellae, cylinders, spheres, and gyroid. However, these basic nanostructures are obviously not enough to meet the requirement of applications. Therefore, chemical functionalization or physical addition has been utilized to enable LCBCs to be capable of formation of novel hierarchical structures, which also enriches the nanostructures formed by the self-assembly of LCBCs and makes the LCBCs radiate new brilliance and vitality, thus attracting more scientific researchers to be engaged in them. For instance, aramid groups were elegantly introduced into LCBC to form HBs in the matrix, which can bring about more novel nanostructures by supramolecular self-assembly.\[86\] Both HBs and mesogenic ordering can influence the MPS process, promising them to form hierarchical structures by supramolecular self-assembly. The introduction of aramid groups with HBs not only improves the stability of the self-assembled nanostructures, but also contributes to macroscopic regular arrays of perpendicularly orientated nanocylinders.

Interestingly, MPS nanostructures in LCBCs have also been prepared by introduction of HBs in the mesogenic side chain without any dopants. As shown in Fig. 14, both out-of-plane and in-plane orientations of MPS nanocylinders were successfully obtained in the PEO-based amphiphilic LCBCs depending on the film thickness. However, the newly-introduced urethane groups in the side chain of the hydrophobic block of LCBCs also interact with the ether groups of the hydrophilic PEO block, which should affect the crystallization process of the PEO blocks in the nanoscale separated phase. Thus, a sub-10 nm inner-phase nanostructure was observed in the LCBC film.\[87\]

4.2 Halogen Bonds (XB)
Compared with HB, XB is one of the most promising candidates to prepare LC supramolecules due to its larger strength tunability and higher directionality.\[88–93\] The introduction of XBs into BC systems especially for LCBCs to form new hierarchical structures has now aroused interests in LCBC supramolecule fields. Very recently, we designed a novel XB-involved LCBC supramolecule and studied the effect on its photoalignment behaviors.\[85\] The LCBC supramolecule was formed by the selective bonding between 1,2-diiodo-3,4,5,6-tetrafluorobenzene (1,2-DITFB) as the XB donor and the azopyriding (AzPy)
containing BC, PEO-b-PazPy as the XB acceptor. Upon self-assembly, the pristine BC formed a mixed micromorphology, as shown in Fig. 15. When 1,2-DITFB was added into PEO-b-PazPy, the supramolecule exhibits obvious LC textures, that is, the degree of order was improved. In addition, the micromorphology of this LCBC supramolecule is more regular, reassembled into a cylinder morphology arranged perpendicular to the substrate. Therefore, the addition of XB improves the order of the supramolecular system when the XB donor and the BC were added in an equimolar ratio. Similar to other azobenzene-containing LCBCs, reorientation of the nanostructure was also obtained in XB LCBC supramolecules through LPL irradiation.

**Fig. 14** Morphologies of the out-of-plane alignment, in-plane alignment and the internal phase structure in the hydrogen-bond-containing LCBC. (Reproduced with permission from Ref. [87]; Copyright (2018) WILEY-VCH).

**Fig. 15** Morphologies of the annealed film, the film after the first irradiation with LPL of 460 nm at 75 °C, and the film after successive irradiation with orthogonal LPL at 75 °C. (Reproduced with permission from Ref. [85]; Copyright (2020) American Chemical Society).
These indicate that the supramolecular interaction with high directionality and mesogenic ordering are two necessary conditions to generate well-ordered MPS nanostructures for LCBC supramolecules. The formation of XBs gives LCBC supramolecules a new ordered structure, and subsequent illumination can achieve the reorientation of the ordered structure, which is promising for their further applications in various fields of supramolecular chemistry, nanotechnology and optical materials.

