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Lytropic Liquid Crystals Incorporated with Different Kinds of Carbon Nanomaterials or Biomolecules

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<http://dx.doi.org/10.5772/intechopen.70392>

Abstract

Liquid crystals (LCs) are considered as the “fourth state of matter,” which can display properties between crystals and isotropic liquids. LCs can be classified into lyotropic liquid crystals (LLCs) and thermotropic liquid crystals (TLCs), among which LLCs are a kind of self-assemblies formed by amphiphile molecules in a given solvent within certain concentration ranges. The structures and properties of LLCs can be tuned by the incorporation of various kinds of additives, which represents an interesting and novel route for realizing functional composites. This review focuses on recent progress on LLCs-based materials assembled with diverse additives including carbon nanotubes, graphene, graphene oxide, and biomolecules. The thermal stability and mechanical strength of the host LLCs can be greatly improved after the guests are incorporated. In addition, new functions such as conductivity, photothermal effect, and bioactivity can be introduced by the incorporation of the guests, which significantly widens the applications of LLCs-based hybrids in nanotechnology, electrochemistry, drug delivery, and life science.

Keywords: liquid crystals, amphiphilic molecule, carbon nanotubes, graphene oxide, biomolecule

1. Introduction

Liquid crystals (LCs), including lyotropic liquid crystals (LLCs) and thermotropic liquid crystals (TLCs), are an intermediate state between isotropic liquid and ordered crystal [1]. They normally show the anisotropic physical properties because of the long orientational order of the molecular self-assemble aggregates. Thus, LCs are currently of great significance in nanotechnology to act as templates to devise, arrange, or even synthesize interesting composites due to the intrinsic self-assembly speciality [2–9]. Among them, LLCs were a special

kind of self-assemblies of amphiphilic molecules within the scope of the long-range ordered arrangement, and their unique functions cannot be replaced by other materials. For example, the LLCs can be used as mediums for various organic and inorganic reactions that can be carried out in the hydrophilic or hydrophobic domains in confined spaces of those mesophases [10–13]. Moreover, the lamellar, hexagonal and cubic phases of LLCs can also be used as soft templates to control the structure and morphology of desired composites [14]. The Bi, PdS nanoparticles can also be synthesized by the LLCs [15]. A large variety of functional materials possessing mechanical or processing properties, biocompatibility, and so on, could be produced in this way. The LLCs have been the ideal self-organizing templates of carbon nanotubes, graphene oxide, biomolecules, and a large number of functional nanoparticles, because of their alignment regulated by the ordered matrix of LLCs [3, 16]. The preparation of LLCs-based hybrid materials has been proven to be an efficient approach to prepare ordered functional composites.

In the present chapter, a deep review on structure and property of LLCs-based materials is presented. Emphasis will be put on the hybrids composed of LLCs of amphiphilic molecules incorporated with different kinds of additives including carbon nanotubes, graphene oxide, and biomolecules.

2. Carbon nanotubes/LLC hybrid materials

Carbon nanotubes (CNTs) possess wide potential applications in physics, chemistry, and material and life sciences due to their distinct cylindrical π -conjugated structure and remarkable mechanical, electronic, optical, and thermal properties [17, 18]. The orienting and aligning of CNTs in CNTs-based composites is crucial for the advancement of their applications. Great efforts have been paid to disperse single-walled carbon nanotubes (SWNTs) into aqueous solutions by noncovalent method typically with surfactants, polymers, and polyelectrolytes [19, 20]. One of the efficient methods to develop aligned CNTs is to make use of the order and fluidity of LLCs [21]. The incorporation of CNTs in LLCs has achieved well-dispersed and uniformly-aligned CNTs, which are two key prerequisites during the application of CNTs.

Studies about the dispersion and alignment of CNTs in LLCs have been reported [4, 16, 22–24]. For example, Lagerwall et al. presented an approach of using self-organized lyotropic nematic LC to align and disperse SWNTs [21]. This work also pointed out the possibility of using other LLCs with higher orientational orders such as lamellar and hexagonal phases to align CNTs. However, the above LC composites must be presented in a test cell to avoid the fluiding of the materials. Okano et al. proposed an approach of using sulfonated polyamide to prepare ordered SWCNTs/LLCs film. The fabrication process of this system is simple (LLCs in water) and low-cost, endowing the broad versatility performance of LLC polymer film with SWCNTs [25]. These characteristic properties also demonstrated that the LLC/SWNTs systems took an advantage over the TLC/SWCNTs systems.

Although using LLCs to align CNTs is a promising method to promote the application of CNTs, the direct incorporation of SWNTs into the LLCs with high viscosity is usually difficult.

A modified method for the introduction of the CNTs into LLCs is accompanied by rigorous sonication and heating, which is complicated and harmful for the LLC matrix. The heating process may also induce the desorption of the amphiphilic molecules from the surface of the CNTs, leading to the aggregation of the CNTs [26]. To overcome these problems, Xin and coworkers developed a nondestructive strategy to incorporate SWNTs into LLCs utilizing the spontaneous phase separation between a nonionic surfactant (n-dodecyl hexaoxyethylene glycol monoether, $C_{12}E_6$) and a hydrophilic polymer (poly(ethylene glycol), (PEG)) [27]. After phase separation, an upper phase contains hexagonal LLCs incorporated by SWNTs together with a bottom isotropic phase consisting of PEG (Figure 1A and B). The type of the LLC phase (hexagonal or lamellar phase) could be regulated by varying the ratio of PEG and $C_{12}E_6$. The quality of SWNTs/LLC composites was characterized by polarized microscopy (POM) observations (Figure 1C and D) and small-angle X-ray scattering (SAXS) measurements (Figure 1E and F). The d-spacing of the upper hexagonal phase was improved with increasing amount of SWNTs, which was consistent with the results obtained from POM observations.

