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Additive-stabilized hexagonally ordered mixed lyotropic liquid crystal

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Abstract

A strategy for preparing mixed lyotropic liquid crystals (LLCs) possessing a stable 2-D hexagonal mesostructure is demonstrated, which can be controlled easily and reproducibly through the use of both hydrophobic dopings and inorganic cations serving as additives. By using small molecules such as LiCl and anthracene, respectively, the cylindrical micelles of mixed amphiphiles can spontaneously assemble into 2-D hexagonal mesophase. This kind of mixed amphiphiles may be used as stable templates for synthesis of templated nanomaterials.

Keywords: Lyotropic liquid crystal; Mixed surfactants; Hexagonal; Mesostructure; Self-assembly

1. Introduction

The use of cylindrical micelles of surfactants in the synthesis of templated ordered nanomaterials is currently an active area of material researches, because resulting products such as mesoporous and nanotubular materials are of interest for potential applications in catalysts, molecular sieves, batteries, fuel cells and electronics. A key of the formation of ordered mesostructured solids generally requires an ordered self-assembling mesophase built from cylindrical micelles as a template such as 2-dimensional (2-D) hexagonal cylinder assemblies where the hydrophobic alkyl chains are gathered in the center of the cylinders and the hydrophilic groups are in contact with the continuous aqueous region that lies between the cylinders [1–16]. Among a variety of self-assembling templates, direct lyotropic liquid crystal (LLC) with high surfactant concentration (>30 wt.%) [7–16] has advanced the techniques for the synthesis of ordered mesostructured materials that directly reproduce dimensions and symmetry of the ordered LLC assemblies serving as the template.

Polyoxyethylene alkyl amphiphile $C_nH_{2n\pm1}$–$(CH_2CH_2O)_mOH$ (or C_nEO_m) non-ionic surfactants, comprised of a hydrophobic alkane $C_nH_{2n\pm1}$ tail and a hydrophilic oligo (ethylene oxide) $(CH_2CH_2O)_m$ head group (Scheme 1), represent a class of self-assembling LLC system that can form 2-D hexagonal LLC. Utilizing 2-D hexagonal LLC mesophase as a template for the syntheses of ordered mesoporous structures involves the synthesis of a self-supporting LLC nanocomposite, consisting of 2-D hexagonal amphiphilic template and an aqueous solution of the inorganic precursors that remain in the hydrophilic segments of the amphiphile, and post-treatment such as heat-treatment [7] or chemical reduction [8–13]. For successful direct templating processing of the mesostructured materials, the template is required to possess three necessary conditions to define the synthesis as direct templating. First of all, the template would be controlled in mesophase and dimension; then, it is necessary to prove that the temperature and composition of the inorganic precursors do not disrupt the long-distance order of the LLC; thirdly, the ordered mesostructure in the LLC paste should be stable in air over a relatively long period in order to preserve its original structure at all stages of templating processes. Furthermore, in view of controlling the dimension of the template, one of the important advantage of direct LLC template is that it is possible to exploit a mixture of the amphiphiles with the different type and relative length of the respective segments to construct micelles with a larger diameter than are achievable in single amphiphile, so as to produce larger pore size in the templated

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Polyoxyethylene (10) oleyl ether

Polyoxyethylene alkyl amphiphiles: C_nEO_m

Scheme 1. Amphiphiles.

materials. For example, recently our group synthesized noble metal nanotubes of 3 nm diameter using 2-D hexagonal mesophase of mixed LLC as a template [17], whereas the pores of not more than 2 nm in diameter had been obtained through using single component LLC [9]. It is expected that the control in nature and dimensions of the mesostructured LLC template through mixing some amphiphiles with different natures provides us with a powerful method for obtaining controlled nanostructures. However, poly (oxyethylene oxide)–alkyl amphiphiles can form various LLC mesophases including 2-D normal topology hexagonally (H_I), normal topology cubic (Ia3d) and lamellar (Lα) phases in water [14]. A main drawback of the C_nEO_m surfactant is that the mesophases can be manifold and unstable because the LLC mesophase is considerably sensitive to ambient conditions including temperature, reaction time, concentration, and composition of the parent solution, largely due to a rich polymorphism of the LLCs. The constrained synthesizing processing apparently limits the degree of conversion of the LLC to 2-D hexagonal phase, imparting different mesophases than the original ones when it is exposed in air. The stability of the LLC mesophase in air is so poor that its mesostructure changed just during XRD measurements. Particularly when LLC is used to construct the ordered mesostructured LLC nanocomposite with the metal sources such as H_2PtCl_6 for synthesizing mesoporous metals, subsequent electrochemical or chemical reduction of metal salts usually destroys most of the ordered mesostructure due to disruption from reduction reaction, leading to a low yield of mesostructured metal and poor reproducibility.

