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Solid mesostructured polymer–surfactant films at the air–liquid interface

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ABSTRACT

Pioneering work by Edler et al. has spawned a new sub-set of mesostructured materials. These are solid, self-supporting films comprising surfactant micelles encased within polymer hydrogel; composite polymer–surfactant films can be grown spontaneously at the air–liquid interface and have defined and controllable mesostructures. Addition of siliconalkoxide to polymer–surfactant mixtures allows for the growth of mesostructured hybrid polymer–surfactant silica films that retain film geometry after calcinations and exhibit superior mechanical properties to typically brittle inorganic films. Growing films at the air–liquid interface provides a rapid and simple means to prepare ordered solid inorganic films, and to date the only method for generating mesostructured films thick enough (up to several hundred microns) to be removed from the interface. Applications of these films could range from catalysis to encapsulation of hydrophobic species and drug delivery. Film properties and mesostructures are sensitive to surfactant structure, polymer properties and polymer–surfactant phase behaviour: herein it will be shown how film mesostructure can be tailored by directing these parameters, and some interesting analogies will be drawn with more familiar mesostructured silica materials.

Contents

1. Introduction

Surfactant-templated mesostructured bulk materials have received much attention in the literature since the first reports of MCM-41 [1,2] and SBA [3] mesoporous silica [4–11]. However, less time and energy seem to be directed to non-inorganic or hybrid inorganic–organic materials, and seemingly even less to films. This review seeks to bring together some of the recent advances in self-assembled mesostructured polymer–surfactant materials. Particular focus shall be given to mesostructured films formed spontaneously at interfaces.

Interactions and general phenomena of polymer–surfactant systems in the bulk and at interfaces have been topics of intense interest for some time [12–15]. Meso-ordered polymer–surfactant materials were first reported around two decades ago [16]. Fairly recently polymer–surfactant complexes have been used as templates for porous silica [17–19]. However, in most of these studies powders have been prepared lacking regular morphologies, high degrees of long range order or hydrothermal stability. It is envisaged that films have the potential to fulfil this list of criteria, but have largely been over looked since they are often considered too brittle.

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Common strategies used to prepare mesostructured inorganic films rely on some form of solid support. For example in dip [20] and spin [21,22] coated films are templated from surfactants and precursor sols on a solid supports. Micelles form and then arrange on a solid substrate; evaporation of the solvent drives the self-assembly of organic and inorganic species. Layer-by-layer approaches have also been used to prepare inorganic films [23]. However, fabrication of films at the air–liquid interface, whereby surfactants (and polymers) spontaneously self-assemble and accumulate at the interface, is a more rapid and efficient means (and do not involve controlled humidity and temperature) to prepare self-supporting films with thicknesses spanning from nanometers to micrometres. Recent work has shown that under certain conditions it is possible to spontaneously form free-standing polymer–surfactant films with highly ordered mesostructures, at the air–liquid interface [24,25]. If a silica precursor is added to the polymer–surfactant mixture then a film may again form at the air–liquid interface, and removal of the surfactant template framework leaves behind micron-thick mesoporous polymer silica membranes [26]. Not only are the mesostructures retained (something seldom reported in silica films) but these films are also thicker and more robust than typically brittle inorganic films. Polymers may remain stable to calcination and so this also provides a very simple way of imparting functionality into the mesoporous silica walls.

This review will explore recent developments concerning polymer–surfactant films and polymer–surfactant–silica films formed primarily at air–liquid interfaces. Significantly these films show ordered mesostructures courtesy of their self assembly properties and phase behaviour with polymers. Efforts have been made, wherever possible, to illuminate how the fundamental science of polymer–surfactant systems can be related to fabrication of films. Indeed Section 1 is dedicated to giving a short account of the basic polymer–surfactant mixture behaviour which underpins much of what follows in the text. The synthetic procedures and conditions affecting film properties and mesostructure will also be discussed.

2. Polymer–surfactant interactions

When mixed with polymers, surfactants commonly form micelles at a concentration lower than the critical micelle concentration (CMC); this lower point is termed the critical association concentration (CAC). Surfactant monomers may bind to polymer chains at dilute surfactant concentrations, the high local concentration of surfactant monomers along the polymer chains allows micelles to be formed at very low concentrations. The formation of micelles on a polymer chain is often conceptualised as a *pearl necklace*, with discrete micelle aggregates bejewelling a random coiled polymer. At higher polymer concentrations, polymer chains can wrap around and 'encase' the micelles [27].