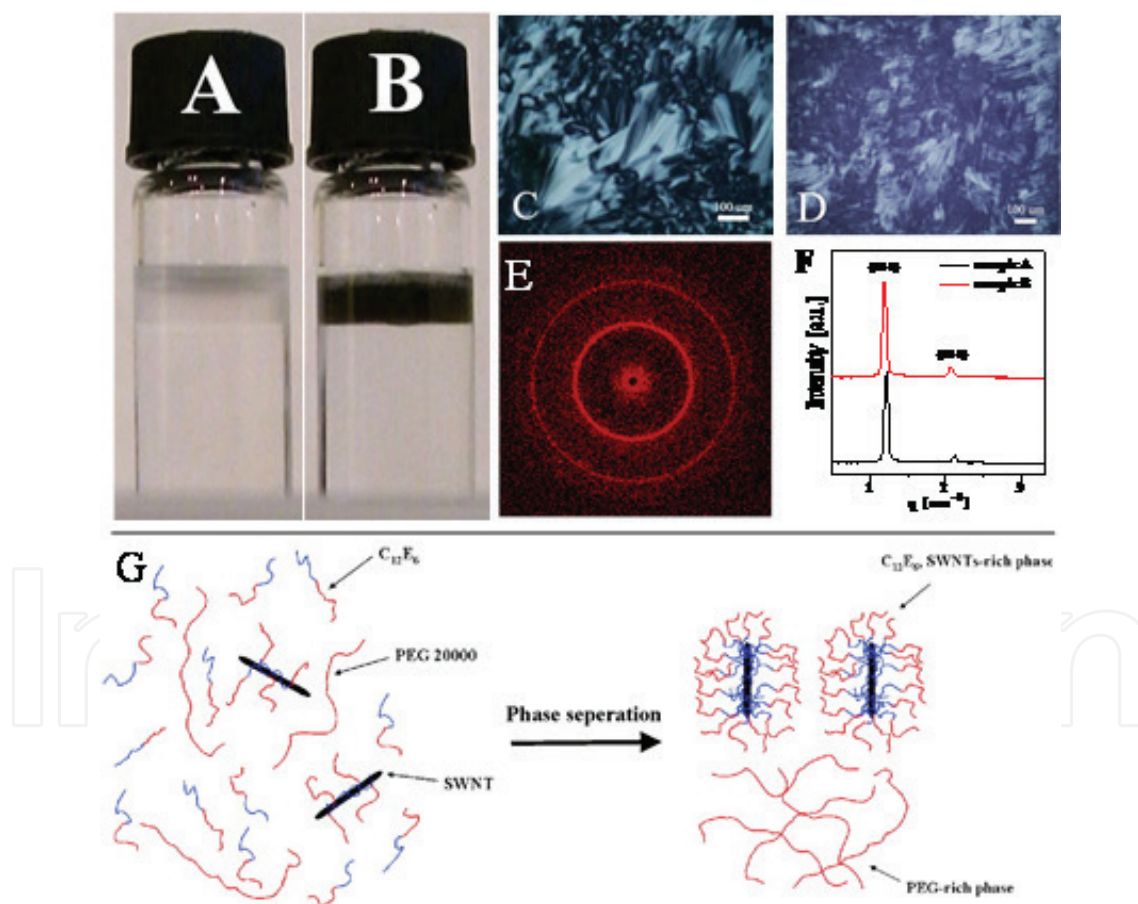


Figure 1. SWNTs embedded in the upper hexagonal phase formed by $C_{12}E_6$ (10 wt%) after phase separation induced by PEG 20,000 (20 wt%). The percent of SWNTs in the upper phase was calculated to be (A) 0 wt% and (B) 0.25 wt%. Corresponding polarized micrographs of the upper $C_{12}E_6$ hexagonal phases without (C) and with (D) incorporated SWNTs. (E) Small-angle diffraction rings of sample B and (F) SAXS results of SWNTs/LLC composites. (G) Schematic representation of the phase separation process in the four-component mixture of the surfactant $C_{12}E_6$, PEG 20,000, SWNTs, and water [27].

Next, the incorporation of CNTs into the LLC phase formed by n -dodecyl tetraethylene monoether ($C_{12}E_4$) through phase separation at the presence of PEG with different molecular weights has been systematically studied (**Figure 2**) [28]. The LLC/CNTs hybrid material maintained the lamellar organizations of the host LLCs according to POM observations and SAXS measurements. The increase of the d -spacing of the LLC/CNTs hybrid with increasing concentration of incorporated CNTs indicated that the CNTs have been successfully integrated within the layer of lamellar LLCs. UV-vis and Raman spectra further confirmed that CNTs have been incorporated into the LLC phase, which also revealed the alignment of CNTs in the LLC matrix. The mechanical strength of the hybrid material has also been improved after the introduction of CNTs.

Furthermore, the LLCs formed by ionic surfactants such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) have also been selected as the host matrix for SWNTs incorporation. In these cases, polyelectrolytes such as poly(sodium styrenesulfonate) (PSS) or poly(diallyldimethylammonium chloride) (PDADMAC) instead of PEG were utilized to induce phase separation (**Figure 3**) [29]. The final concentration of the SWNTs in the upper LLC phase was increased a few times compared with that in the initial aqueous dispersion. Thus, it can be concluded that incorporation of SWNTs into LLC by phase separation method provides a practical way to achieve highly concentrated SWNTs aqueous

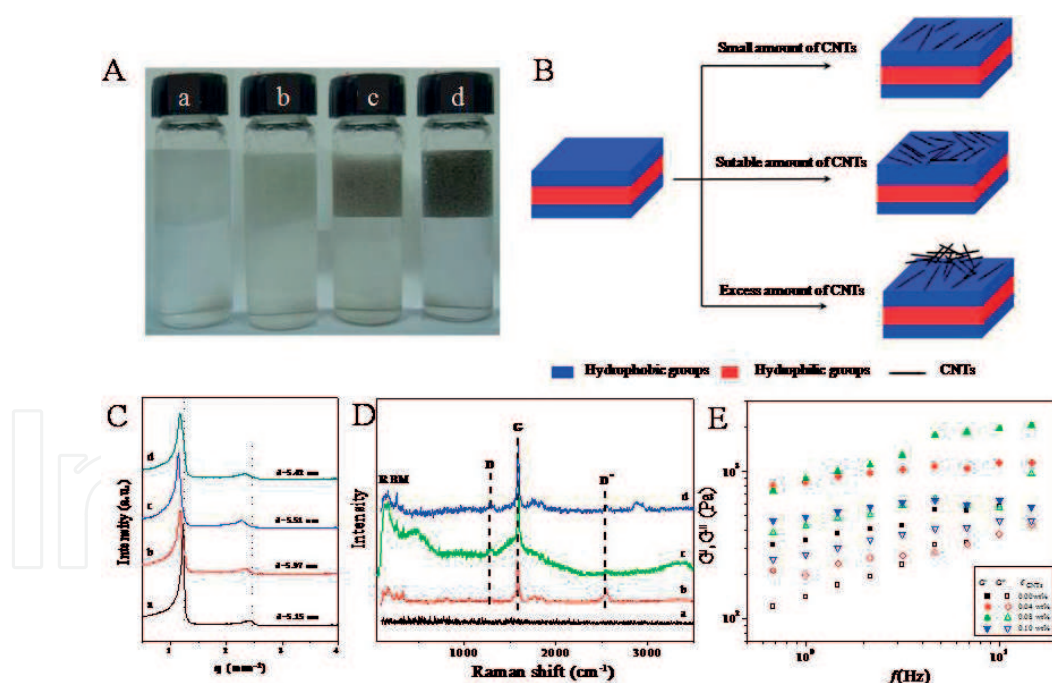


Figure 2. (A) CNTs embedded in the upper LLC phase formed by $C_{12}E_4$ (10 wt%) after phase separation induced by PEG 20,000 (20 wt%). (B) Schematic illustrations of the states of LLC/CNTs composites as a function of the concentration of incorporated CNTs in the upper LLC phase: (a) 0, (b) 0.04 wt%, (c) 0.08 wt% and (d) 0.10 wt%. (C) SAXS results of LLC/CNTs composites as a function of the concentration of incorporated CNTs in the upper LLC phase. (D) Raman spectra excited at 1064 nm of (a) pure $C_{12}E_4$ LLC, (b) the raw CNTs, (c) 0.05 wt% CNTs dispersed in 10 mL of 0.1 wt% $C_{12}E_4$ and (d) $C_{12}E_4$ LLC/CNTs composites. (E) Rheological results for LLC/CNTs composites with increasing concentration of CNTs [28].