4.3 Chirality Transfer
The above-mentioned two methods improve the ordering of MPS nanostructures and introduce new hierarchical structures in LCBC supramolecules through HB or XB interactions. Then, if small functional molecules with a specific configuration are added to the LCBC, will the resultant supramolecular system form a more bizarre nanostructure while exhibiting more excellent performance? Obviously, the introduction of chirality into LCBCs could induce unique helical nanostructures which have potential applications as nanotemplates for fabricating complicated nanostructures. As shown in Fig. 16, chirality transfer effect and the controllable MPS were combined together in one LCBC system consisting of hydrophilic PEO and hydrophobic azobenzene-containing poly(methylacrylate), which was used to prepare helical nanostructures via doping with chiral additives. Through HB interactions, chirality was transferred from dopants to the aggregates, leading to formation of the hierarchically self-assembled nanostructures in the composite system. Upon thermal annealing and adjusting the amount of chiral dopants, helical structures in film were successfully prepared by the induced aggregation chirality. Consequently, the photosensitive azobenzene mesogens in LCBCs may help photo-regulation of the self-assembled helical morphologies. This provides a simple but elegant method for construction and non-contact manipulation of complicated nanostructures. Moreover, Zhang et al. reported another chirality transfer method named polymerization-induced chiral self-assembly. Firstly, the helical azobenzene-containing monomer was polymerized to form LCBC. During polymerization, the chirality transferred from the terminal chiral group to azobenzene and finally built the supramolecular chirality in LCBC assemblies. Therefore, the chirality transfer can be achieved in situ in a controlled method and the method is also suitable for other azobenzene-containing materials.

5 STABILIZATION OF NANOSTRUCTURES IN LCBCS
The MPS of the azobenzene-containing LCBCs has been

![Fig. 16 Illustration for the transfer, photoinduced breaking, and regeneration of the aggregation chirality in film of an amphiphilic azobenzene-containing LCBC doped with chiral tartaric acid. (Reproduced with permission from Ref. [61]; Copyright (2018) WILEY-VCH).](https://doi.org/10.1007/s10118-021-2551-1)
manipulated by the rubbing technique or photo-controllable method. However, the obtained nanostructures have a poor optical durability and environmental stability at room light. Moreover, there still lacks efficient technology to store the obtained MPS nanostructures of LCBCs due to their tendency to be contaminated by defects and impurities, which greatly limited their further applications. Then one confined self-assembled strategy was proposed for thermal stabilization and convenient patterning of MPS nanostructures in LCBCs enabled by top coating of poly(sodium-4-styrenesulfonate) (PSSNa), a water-soluble ionic polymer. PSSNa was chosen to cover the LCBC film for providing a confined self-assembly environment sandwiched between the top coating and the substrate. The LCBC film top-coated PSSNa can maintain the initial nanostructures unchanged during the thermal annealing at 125 °C and even UV irradiation, as shown in Fig. 17. It was considered that thermal stabilization of MPS nanostructures of the PSSNa-covered LCBC might be attributed to the coordination interaction between PEO and PSSNa. Therefore, the PSSNa-caused stabilization effect provides a novel and versatile way for long-term nondestructive preservation of MPS nanostructures, extending applications of the LCBC films.

The ordered nanostructures formed in LCBCs can be used as nanotemplates in the field of semiconductor chips, information storage and even encryption. The process of assembly, molding and equipment of semiconductor devices is complicated and very delicate, which has extremely high requirements on the cleanliness and stabilization of the template. However, the template will be inevitably stained with dust during utilization and transportation, which will affect the precision of the chip and cause inestimable losses. Therefore, it is particularly important to improve the stability of the template. By using the water-soluble polymer PSSNa, the stability of the MPS nanostructures has been improved, and at the same time, it can withstand a certain temperature to meet the template application in different occasions, so it is of great significance. It is believed that there will be more excellent work for improving the stability of these nanotemplates in the future.

6 APPLICATIONS

The ordered nanostructures of LCBCs are tunable over a broad variety of morphologies hierarchically assembled from intrinsic to extrinsic structures. Their synthetic nature allows the design of interfaces with different functional groups and geometrical properties. This, in combination with molecular architecture, determines the level of ordering in self-organizing polymeric materials. Because of the integration of advanced properties of LCP blocks with the additional MPS nanostructures of BCs, LCBCs possessing intrinsic and extrinsic nanostructures are finding applications in several areas, ranging from nanocomposites to photonic devices.