Mixtures of polymers and surfactants can phase separate, analogously to polymer–polymer systems. For two polymer systems, two types of phase separation can be distinguished, associative and segragative. Common sense dictates that a mixture of two polymers in a common solvent is expected to separate into two separate phases, owing to the weak entropic driving force of mixing of high molecular weight molecules (segragative separation).This is true if no attractive interaction exists between polymers. If, however, there are sufficiently strong attractive interactions between polymer pairs, associative phase separation can occur, where both polymers are collected in the same phase [28]. If in a polymer–surfactant pair, both polymer and surfactant are neutral, a segragative phase separation is observed for all but a few examples of polymer–surfactant pairs. (Associative phase separation can occur for less polar polymers at high temperatures). Introducing additional charge onto one of either the polymer or surfactant often prohibits phase separation.

Consider again a two-polymer system; there is a relatively small entropic penalty for combining large polymer molecules to a single phase. But now consider that one of the polymers is charged; in this case there is a much more undesirable entropic condition resulting from confining the far more numerous counter-ions to a single phase. Incidentally this is also a reason for the greater solubility of a polyelectrolyte compared to its neutral polymer equivalent. Ionic surfactants in most cases tend to associate with non-ionic polymers. Oppositely charged polyelectrolytes and surfactants will associate strongly through electrostatic interactions between oppositely charged functional groups. As such there will be an associative phase separation (also known as complex coacervation) and evolution of higher ordered structures of either a precipitate or concentrated liquid-phase droplets [14,28].

Coacervates are only able to aggregate and so form phase separated particles at certain polymer concentrations, and above a threshold polymer molecular weight, which together equate to the point of charge neutrality. Plotting polymer molecular weight against the ratio of polymer to surfactant (effectively the charge of the complex) yields a U-shaped relationship (Fig. 1) [29]. At low and high concentrations of polymer, polyelectrolyte–surfactant complexes are soluble. At low polymer concentrations micelles will only partially be coated by polyelectrolyte chains and so micelles of ionic surfactants will repel one another electrostatically. At high polymer concentrations micelles are well coated in polyelectrolyte chains. Excess charge originating from the polyelectrolye chains will act to repel neighbouring polyelectrolyte–surfactant complexes. Only at intermediate concentrations, at the point in which the polyelectrolyte charge exactly matches the micelle charge will neutral complexes form and aggregate [28,29].

3. Silica materials: analogies with polymer–surfactant systems

Any discussion on mesoporous/mesostructured materials must consider the nature of silica materials, which is by far the mostly widely researched mesostructured material. Beyond historical relevance, surfactant/silica systems provide interesting comparisons with long studied polymer–surfactant systems. Thus this section will bridge the apparent disparate nature between ordered surfactant templated silica films and purely organic polymer–surfactant films.

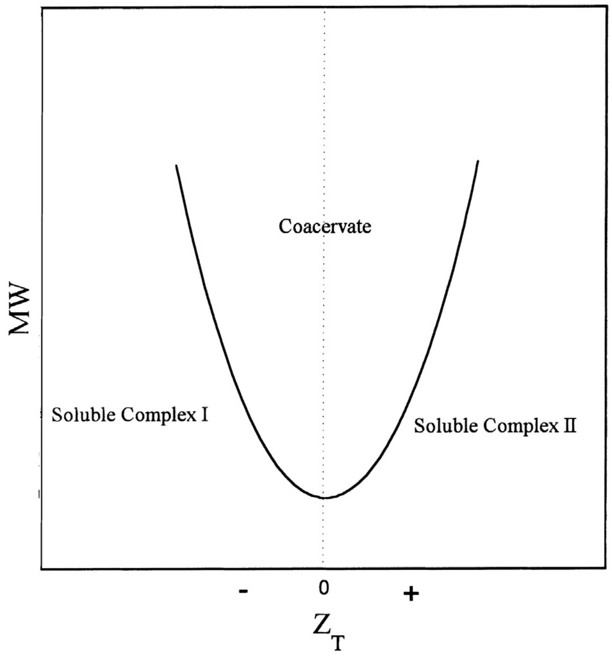

Fig. 1. Representation of the U-shaped phase behaviour for polymer–surfactant coacervate formation. MW is the molecular weight and Z_T is a measure of the net charge on the polymer–surfactant complex, i.e. polymer:surfactant ratio. Reprinted with permission from ref. [29]. Copyright 2001 American Chemical Society.

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