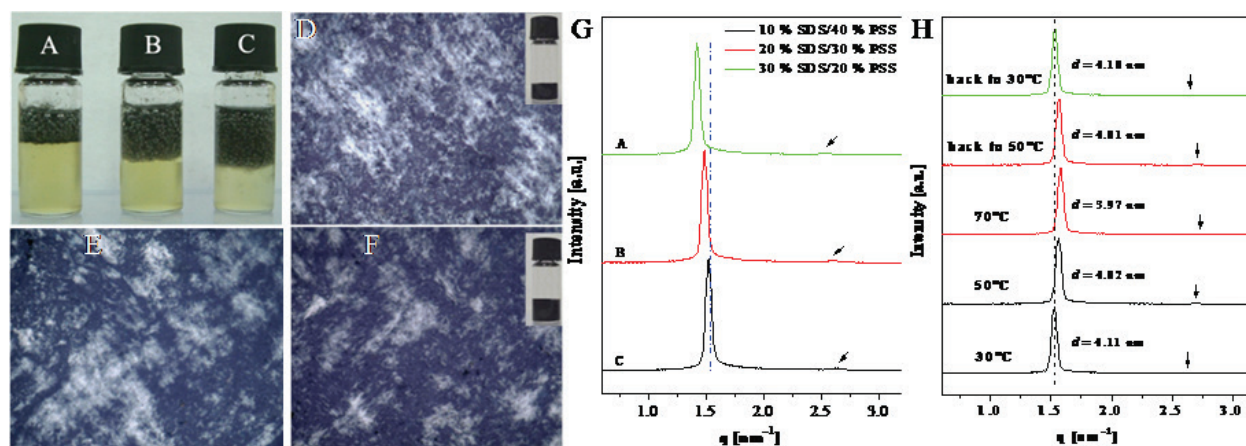


Figure 3. (A–C) Photographs of three typical samples of SWNTs/SDS/PSS/H₂O system after phase separation. (D–F) Corresponding polarized micrographs of the upper SWNTs/LLC hybrids. The weight percent of SDS and PSS to water are 10 wt%/40 wt% (D), 20 wt%/30 wt% (E), and 30 wt%/20 wt% (F). (G) SAXS results of the three typical samples of A–C. (H) SAXS results of one typical sample of SWNTs in CTAB/LLC as a function of temperature. The weight fractions of CTAB and PDADMAC to water are 20 and 15 wt%, respectively [29].

dispersion. Moreover, it is surprising to find the stability of SWNTs/LLC hybrids fabricated from ionic surfactants is much better than those prepared from nonionic surfactants, which indicates that the SWNTs/LLC hybrids prepared by the combination of ionic surfactant/polyelectrolyte may find potential applications at higher temperatures.

CNTs possess hollow lumens with diameters of a few to hundred nanometers, which are an ideal geometry for drug transport and delivery. However, CNTs are observed to exhibit weak infrared emissions. For diagnosis, the nanotubes must be functionalized with spectroscopically characteristic fluorescent dyes [30]. Xin and coworkers fabricated a luminescent CNTs-based hybrid material by anchoring lanthanide complexes (Eu or Tb) onto the surfaces of multi-walled CNTs (MWNTs) (**Figure 4A**). UV-vis measurements was used to demonstrate the successful coupling of Eu(III) complexes to MWCNTs (**Figure 4B**). Then, they incorporated the luminescent Eu-MWCNTs into the C₁₂E₆ LLC phase with a phase separation method using PEG [31]. The hexagonal phase of C₁₂E₆ was remained, and the Eu-MWCNTs were ordered in the hexagonal liquid crystal phase (**Figure 4C**). The introduction of the Eu-MWCNTs merely induced the swollen of the hexagonal lattice, and the luminescent property was retained (**Figure 4D**).

Cellulose nanocrystals (CNCs), obtained from hydrolysis of the cellulose, have attracted considerable attention due to their anisotropic properties and their self-assembly behavior [32]. Recently, Yuan and coworkers firstly fabricated the composite films with ordered oxidized CNTs (o-CNTs) using the lyotropic nematic liquid crystals (CNLCs), and the framework of the CNLCs can be retained in the final solid films (**Figure 5**) [33]. The randomly oriented o-CNTs in the aqueous dispersion were aligned orderly due to the confinement of the liquid crystal matrix of CNCs. The composite films were endowed with the anisotropic conductivity with the help of ordered arrangement of o-CNTs and the anisotropy of the CNLCs. Their work provides a new approach of fabricating LCs/CNTs material with application in sensors and photoelectronics.

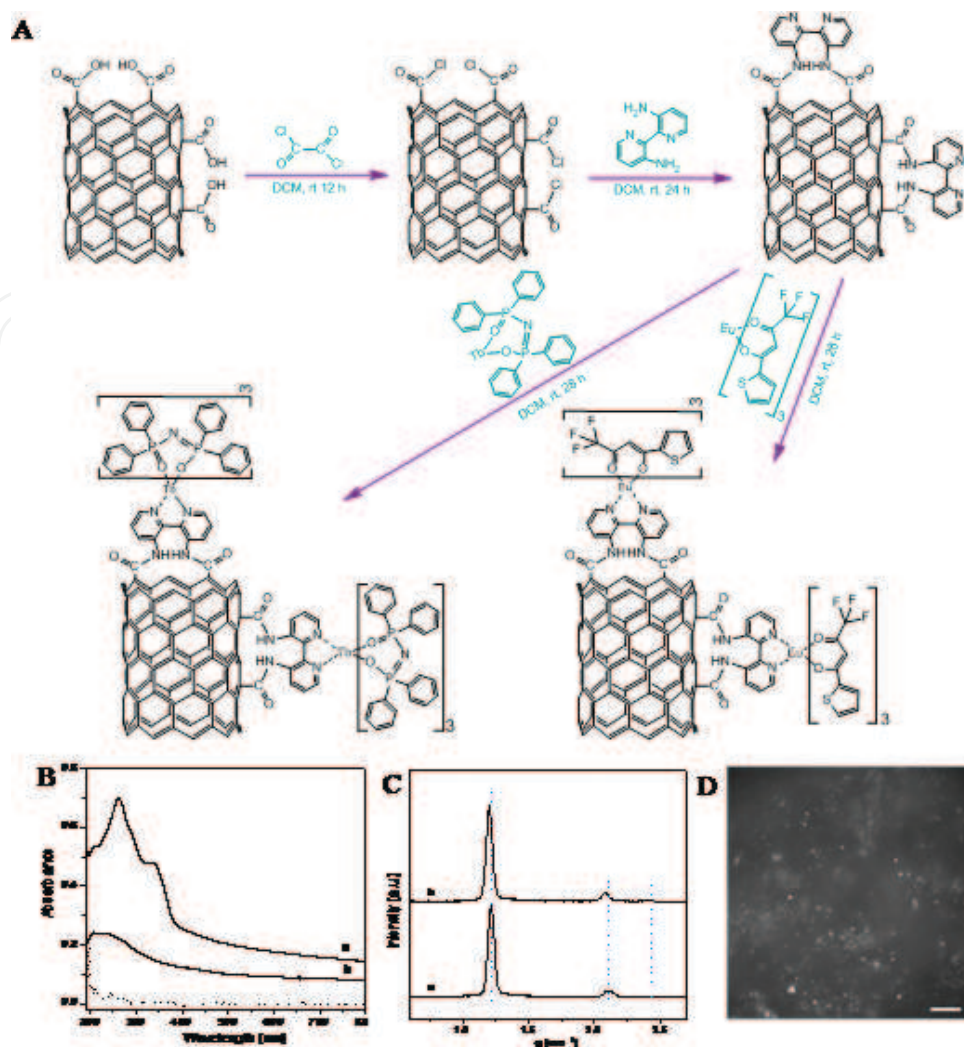


Figure 4. (A) Synthetic procedure for Eu(III) and Tb(III)-coupled MWNTs (Eu or Tb-MWNTs). (B) UV-vis spectra of Eu-MWNTs (a) and ligand-modified MWNTs (b) dispersed in 1 wt% SDS. (C) Typical SAXS results of the upper condensed phase formed by C_{12}E_6 at the presence of PEG without (a) and with (b) Eu-MWNTs incorporated. The dotted lines are guides for the eyes to highlight the peaks. (D) A typical image obtained under a fluorescence microscope for the upper C_{12}E_6 hexagonal phase incorporated with 0.1 wt% Eu-MWNTs [31].