6.1 Holographic Gratings and Storage

LCBCs are promising materials that can combine photosensitive features of azobenzene materials with the optical properties of LCPs. Azobenzene moieties can undergo a reversible isomerization from stable trans to a semi-stable cis state irradiated by UV light; a reverse transition can be obtained upon heating or irradiation with visible light.[96] Holographic gratings are low-cost components with photonic and optoelectronic applications and require that the index of refraction or the absorption coefficient of materials can be modulated throughout the volume. From this point of view, LCBCs are good

![Fig. 17](https://doi.org/10.1007/s10118-021-2531-1)
candidates to control diffraction efficiency by enhancement of surface relief upon MPS processes under a suitable condition.\cite{97}

As shown in Fig. 18, both a surface-relief grating and a refractive-index grating were simultaneously recorded in LCBC films upon irradiation of an interference pattern of two coherent laser beams, in which selective photoisomerization and the isotropic-to-LC phase transition were induced in the bright areas and little changes remained in the dark areas. The diffraction efficiency of the gratings depended strongly on the polarization of the reading beam because of the photoalignment of azobenzene mesogens in the selective areas. As shown in Fig. 18, the surface-relief structure with a sinusoidal curve was clearly observed after the grating formation possessing one fringe spacing of 2.0 μm. After thermal annealing, the amplitude of the surface relief was increased to about 110 nm and the peak-to-valley contrast became more evident. Moreover, the sinusoidal shape of the surface profile became a little irregular, indicating that the mesogenic alignment was partly disturbed upon MPS process at a high temperature (below the clearing point of the LCBC).

Comparing to other methods for controlling diffraction efficiency, such a thermally-enhanced phase separation method of LCBCs had advantages of being simple and convenient.\cite{98}

### 6.2 Nanotemplates

The well-ordered nanostructures of LCBC films can serve as nanotemplates for preparation of metallic and inorganic materials with specially-designed nanostructures. As shown in Fig. 19(a), templated patterning with CaCO$_3$ nanoparticles was fabricated by immersing the LCBC film into the 0.5 mol/L CaCl$_2$ solution, which was then treated with O$_2$ plasma for 5 min, and placed in the air. Because of the selective coordination between PEO and Ca$^{2+}$, CaCO$_3$ nanoparticles would be controlled in accordance with the alignment of the PEO nanocylinders. With and without the light regulation, different morphologies can be obtained due to the light-regulated MPS nanostructures, as shown in Fig. 19(b). Likewise, various metal nanostructures such as Ag and Ag/Co alloy nanoparticles have been prepared by using the photocontrollable hierarchical nanostructures as nanotemplates (Fig. 19c), providing a fascinating strategy for precise and rapid manipulation of functional nanostructures at room temperature, which would be applied to the field of nanofabrication and nanoengineering.\cite{82}

In addition, silver ion (Ag$^+$) was introduced into the PEO-based LCBC and selectively combined with the hydrophilic PEO segments through coordination interactions.\cite{46} After these processes, both the photoreduction of Ag$^+$ and a con-

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**Fig. 18** Holographic gratings recorded in LCBCs and enhancement of surface relief upon microphase separation.

**Fig. 19** (a) Schematic illustration for fabrication of patterning with CaCO$_3$ using nanotemplates of LCBC MPS nanostructures with and without photo-regulation; (b) AFM height images of CaCO$_3$ nanoparticles prepared on the nanotemplates with and without photo-regulation; (c) AFM height images of Ag and Ag/Co alloy nanoparticles prepared based on the LCBC nanotemplates. (Reproduced with permission from Ref. [82]; Copyright (2017) American Chemical Society).
6.3 The Patterned Porous Polymeric Films