We have sought to develop a more stable 2-D hexagonal mixed LLC system as a template for potential application in synthesizing the mesoporous or nanotubular metals with a high yield. Because the geometry of LLC mesophase depends strongly upon the shape of the amphiphiles [14], mixing amphiphiles with different natures might serve as a means of modulating the hydrophilic headgroup and consequently the internal dimensions of the micelles. An important approach to constructing cylindrical micelles and stabilizing the original mesostructure is the introduction of hydrophobic agents into hydrophobic core of the micelles, and metal cations into the headgroup to open up new possibilities for designing stable 2-D hexagonal LLC assemblies. Incorporation of a small molecule into the different segments of the amphiphiles will modify the geometry and chemical stability of the self-assembling domains. Although such additives are ubiquitous in the polymer, little work has been substantially explored for their application in constructing mixed LLC templates to date. In this work, we demonstrate a strategy for preparing mixed LLC with a stable 2-D hexagonal mesostructure that can be controlled easily and reproducibly through the use of both hydrophobic dopings and inorganic cations serving as additives. Through such an approach, we have constructed a 2-D hexagonal nanocomposite consisting of LLC template and metal salts. The method described here is novel in three respects. First, different amphiphiles with various lengths of hydrophilic chains are used to modulate the area size and length of hydrophilic headgroups. Second, the hydrophobic agencies as monomer in the LLC are locked in the hydrophobic cores, leading to a stable 2-D hexagonal phase. Third, the metal cations are distributed into the hydrophilic headgroup to enhance the 2-D hexagonal mesostructure.

2. Experimental

All of the chemical reagents were purchased from commercial companies and used as supplied by the manufacturers. In a typical synthesis, a mixture of $C_{18}H_{35}EO_{10}$, $C_{16}H_{33}EO_{10}$, anthracene, H_2O, LiCl and H_2PtCl_6 in a 3:1:0.04:4:1:3 weight ratio was stirred at 80 °C in a sealed bottle, then cooled to 25 °C. The resulting gel was aged at room temperature (25 °C) for 3 days, during which the LLC relaxed enough to arrive at an equilibrium state. The polarized optical micrographs (POM) were recorded in a transmittance mode on an Olympus BX50 polarizing microscope with a micro-warm stage by using convergent white light between parallel and crossed polarizers. Small-angle X-ray diffraction (SXRD) patterns were measured in a reflection mode using Cu Kα radiation. All of the SXRD measurements and POM observations were conducted in the air.

3. Results and discussion

A variety of the C_nEO_m amphophile mixtures were prepared in order to study the liquid-crystalline behavior of the mixed amphiphiles in the presence of water. Two or three of the C_nEO_m amphiphiles were mixed with water at 80 °C in the form of fluid

Table 1
Studied mixtures of amphiphiles and their mesostructure

Mixed $C_nH_{2n\vee1}EO_m$	Mesostructure
$C_{16}H_{33}EO_{10}+C_{16}H_{33}EO_{20}$	Lamellar
$C_{18}H_{37}EO_{10}+C_{18}H_{37}EO_{20}$	Lamellar
$C_{16}H_{33}EO_{10}+C_{16}H_{33}EO_{20}+C_{16}H_{33}EO_2$	Lamellar
$C_{16}H_{33}EO_{10}+C_{18}H_{37}EO_{10}$	Lamellar
$C_{16}H_{33}EO_{10}+C_{18}H_{37}EO_{20}$	Lamellar
$C_{16}H_{33}EO_{10}+C_{18}H_{35}EO_{10}$	Lamellar, hexagonal, unknown
$C_{16}H_{33}EO_{10}+C_{18}H_{35}EO_{10}+$Anthracene	Hexagonal+lamellar
$C_{16}H_{33}EO_{10}+C_{18}H_{35}EO_{10}+$Anthracene+LiCl	Hexagonal
$C_{16}H_{33}EO_{10}+C_{18}H_{35}EO_{10}+$Anthracene+LiCl+$H_2PtCl_6$	Hexagonal
$C_{16}H_{33}EO_{20}+C_{18}H_{35}EO_{10}+$Anthracene+LiCl+$H_2PtCl_6$	Hexagonal
$C_{16}H_{33}EO_{10}+C_{18}H_{35}EO_{10}+C_{16}H_{33}EO_2+$Anthracene	Hexagonal