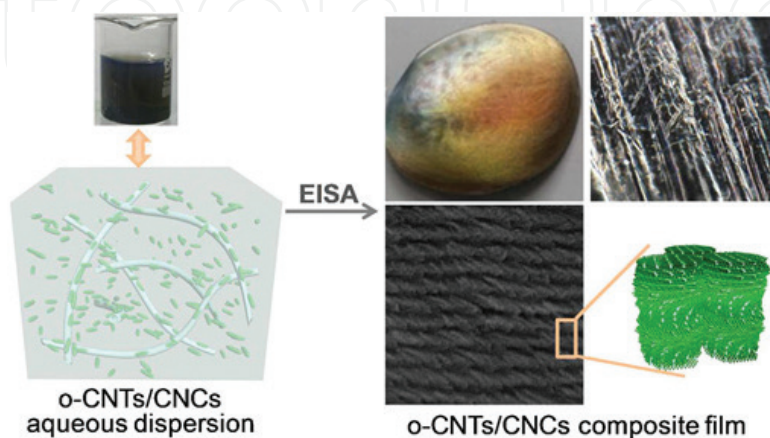


Figure 5. The composite films with ordered CNTs using the chiral nematic liquid crystals (CNLCs) prepared by the cellulose nanocrystals (CNCs) [33].

3. Graphene (or graphene oxide)/LLC hybrid materials

Apart from one-dimensional (1D) CNTs, the two-dimensional (2D) carbon-based nanomaterials, i.e., graphene nanosheets, have also attracted a great deal of attention. Graphene, a single-layer and 2D carbon lattice, is one of the most promising materials with great potential applications due to its unique mechanical, quantum, and electrical properties [34–36]. The properties of superior dispersibility, stability, and processability in water also promote the exploration of graphene assemblies [37]. For example, Behabtu et al. reported the formation of LC phase of graphene at high concentrations ($\sim 20\text{--}30\text{ mg ml}^{-1}$) [38]. The graphite can be spontaneously exfoliated into single-layer graphene in chlorosulphonic acid without the need for surfactant stabilization and sonication. The LC phases are promising for functionalization, and for scalable manufacturing of nanocomposites, films, coatings, and high-performance fibers. The oxidized derivative of graphene, i.e., graphene oxide (GO), is a good hydrophilic and biocompatible material. Due to the presence of a variety of hydroxyl, epoxide, and carbonyl groups at their basal planes and edges, GO has been regarded as the most important substitute for graphene to form stable colloidal carbon-based composites in water and polar organic solvents [39–43]. Kim et al. prepared nematic LCs of exfoliated graphene oxide by a modified Hummer's method [44]. The ionic strength and pH are the influencing factors on the stability of the LCs. They also successfully tuned the macroscopic orientation of GO in LCs by applying a magnetic field (**Figure 6**). This method provided a viable route to engineering high-performance nanocomposites.

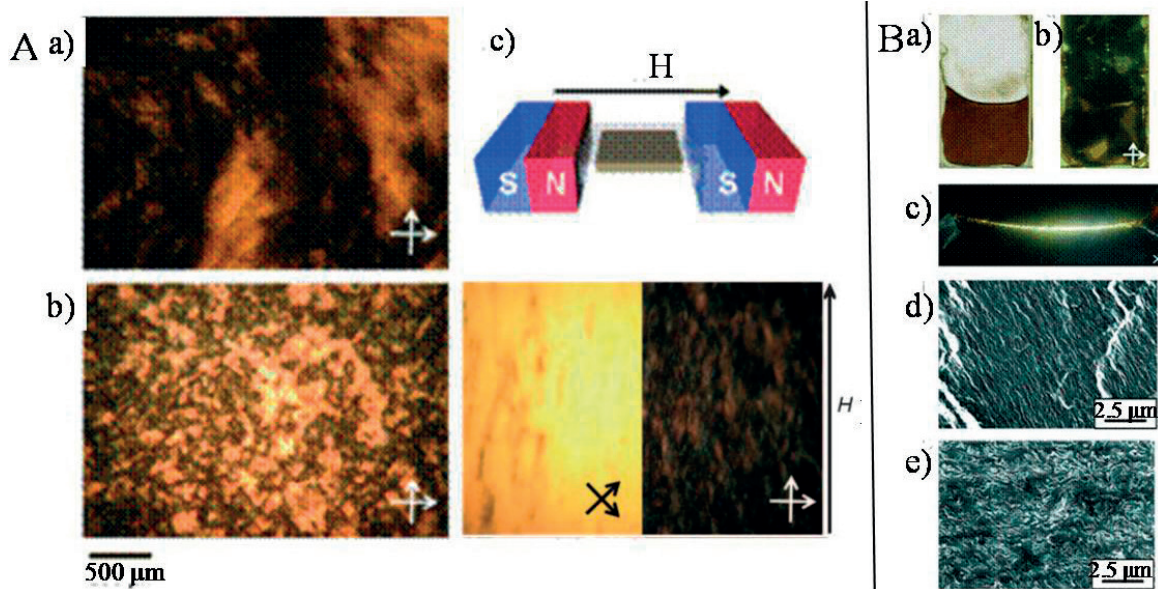


Figure 6. (A) Magnetic-field-induced alignment of graphene oxide liquid crystals. a) Shear-induced birefringent morphology formed after sample preparation. b) Nematic schlieren morphology formed about 3 h after sample preparation without any external field. c) Top: experimental scheme for magnetic field application; bottom: magnetic-field-induced highly aligned liquid-crystal texture. (B) Mechanical-deformation-induced alignment of PAA/graphene oxide composites. Water/PAA/graphene oxide three-component liquidcrystal mixtures: a) without and b) with crossed polarizers. c) Handdrawn gel composite fiber. The strong optical birefringence was caused by homogeneously dispersed, uniaxially oriented graphene oxide platelets. d) Highly aligned graphene oxide morphology along the fiber axis. e) Randomly oriented graphene oxide morphology in the fiber cross section [44].