Porous polymer films are very essential in many fields of scientific research and technology. Although highly ordered nanostructures have been obtained by self-assembly of LCBCs, it is difficult to form microporous films via MPS processes of LCBCs. The general methods are imprint and lithography to fabricate porous polymer film, which requires mold to directly contact the film by external force. Because of the facile and high throughput, breath figure (BF) method has been employed to prepare the ordered porous films in the past several years. Recently, LCBCs has also been used to fabricate microporous films via BF method. For example, Lin et al. developed a light manipulation method to regulate the porous shapes of azobenzene-containing LCBC polymer films. As shown in Fig. 20, round pores can be transferred into rectangular, and rhombic-shaped structures, according to the polarization direction of the incident light. Moreover, they also prepared the photo-driven shape-memory porous LCBC films by BF method, followed by vapor crosslinking and photo-manipulation. Microporous structures can be converted into other shapes such as rectangle and rhombus. More interestingly, the new obtained micropores could be recovered to their original shapes by UV irradiation or thermal annealing. As is well known, high humidity is indispensable to prepare the microporous polymer films by conventional BF method. So-called traditional is not absolute or static. We fabricated regularly ordered microporous films with LCBC under a dry environment. Addition of 4.5 wt% water into a tetrahydrofuran solution of LCBCs results in the formation of ellipsoidal microporous film upon spin-coating. Moreover, we also study the influence of different rotational speeds in spin-coating on microporous size, and the obtained patterned polymer films showed good photo and thermal stability. Thus, highly ordered microporous LCBC film was successfully fabricated by a simple and highly effective approach to BF arrays. This approach could render LCBCs hierarchical structures, which can serve as functional materials for pattern transfer, release of drugs and tissue engineering.

6.4 Surface Functionalization

The surface coatings of polymer materials are of particular importance in industrial applications. Currently, the surface segregation of a selective polymer in blend amorphous polymer films has been extensively studied because it allows for low-cost, easy, and reliable surface modifications of polymer materials. Seki et al. proposed that the azobenzene-containing polymer chains with high flexibility and low surface tension tend to migrate towards the free surface under thermal stimulation. Therefore, blending the LCBC with a homopolymer derived from a non-azobenzene monomer such as PS can promote surface migration of azobenzene moieties upon thermal annealing (Fig. 21). Then photoalignment could be effectively achieved via LPL irradiation. Therefore, the method of surface segregation and self-assembly could introduce the azobenzene moieties into the substrate materials surface based on LCBCs. Thus, one can design the molecular structure of non-LCP block which is the same as or similar to that of the substrate materials. Moreover, various functional moieties can be readily introduced to the materials surface by this approach.

However, the alignment of the polymer materials soon diminishes during elastic deformation of the polymeric substrate due to the weak interaction between the copolymer and polymeric substrate. To address this challenge, Lu et al. introduced rigid segments composed of N-p-anislymaleimide (NPAMI) via copolymerization into the well-defined LCBC as “anchors” to resist the “drift” of the copolymer from a poly(methyl methacrylate) (PMMA) substrate at a temperature above its $T_g$. They prepared well-defined diblock copolymers with one block of azobenzene-containing LCP and another block of alternating polymer P(MMA-NPAMI) in which PMMA serves as a compatibilization segment and NPAMI as a rigid “anchor”. The LCBC was spin-coated onto a PMMA substrate, and thermally annealed at a temperature above the $T_g$ of PMMA to trigger self-assembly arrangement of azobenzene LCP chains towards the substrate surface to form an azobenzene polymeric layer. LPL irradiation was then applied to align the layer (Fig. 22). Owing to the introduction of rigid NPAMI as “anchors”, the LCBC exhibited enhanced stability of the photoalignment layer. The degree of alignment for the azobenzene groups was 1.7-fold higher than that for a control sample when the treatment temperature approached to the $T_g$ of PMMA substrate. This approach may be useful for fabrication of more stable ordered layers through self-assembly of LCBCs.
6.5 Light-induced Reworkable Adhesives

