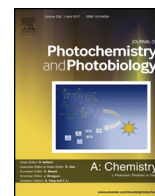




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Invited paper

Transfer of molecular chirality to spiral nanostructure in the interfacial mixed amphiphilic diacetylene/histidine monolayers via in situ topochemical photopolymerization

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ABSTRACT

The photopolymerization in the monolayers consisted of an equivalent mixture of 10, 12-pentacosadiynoic acid and amphiphilic histidine derivatives L-HC18 or D-HC18 has been investigated. It is found that the diacetylene derivatives can be incorporated into the monolayer and polymerized to polydiacetylene (PDA) backbone with a red phase by in situ UV irradiation at the air/water interface. The chiral amphiphiles L-HC18 or D-HC18 can transfer the molecular chirality to PDA through the ordered alignments of the two components. AFM images of the transferred films further revealed the chiral nanostructures from PDA/L-HC18 or PDA/D-HC18. The topochemical polymerization of the mixed films at a low surface pressure as a function of time is carried out to characterize crimp behaviors from straight nanobelts to more curly bands even spiral nanostructures in a clockwise or anti-clockwise direction, in which the curling direction is depended on the molecular chirality of the two enantiomers. The research has well established the connection between molecular chirality and mesoscopic chirality using the Langmuir as well as Langmuir-Blodgett methods.

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1. Introduction

Chirality is a fascinating phenomenon in nature and appears at various hierarchical levels from molecular to supramolecular levels [1]. Compared to the molecule chirality resulting from an asymmetric arrangement of the atoms on a central carbon or along an axis, supramolecular chirality aroused from the non-symmetric arrangement of the molecules through a non-covalent bond such as $\pi - \pi$ stacking, hydrogen bonding, electrostatic interaction and van der Waals interactions [2]. Supramolecular chirality can be obtained through chiral component molecules, non-covalent interactions between chiral and achiral molecules, or symmetry breaking of achiral molecules [3–5]. During the formation of the chiral supramolecular system, an important issue is how a molecular chirality can be transferred into an assemblies and

how the supramolecular chirality can be expressed at a supramolecular level?

Polydiacetylene (PDA) has been extensively investigated with excellent optical, electrical, and sensing properties, where well-aligned diacetylene monomers can undergo 1,4-photopolymerization labeled as topochemical photoreaction to form conjugate polymer with alternating ene-yne backbone structure [6,7]. PDAs also show two main phases like blue ($\lambda \sim 640$ nm) and red ($\lambda \sim 530$ nm) phases. Moreover, the blue phase can change into the red phase upon external stimulus, such as pH [8], temperature [9], mechanical stress [10] or metal-ligand interaction [11,12] and so on. Thus, PDAs have been regarded as potential chemosensors and biological sensing units [13–17]. Since the topochemical photopolymerization of DAs requires a high ordered arrangement of diacetylene units, interfacial assembly through the Langmuir and Langmuir-Blodgett (LB) technique can control molecular orientation and packing in a two-dimensional manner and further facilitates photopolymerization [18–20]. The introduction of chirality into polydiacetylene (PDA) is expected to fruit novel organic devices with special electro-magnetic functions [21–24]. We have reported that chiral PDA LB films can be prepared from

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achiral diacetylene monomers by UV irradiation [25]. However, the circular dichroism (CD) signals of above prepared PDA films were very weak and the direction of the signals was not determined. Here, we tried to introduce the chiral component to control the supramolecular chirality of the PDA. Previously, we have investigated that the chaperone gelator L- or D-HC18 could co-assemble with amino acids or naphthoic acids and form stable supramolecular gel through the interaction between imidazole and carboxylic groups [26,27]. The amphiphilic L/D- histidine ester derivatives were mixed with some diacetylene (DA) monomers and the fabricated organogels (Scheme 1) could undergo topochemical polymerization, displaying not only colorimetric and fluorogenic detection capability but also chiroptical sensing property [28]. Herein, we focused on the polymerization of diacetylene and L- or D-HC18 on the air/water interfaces to see if the chirality transfer can occur in monolayers.

We have found that the diacetylene/L- or D-HC18 mixed film really showed chirality transfer from L- or D-HC18 to achiral polydiacetylenes. In addition, chiral nanostructures were obtained in the monolayers. The topochemical polymerization at low surface pressure as a function of time further revealed interfacial crimp behaviors from straight nanobelts to more curly bands in clockwise or anti-clockwise direction differing from two chiral enantiomers. Thus, we have well realized the construction of PDA systems which bridge the connection between molecule chirality and mesoscopic chirality using the Langmuir as well as Langmuir-Blodgett technique.