LLC phases containing graphene and GO sheets have received considerable attention because of the new dimension to soft self-assembly science. A series of LLCs containing graphene and GO have been fabricated employing novel amphiphilic molecules, which achieved functional materials with enhanced properties, self-assembly, and alignment of graphene and GO [45, 46]. Pasquali et al. explored the lyotropic phase behavior of giant GO flakes in water with an order of magnitude higher than other works in 2011 [47]. Wallace and coworkers produced the GO LLC phase in a wide range of organic solvents (ethanol, acetone, tetrahydrofuran, and some other organic solvents) fully using the ultralarge GO sheets (**Figure 7A**) [48]. The GO LLC phase could be used to take the exploitation of organizing and aligning SWNTs through the addition of LC GO to the SWNT dispersions (**Figure 7B**). The presence of fine interband transitions of the UV/vis-near-IR spectra of the LC GO and LC GO-SWNT demonstrated that SWNT sizes have been preserved in the composite formulation (**Figure 7C**).

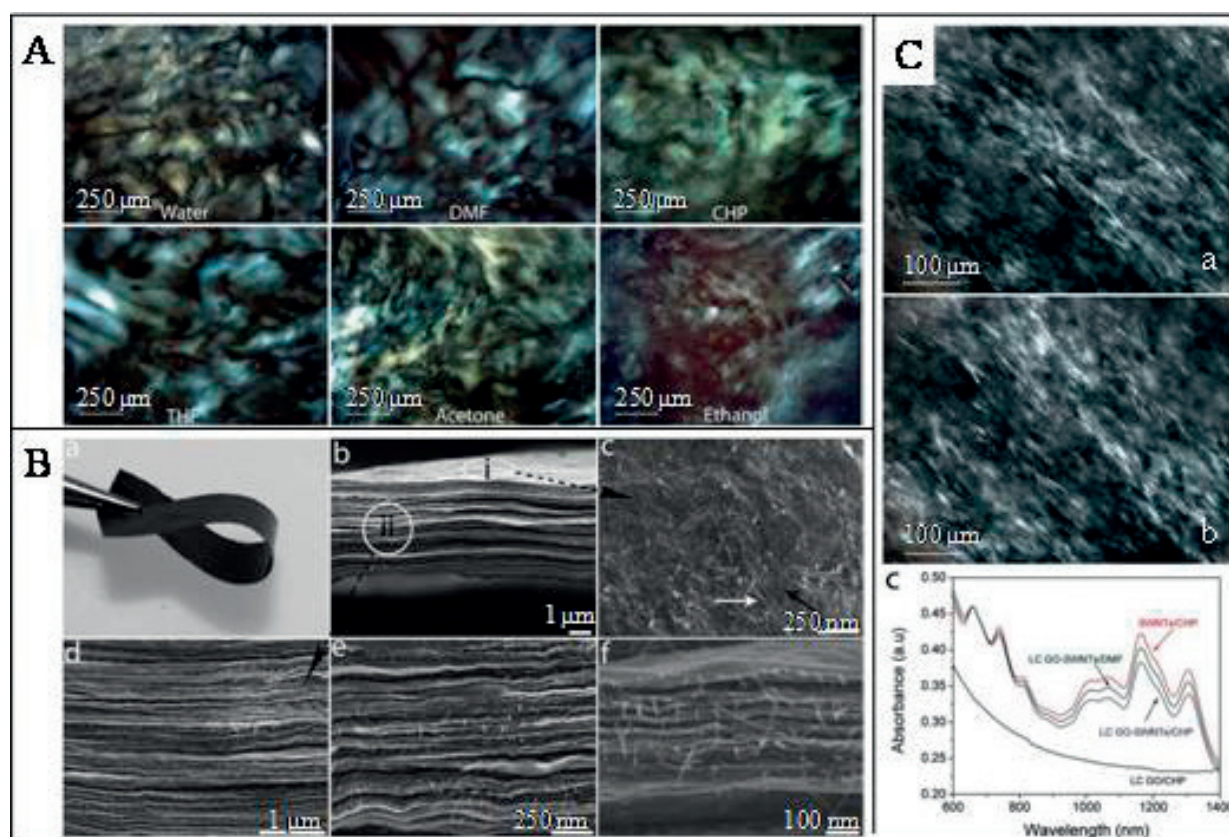


Figure 7. (A) Representative POM images of LC GO in various organic solvents at a concentration of 2.5 mg mL^{-1} . (B) (a) Representative photograph of a flexible free-standing paper of LC GO-SWNT made by cast drying method. (b) SEM image of the cross section of as-cast dried LC GO-SWNT paper. (c) SEM image of the surface of the layer-by-layer composite, which is marked as region (i) in (b). Some of the SWNTs are laid on the surface of the paper (white arrow), while others are placed between layers of GO sheets (black arrow). Transparency of the monolayer/few layers of GO sheets allows observing tube sites in different layers. (d-f) Cross section of composite paper at different magnifications (marked as (ii) in (b)) confirmed the self-oriented nature of the composite as well as maintaining SWNTs debundled after the fabrication of composite. (C) POM micrographs of LC GO-SWNTs/CHP (a), (b) LC GO-SWNTs/DMF. (c) UV-vis-near-IR spectra of SWNTs and LC GO dispersions before and after mixing together [48].

Xin and coworkers successfully incorporated graphene and GO into LLC matrix constructed by $C_{12}E_4$ (**Figure 8A and B**) [49]. Typical TEM images showed that graphene and GO were all fully exfoliated and well-dispersed in aqueous solutions, indicating that the carbon nanosheets can be efficiently stabilized by the steric repulsions created by $C_{12}E_4$ (**Figure 8C and D**). According to the polarized optical microscope (POM) and small-angle X-ray scattering (SAXS) results, all of the composites including graphene- $C_{12}E_4$ (**Figure 8E-G**) and graphene oxide- $C_{12}E_4$ (**Figure 8H and I**) are characteristic of lamellar structures. The strength of the composite could be enhanced by the addition of a small amount of well dispersed graphene and GO. A phase separation method was taken to demonstrate the difference between the interaction mechanisms of graphene and GO with $C_{12}E_4$ LLC because of the different nature of graphene and GO. The schematic illustration of graphene and GO incorporated into the $C_{12}E_4$ LLC phase is presented in **Figure 9**. The results indicated that the improved mechanical and electrical properties of the $C_{12}E_4$ LLC by graphene and GO facilitated the manipulation and processing of graphene and GO in nanotechnology, electrochemical and biochemical areas.

