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Solid, Mesostructured Polymer-Surfactant Films Formed 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. Solid, self-supporting films comprising surfactant micelles encased with a polymer hydrogel- surfactant-polymer films, that can be grown spontaneously at the air-liquid interface. These films can be prepared with defined and controllable mesostructures. Addition of a siliconalkoxide to polymer-surfactant mixtures allowed for the growth of mesostructured hybrid polymer-surfactant silica films that retained film geometry after calcination and exhibit superior mechanical properties to typically brittle inorganic films. Growing films at the air-liquid interface provides the most rapid and simple means to prepare ordered solid inorganic films and to date the only method to form mesostructure 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 mesostructure are sensitive to surfactant structure, polymer properties and polymer-surfactant phase behaviour: herein it will be shown in particular how the film mesostructure can be tailored by directing these parameters and some interesting analogies will be drawn with more familiar mesostructure silica materials.

KEYWORDS

Mesostructure, polyelectrolyte-surfactant interactions, air-liquid interface, polymer-surfactant films, polymer-surfactant-silica films.

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13 Nomenclature

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16 1. Introduction

17 Surfactant-templated mesostructured bulk materials have received much attention in the
18 literature,[1,2,3,4,5,6,7,8] since the first reports of MCM-41,10 and SBA11 mesoporous silica. But less
19 time and energy seems to be directed to non-inorganic or hybrid inorganic-organic materials and seemingly
20 even less time to films or membranes. This review seeks to bring together some of the recent research into
21 self-assembled mesostructured polymer-surfactant materials. Particular focus shall be given to
22 mesostructured films or membranes formed spontaneously at interfaces.

23 Interactions and general phenomena of polymer-surfactant systems in the bulk and at the interface
24 have been a topic of intense interest for some time. [12,13,14,15] Meso-ordered polymer-surfactant
25 materials were first reported around two decades ago. [16] Fairly recently polymer-surfactant complexes
26 have been used as templates for porous silica.[17,18,19] However in most of these studies, powders have
27 been prepared lacking regular morphologies, high degree of long range order and hydrothermal stability. It
28 is envisaged that films (or membranes) have the potential to fulfil this grocery list of criteria, but have often
29 been over looked since they are often too brittle.

30 Common strategies used to prepare mesostructured inorganic films rely on some form of solid
31 support. In dip [20] and spin [21,22] coating films are templated from surfactants and a precursor sol on a
32 solid support. Micelles form and then arrange on a solid substrate, evaporation of the solvent drives the self-
33 assembly of organic and inorganic species. Layer-by-layer approaches have also been used to prepare
34 inorganic films. [23] However, fabrication of films at the air-liquid interface, whereby surfactants (and
35 polymers) spontaneously self-assemble and accumulate at the interface, is a more rapid and efficient means
36 (and do not involve controlled humidity and temperature) to prepare self-supporting films with thickness
37 spanning from nanometers to micrometers. Recent work has shown that under certain conditions it is
38 possible to form free-standing (macroscopic) polymer-surfactant films with highly ordered mesostructures,
39 spontaneously at the air-liquid interface. [24,25] If a silica precursor is added to the polymer-surfactant

1 mixture then a film again forms at the air-liquid interface, removal of the surfactant template framework
2 leaves a micron-thick mesoporous polymer silica membrane. [26] Not only is the mesostructures retained
3 (something seldom reported in silica films) this membrane is also thicker and more robust than typically
4 brittle inorganic films. Polymer remains stable to calcination and so this also provides a very simple way of
5 imparting functionality into the mesoporous silica walls.

6 Herein this review will explore recent developments concerning polymer-surfactant membranes and
7 polymer-surfactant-silica formed primarily at air-liquid interfaces and also time will also be given to
8 membranes formed at the liquid-liquid interface. Significantly these films show ordered mesostructure,
9 courtesy of their self assembly properties and phase behaviour with polymers. Efforts have been made,
10 wherever possible, to illuminate how the fundamental science of polymer-surfactant systems can be related
11 to fabrication of films. Indeed Section 1 is dedicated to giving a short account of the basic polymer-
12 surfactant mixture behaviour that underpins much of what follows in the text. The synthetic procedures and
13 conditions that govern film properties and mesostructure will also be discussed.

15 **2. Polymer-Surfactant interactions**

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

23 Mixtures of polymers and surfactants can phase separate analogously to polymer-polymer systems.
24 For two polymer systems we can distinguish between two types of phase separation, associative and
25 segregative. Common sense dictates that a mixture of two polymers in a common solvent ought to separate
26 into two separate phases, owing to the weak entropic driving force of mixing of high molecular weight
27 molecules (segregative separation.) This is true if no attractive interaction exists between polymers. If,
28 however there are strong attractive interactions between polymer pairs an associative phase separation can
29 occur, where both polymers are collected in the same phase. [28] If in a polymer-surfactant pair, both
30 polymer and surfactant are neutral, a segregative phase separation is observed for all but a few examples of
31 polymer-surfactant pairs. (Associative phase separation can occur for less polar polymers at high
32 temperatures). Introducing additional charge to one of either the polymer or surfactant often prohibits phase
33 separation.