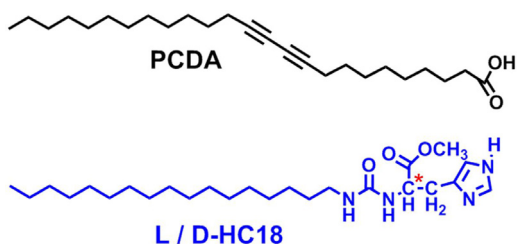
2. Experiment

2.1. Materials

All the starting materials and solvents were obtained from commercial suppliers and used as received. 10,12-pentacosadiynoic acid (PCDA) was purchased from TCI. The amphiphilic compound (L/D-HC18) containing L- or D- histidine group and long alkyl chain were synthesized by following the method previously reported by our group [26].

2.2. Characterization

The surface pressure-area (π -A) isotherm was recorded on a computer-controlled KSV-minitrough system with a surface area of 273 cm² (L364 mm, W75 mm) (KSV Instruments, Helsinki, Finland). The UV/Vis and CD spectra for the samples before or after photopolymerization were measured with JASCO UV-550 and JASCO J-810 spectrophotometers, respectively. The parameter setting: scan speed, 1000 nm/min; bandwidth, 1 nm; data pitch, 0.5 nm. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-660 plus spectrophotometer with a wavenumber resolution of 4 cm⁻¹ at room temperature (scanning velocity, 10 kHz; acquisition time, 52.77s; an average of 64 scans in the wavenumber ranging from 1400 cm⁻¹ to 3600 cm⁻¹). The atomic



Scheme 1. Molecular structures of amphiphilic diacetylene monomer (PCDA) and L- or D- histidine ester derivative (L/D-HC18).

force microscope (AFM) was performed to analyze the morphologies of the samples by using ScanAsyst mode (Nanoscope IIIa, Digital Instruments) with a pyramidal Si3N4 tip.

2.3. Langmuir–Blodgett films

The mixed PCDA/L or D-HC18 (5×10^{-4} mol/L, 1:1), the pure PCDA (5×10^{-4} mol/L) and L- or D- HC18 (5×10^{-4} mol/L) were all prepared in a mixture of chloroform and methanol with a ratio of 10:1 (v/v) which was used as co-spreading solvent. The Milli-Q water (18.2 M Ω -cm) was used as a subphase. The subphase temperature was 20 °C with pH 7. A few microliters of the solution were spreading onto the air/liquid interface. After 20 min for solvent evaporation, the surface pressure-molecular area (π -A) isotherm was recorded by compressing the floating film with a rate of 5 cm². min⁻¹. After interfacial photopolymerization of PCDA/L or D-HC18 mixed films at a selected surface pressure, the polymeric films were transferred onto freshly cleaved mica by a vertical dipping method with the lifting speed of 1 mmmin⁻¹. Then, the mixed films were subsequently transferred onto clean quartz substrate by a horizontal lifting method for UV/Vis spectra and onto the CaF2 substrate for FT-IR spectra.

2.4. Interfacial photopolymerization

For interfacial Photopolymerization, a UV lamp ($\lambda = 254$ nm, W = 30 W) was set on top of the trough, keeping a distance of 10 cm from the floating film with a surface pressure equilibrated at 1 mN. m⁻¹, 5 mN.m⁻¹, 10 mN.m⁻¹, 30 mN.m⁻¹, respectively. In order to monitor the polymerization process, the samples were irradiated for different time intervals and after the UV irradiation, the mixed films were transferred by vertical or horizontal lifting method onto the substrates and then dried in the clean room.

3. Results and discussion

3.1. Surface Pressure–Area isotherms

Surface pressure-area (π -A) isotherms of the PCDA/L-HC18 (1:1) and PCDA/D-HC18(1:1) mixed films on the water subphase were shown in Fig. 1, as well as pure components PCDA and L-HC18. The spreading film of pure PCDA exhibited a phase transition point at 20 mN.m⁻¹ and the limiting areas extrapolating from the linear part of the isotherm to zero surface pressure was ca. 0.22 nm²/molecule, corresponding to a tight packing of PCDA monomers. Upon overcompression of the film, a solid phase formed with the limiting molecular area of 0.08 nm², showing that the formation of

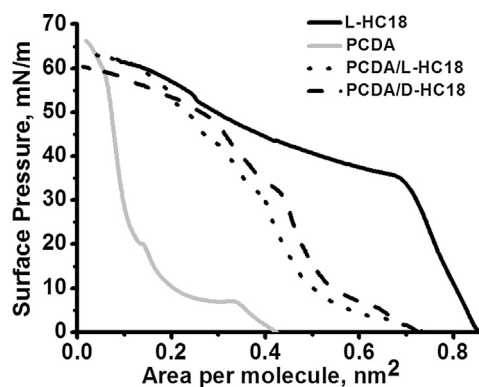


Fig. 1. Surface pressure–area (π -A) isotherms of pure L-HC18 (black line), pure PCDA (green line), and PCDA/L-HC18 = 1:1 (red line), PCDA/D-HC18 = 1:1 (blue line) mixed films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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