The graphene (or GO)/LLC matrix could be facily regulated by changing its composition, for example, the type of amphiphilic molecules. Following the above work, Xin and coworkers successfully incorporated GO into a hybrid LLC matrix constructed by the mixture of $C_{12}E_4$ and 1-dodecyl-3-methylimidazolium bromide ionic liquid ($C_{12}mimBr$) [50]. The GO was well-dispersed in the $C_{12}E_4/C_{12}mimBr$ hybrid LLC matrixes at room temperature according to POM observations and SAXS results, which indicated that GO/60 wt% $C_{12}E_4$ /10 wt% $C_{12}mimBr$ LLC composite is the lamellar phase and GO/10 wt% $C_{12}E_4$ /60 wt% $C_{12}mimBr$ LLC composite exhibits a hexagonal structure. GO could not only improve the mechanical properties, but also tune the phase state of hybrid LLC matrixes from lamellar to hexagonal state. The addition of large amounts of $C_{12}mimBr$ greatly increased the thermal stability of GO/ $C_{12}E_4$ / $C_{12}mimBr$ LLC

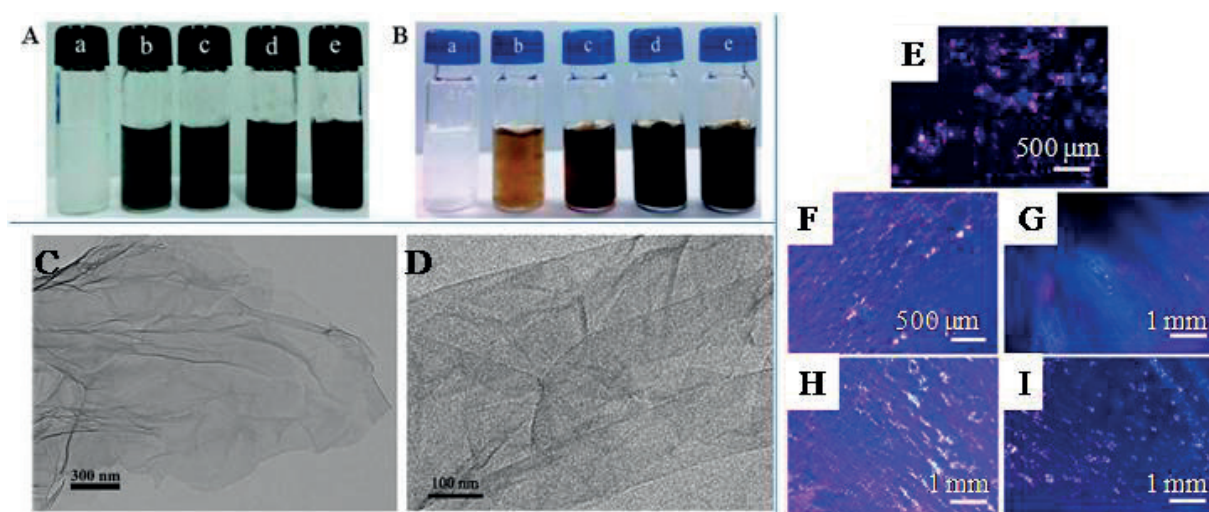


Figure 8. Graphene (A) and graphene oxide (B) incorporated into the LLC phase formed by 35 wt% $C_{12}E_4$. The weight percent of graphene and GO is 0 (a), 0.03 (b), 0.09 (c), 0.15 (d), 0.20 (e) mg mL⁻¹ in (A) and 0 (a), 0.1 (b), 0.5 (c), 1.0 (d) 1.5 (e) mg mL⁻¹ in (B), respectively. (C, D) Typical TEM images of graphene and GO dispersed in water. POM images for graphene- $C_{12}E_4$ (E-G) and GO- $C_{12}E_4$ (H, I) LLC composites [49].

and there was no obvious structural change during the heating or cooling process (**Figure 10**). **Figure 11** gives the schematic illustration of the formation of GO/C₁₂E₄/C₁₂mimBr lamellar and hexagonal LLC composites.

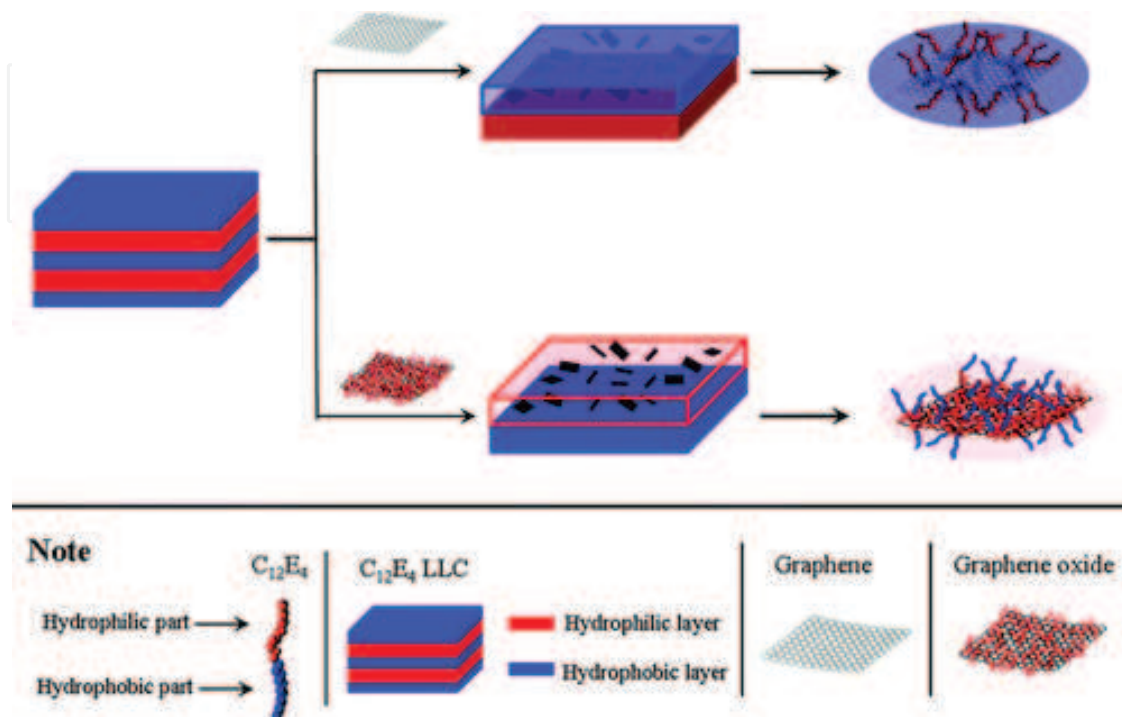


Figure 9. Schematic illustration of graphene and GO incorporated into the C₁₂E₄ LLC phase. Graphene incorporates into the hydrophobic layers of the C₁₂E₄ LLC phase while GO tends to stay in the hydrophilic layers [49].