Adhesives are of immense practical and technological importance in industry. Nowadays, sustainability is an important objective during the material service cycle. To achieve the requirement, reworkable adhesives that enable repeatable bonding and debonding have been developed. Obviously, photoinduced reworkable adhesives are particularly interesting because light can activate the adhesives by an athermal process. Recently, certain azobenzene derivatives have shown to reversibly convert from solid to liquid upon UV irradiation.\textsuperscript{[109]} Thus, Kihara et al. synthesized an ABA-type triblock copolymer consisting of poly(meth)acrylates bearing an azobenzene moiety (A block) and 2-ethylhexyl (B block) side chains utilized as photocurable adhesives.\textsuperscript{[110]} Compared to the azobenzene homopolymers, the LCBCs incorporate the soft middle block actualized a low concentration of the azobenzene moiety, thus acquiring higher flexibility. This makes sure the film formation of the azobenzene-based adhesives. Due to the photo-isomerization of azobenzenes, changes in their viscoelastic properties of the LCBCs were induced by UV irradiation at 365 nm and green light irradiation at 530 nm, respectively. In fact, two glass substrates were bonded with the free-standing polymer film, which was sequentially softened and hardened upon UV and green light irradiations. They exhibited shear strengths of 1.5–2.0 MPa, and UV irradiation lowered the adhesion strength to 0.5–0.1 MPa (Fig. 23). Therefore, appropriate molecular design of the azobenzene-containing LCBC enables the film to show photochemical bonding and debonding performances, serving as novel light-induced reworkable adhesives.

6.6 LC Elastomer

The most classic application of BCs should be thermoplastic elastomer SBS, which is an ABA-type triblock copolymer obtained by anionic polymerization of styrene and butadiene. PS micro-regions with a higher \( T_g \) can serve as a physical cross-linking point, and polybutadiene as a continuous phase with a lower \( T_g \) can provide elasticity of rubber. The polymer can be processed by heating above the \( T_g \) of PS. Therefore, SBS has both the elasticity of rubber and the thermoplastic processability of plastics,\textsuperscript{[62,63]} called the third-generation synthetic rubber. If the azobenzene-containing LCP is introduced into this triblock copolymer, the resulting polymer will have both rubber elasticity and liquid crystallinity. This new type of polymer is an LC elastomer (LCE), which has attracted much attention for applications in soft robots and energy generators due to its combination of the anisotropic nature of LCPS and the rubber elasticity of polymer networks.\textsuperscript{[111,112]}

In general, LCE possesses reversible macroscopic shape
changing behaviors; when one LCE film with uniaxial orientation is uniformly heated to the isotropic phase, the length of film contracts and its width elongates, while when it is cooled back to the LC phase, the length extends and the width contracts. However, Zhao et al. reported a novel LCE based on the triblock copolymer SBS with a side-chain azobenzene-containing LC polymer, \cite{113} which exhibited an anomalous shape change. The LCE film was formed by uniaxial stretching and crosslinking within the LC state, but the film contracts in both length and width on heating to the isotropic phase, while it elongates in both length and width on cooling to the LC phase, as shown in Fig. 24. They proposed a possible mechanism for the reverse action of the orientation of the main chain and the side chain. In uniaxial stretching orientation, the main chain is oriented in the stretching direction, and the side chain azobenzene is oriented perpendicular to the stretching direction. When the oriented polymer film is heated up to an isotropic state, the main chain shrinks in the stretching direction and extends perpendicular to the stretching direction, and the side chains are opposite, extending in the stretching direction and shrinking perpendicular to the stretching direction. In the stretching direction, the contraction effect of the main chain is stronger than that of the side chain, and in the direction perpendicular to the stretching direction, the contraction effect of the side chain is stronger than that of the main chain. For cooling to the LC phase, vice versa. In addition, the author used this special LCE to prepare several shapes of actuators. Therefore, LCEs of this kind exhibit distinguished shape change and may be explored in soft actuator and robot applications.

The preparation of elastomers based on azobenzene-containing LCBCs has attracted more and more attention and re-

![Fig. 23](image1)

**Fig. 23** Synthesis of ABA-type LCBC and preparation of the light-induced reworkable adhesives. (Reproduced with permission from Ref. [110]; Copyright (2018) American Chemical Society).

![Fig. 24](image2)

**Fig. 24** Schematic illustration and photos showing the thermally induced anomalous shape change of an oriented SBS-Azo strip between 80 °C (isotropic phase) and room temperature (LC phase). (Reproduced with permission from Ref. [113]; Copyright (2020) WILEY-VCH).
search. Our group is also conducting related research, hoping to enrich the application range of LCBCs and promote the development of elastomers.