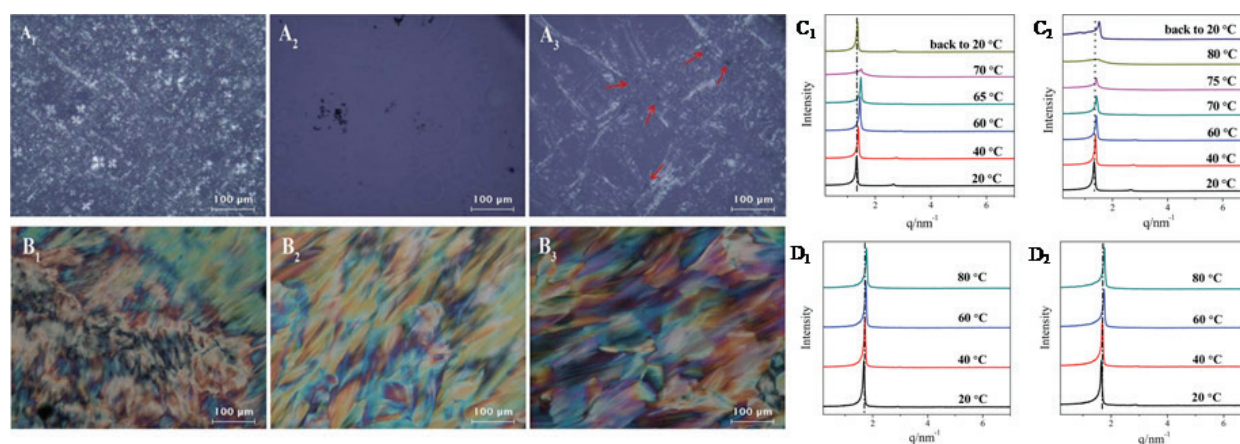


Figure 10. POM images of liquid crystal composites as the change of temperature, $c_{GO} = 0.3 \text{ mg mL}^{-1}$, (A) 60 wt% C₁₂E₄/10 wt% C₁₂mimBr and (B) 10 wt% C₁₂E₄/60 wt% C₁₂mimBr. The temperature is (A₁ and B₁) 20°C, (A₂) 80°C, (B₂) 90°C and (A₃ and B₃) back to 20°C from high temperature. The SAXS results of LLC composites: 60 wt% C₁₂E₄/10 wt% C₁₂mimBr (C₁ and C₂); 10 wt% C₁₂E₄/60 wt% C₁₂mimBr (D₁ and D₂). The concentration of GO is 0 mg mL⁻¹ (C₁ and D₁) and 0.3 mg mL⁻¹ (C₂ and D₂) [50].

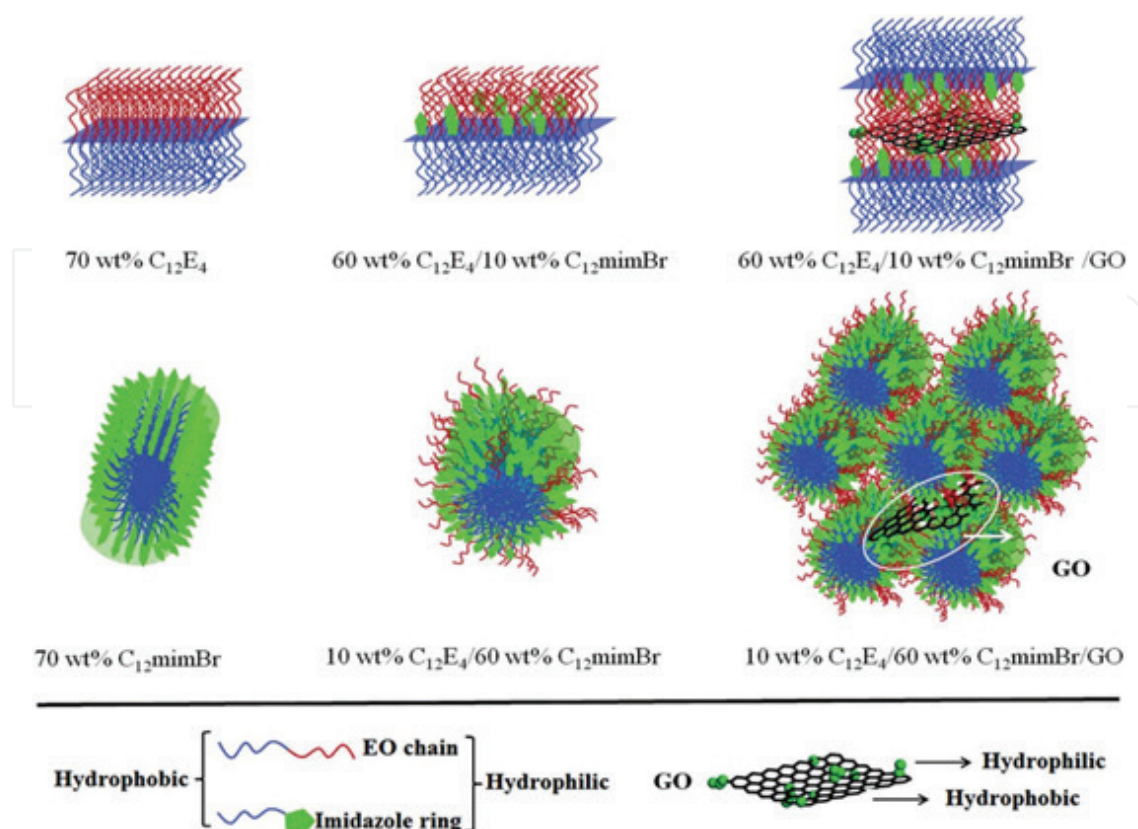


Figure 11. Schematic illustration of the formation of GO/C₁₂E₄/C₁₂mimBr lamellar and hexagonal LLC composites [50].

4. Manipulation of LLC behavior of amphiphilic molecules by biomolecules

Apart from varying the type of amphiphilic molecules, the structure and properties of LLC can also be tuned by changing the additives to the LLC composites. Much attention has been paid to study the effect of biomolecules to the amphiphilic molecules LLCs with new types of functions. The literatures have shown that LLCs with biomolecules are useful for biological sensing and NMR RDC analysis [51]. Clark et al. have reported the formation of LLC phases of double-stranded DNA and RNA oligomers in water [52, 53]. The formation of LLC by hydrated duplex DNA plays a crucial role in deciphering the structure of DNA and enables the alignment of the DNA chains.

Amino acids are the basic units of proteins and peptides, which give the proteins and peptides specific molecular structure features [54]. Oligomers of the β -amino acids (β -peptide), a second class of biomolecules, can aggregate into diverse nanostructures [55, 56]. Gellman et al. investigated the effect of β -peptide modifications on the propensity of these helical molecules to form LLC in water [57]. The side chain of β -peptides displayed an important role to well-defined nanostructures and rules for creating LLC phases, which can also endow

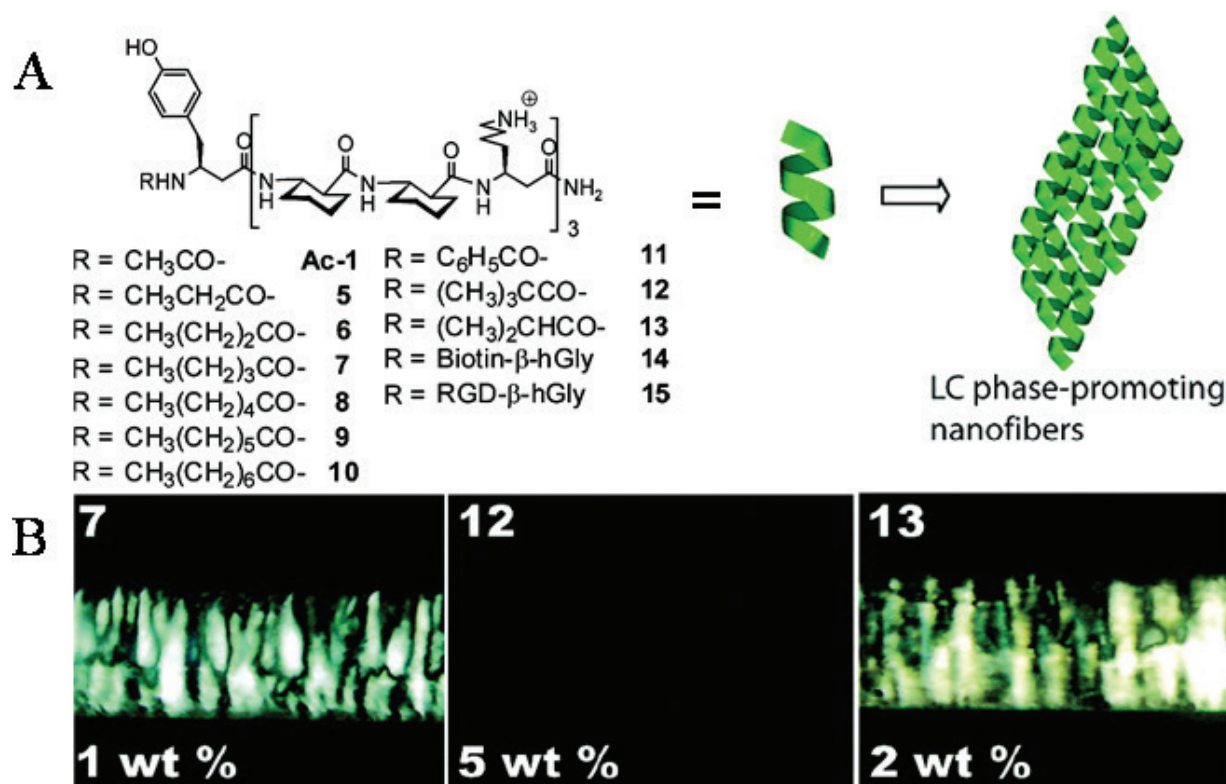


Figure 12. (A) Acylated β -peptides containing hydrocarbon acyl tails, Ac-1 and 5-13, and biological recognition groups, 14 and 15. Model for the multistate assembly of amphiphilic β -peptides, progressing of formation of nanofibers directly from monomeric β -peptides. (B) Optical micrographs of aqueous solutions of acylated β -peptides 7, 12, and 13 between crossed polarizers [57].

the LLCs useful properties (**Figure 12**). They also demonstrated that LLC formed by the modified β -peptides was useful as NMR alignment media to small organic molecules in aqueous solution and provided initial evidence for enantiodiscrimination [58].

The interactions between the surfactants and amino acids have also been investigated, which is not only of fundamental important in theoretics but also practical in industrial applications [59–62]. Except for traditional surfactants, long-chain alkyl ionic liquids are special kinds of amphiphilic surfactant molecules which can also form LLC. Xin and coworkers systematically studied the effects of alkaline amino acids L-Arginine (L-Arg) and L-Lysine (L-Lys) on the LLC behavior of C₁₄mimBr. C₁₄mimBr/L-Arg system remained the hexagonal phases and merely led to the variation of the mechanical strength (**Figure 13A–F**) [63]. L-Lys could induce a transition of the C₁₄mimBr LLC phase to worm-like micelles (WLMs). The balance among electrostatic interaction, H-bond interaction, and hydrophobic interaction between amino acids, C₁₄mimBr and water contributes to the phase transition. The schematic illustrations for phase transition introduced by the amino acids are shown in **Figure 13G**. These changes can contribute to a better understanding of the effect of the additives on the influence of the structure and macroscopic properties of LLCs.

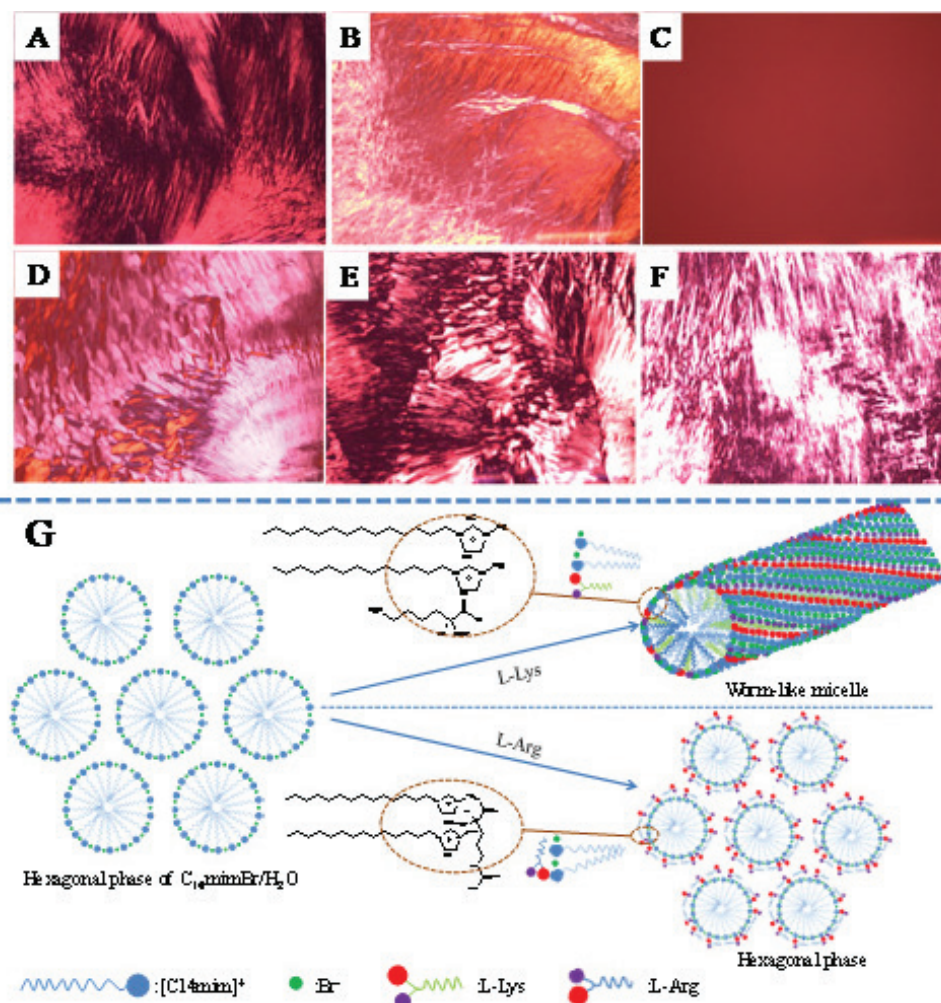


Figure 13. POM images (100 \times) for 38 wt% $C_{14}mimBr$ -amino acids mixtures with different water contents at room temperature. The amount of the amino acids is: (A) 0; (B) 1.0 wt% L-Lys; (C) 5.0 wt% L-Lys; (D) 2.5 wt% L-Arg; (E) 5 wt% L-Arg; and (F) 7.5 wt% L-Arg. (G) Schematic illustrations of the phase transition between LLCs and WLMs by the L-Arg and L-Lys [63].

5. Conclusion and outlook

In summary, LCs, with their fluidity as well as long-range organization, represent an interesting and novel route for realizing functional composites. In the ordered LLC phases, the molecules tend to align along a common direction, forming orientationally ordered macroscopic domains which can provide a way to control the orientation of guest materials. Thus, different kinds of additives including SWNTs, MWNTs, graphene, GO, and biomolecules can be incorporated into LLCs, which will induce various different properties of LLCs. The mechanical, electric, physicochemical properties of the hybrid LLC materials will be improved largely after the incorporation, which will open the door for the applications of these interesting hybrid materials in nanotechnology, electrochemical and biochemical areas.

Acknowledgements

We gratefully acknowledge the financial support obtained from the National Natural Science Foundation of China (21476129, 21203109) and Young Scholars Program of Shandong University (2016WLJH20).

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