7 SUMMARY AND OUTLOOK

The use of self-assembled LCBC technology provides great benefits with micropattern control in the area of photonics and nanotechnology. This review discusses recent investigations and developments in this related area, including fabrication and manipulation of the intrinsic and extrinsic structures of LCBCs, stability and functionalization of nanostructures, and further applications. LCBCs can self-assemble into a primary nanostructure under external stimuli such as heat, solvent, mechanical friction, light and chemical grafting. Simultaneously, due to the photoresponsive characteristics of azobenzene chromophores and the ordering of mesogenic phases, the microscopic deformation of the azobenzene configuration change caused by UV illumination can be extended through the mesogenic arrangement to achieve supramolecular synergy, which ultimately leads to the microstructure of the entire film of LCBCs. Therefore, various fascinating processes such as photoalignment, photo-triggered molecular cooperative motion, photoinduced phase transition and the corresponding volume change can occur, which may greatly impact the MPS nanostructures of LCBCs.

More interestingly, by designing the structure of non-mesogenic blocks, the LCBC has additional excellent chemical properties such as hydrophilicity, crystallization, optical transparency, thermoplasticity, adsorbability, and electrical conductivity to meet more usage requirements. LCBCs and functional small molecules can form LCBC supramolecular systems through supramolecular interaction. This supramolecular system can be assembled on the basis of the pristine LCBC to form a new hierarchical nanostructure. Through the top-down assembly method, the water-soluble and temperature-resistant polymer, PSSNa, is physically deposited on the top of the LCBC film, and the nanostructures can be stabilized at any MPS stage. Based on the controllability of micro-nano morphology, LCBCs are utilized in the fields of optics, templating nanofabrication, porous polymer films, material surface functional modification, adhesives and elastomers. With the development of information technology, new waves are surging, driving the manipulation of such nanostructures leading to industrial applications as the future engineering plastics for functional materials.

Till now, there are not many examples of industrial applications of BCs, and the advances are currently mainly based on laboratory researches. Possible applications for the LCBC nanostructures serving as functional materials encompass many areas, from nanotechnology to photoelectricity. However, it is still difficult to prepare ordered MPS nanostructures in an arbitrary area and in an on-demand control way. Moreover, the spontaneous nature of LCBC self-assembly and its low thermodynamic driving force leads to the simultaneous formation of trapped defects at their boundaries, which significantly limits usability. Furthermore, in films, it is still difficult to prepare periodic nanostructures below 10 nm using LCBCs. These fundamental challenges have motivated researchers to find ways to control orientation and ordering in films, resulting in various successful means to induce LCBC alignment and defect elimination. By using the patterned substrates to direct LCBCs self-assembly, the ordered nanostructures with uniform sizes over large distances may be formed. Simultaneously, the interesting LC property can be introduced into the system, making it applicable to the field of smart displays. In addition, with the selective removal of the non-LCP block via etching, the obtained nanostructure could serve as a mask or a template, which can be used to transfer the self-assembled pattern into different functional materials. Last but not least, the LCBC with a smaller periodic structure should be synthesized through precise molecular design to meet the requirement of templates smaller than 10 nm, so that it can be used to prepare chips for computers or mobile phones.

In summary, previous remarkable success at progress in self-assembled LCBC nanostructures toward functional materials has provided a clear rational for expanding the body of knowledge to match that of other self-assembled LCBC nanoscale patterns or templates for optic and nanotechnology devices. We believe that the elaboration of macroscopic regulation of hierarchical nanostructures in LCBCs could greatly promote the innovative application of LCBCs in a variety of fields.

BIOGRAPHY

Hai-Feng Yu received his PhD degree from Tsinghua University in 2003. Then he went to Japan, where he worked as a researcher at JST-CREST, and then as a postdoc at JSPS at Tokyo Institute of Technology and Kyudo University. In 2008, he started his independent research as Associate Professor by special appointment at Nagaoka University of Technology. In 2012, he joined Peking University as a research professor as the “2011 National Thousand Young Talents Program” recipient. In 2013, he obtained the “NSFC Award” for Excellent Young Scholar. His research interests focus on photoresponsive soft matter, supramolecular self-assembled materials and organic/inorganic hybrid materials.

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