34 Consider again a two-polymer system; there is a relatively small entropic penalty for combining
35 large polymer molecules to a single phase. But now consider one of the polymers is charged; in this case
36 there is the much more undesirable entropic condition resulting from confining the far more numerous
37 counter-ions to a single phase. Incidentally this is also a reason for the greater solubility of a polyelectrolyte

1 comparable to its uncharged polymer equivalent. Ionic surfactants in most cases tend to associate with non-
2 ionic polymers. Oppositely charged polyelectrolytes and surfactants will associate strongly through
3 electrostatic interactions between oppositely charged functional groups. As such there will be an associative
4 phase separation (also known as complex coacervation) and evolution of higher ordered structures of either
5 a precipitate or concentrated liquid-phase droplets.[14,28]

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

17 **3. Silica Materials: Analogies with Polymer-Surfactant Systems**

18 Any discussion on mesoporous/mesostructured materials ought to begin with silica materials; by far
19 the mostly widely researched mesostructured material in terms of both nanoparticles and films. Beyond its
20 historical relevance, surfactant/silica systems provide curious comparisons with long-studied polymer-
21 surfactant systems. Thus this section will bridge the apparent disparate nature between ordered surfactant
22 templated silica films and purely organic polymer-surfactant films.

24 **3.1 Mesostructured Silica particles**

25 In the early 1990s scientists from Mobil reported the preparation of MCM-41, mesoporous silica.
26 [1,2] Templated from cationic quaternary ammonium salts, the silica walls are both amorphous and show
27 long range order. Pore size was shown to be able to be precisely tuned by the surfactant chain length and
28 reaction conditions. Ever since, materials with organised and controllable meso-scale pores have been
29 studied enthusiastically, finding applications in catalysis, sensing and optics, adsorption, separation, drug
30 encapsulation for targeted or controlled release and a myriad of other diverse and seemingly distant fields
31 from pure material chemistry. For instance a review article recently published by Makowski et al. describes
32 so of the potential and eclectic uses of mesoporous materials in the nuclear industry; citing applications in
33 separation chemistry for actinide extraction, in waste management for confining mobile volatile radioactive
34 species, in design of new fuel forms (that may accommodate gaseous fission products and associated high
35 pressures) and for use as model materials in the study of irradiation defects. [30]

36 In their synthesis of MCM-41 the Mobil team put forward two mechanisms for the formation of
37 mesoporous silica. In the first they suggested that silica infiltrated into the aqueous region of the pre-formed

1 surfactant liquid crystalline structure to then condense and cement the final mesostructure. However, this
2 mechanism could quickly be discounted since surfactant solutions were too dilute to form organised liquid
3 crystal domains. The second formation pathway put forward by the Mobil team could be termed as the
4 “Micelle assembly model” and accounts for the inorganic species interacting with the micelles in solution
5 and propitiating an organisation of liquid crystalline phases. [1,2] Chen et al. built upon this idea, suggesting
6 that cylindrical or rod like inorganic/surfactant micelles spontaneously arranged into ordered arrays. [31] On
7 the basis of cryo-transmission electron microscopy, Regev proposed hydrolysis and condensation of the
8 inorganic specie may, in fact, occur on the surface of spherical micelles, decreasing repulsion between
9 charged surfactant head groups within the micelle and in turn mediating formation of clusters of more
10 elongated micelles. [32] A more general treatment of electrostatic interactions between surfactant
11 headgroups and inorganic species was introduced by Stucky and co-workers, in the “cooperative assembly
12 model” or “charge-matching formation model.” They were able to categorise interactions as either S-I+ or
13 S+I-, the former for anionic surfactant and silicate intermediate found in acidic conditions and the later for
14 cationic surfactants and negative silicate intermediates in alkaline syntheses. They first proposed that there
15 was a multidendate binding of silicate to surfactant ions, followed by cooperative assembly of a liquid
16 crystal like phase, driven by the need for charge matching of the charged species. [33,34,35]
17 Studies using NMR and fluorescence probes in soluble silica preparation in alkali conditions seemed to
18 suggest that the direct electrostatic interactions between headgroups and inorganic species may perhaps have
19 been overemphasised. [36,37] Instead of direct binding of silica or hydroxyl ions to the charged micelle
20 surface (under dilute precursor conditions), self assembly of liquid crystalline phases required polymeric
21 silica and then precipitation of a charge neutral mesomorphous surfactant/silica composite occurred in a
22 manner analogous to oppositely charged polyelectrolyte/surfactant complexes.

23 Chan et al. realised an analogy with polyelectrolytes in surfactant templated silica, observing a
24 liquid-liquid phase separation from which droplets of concentrated silica oligomers and surfactant formed.
25 [38] They put forward an inorganic driven phase separation model for the formation of mesostructured
26 precipitates; growth of inorganic oligomers causes a thermodynamically unstable silica
27 oligomer/surfactant/solvent mixture that undergoes liquid-liquid phase separation to give droplets of a
28 second liquid enriched in oligomer and surfactant. It was suggested that these droplets were colloiddally
29 stabilised (by sterics and electrostatic effects) and potentially by excess surfactant. At the high surfactant
30 concentration droplets rearrange and polymerisation of silica network causes a microphase separation within
31 the drops resulting in a defined mesostructure. Finally further polymerisation cements the final
32 mesostructure.

34 **3.2 Mesostructured Silica films**

35 Two groups [39,40] in 1996, separately reported spontaneously forming mesostructured surfactant
36 silica films at the air-liquid interface. It is noteworthy that materials had first been prepared on mica
37 substrates [41] and at the oil-water interface. [42] Almost all reports of mesostructured films form under

1 dilute acidic conditions, in mixed solutions containing the surfactant and usually a metalalkoxide (e.g.
2 tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS)). In a typical synthesis a cationic
3 surfactant (C_n TAB for instance) is dissolved in aqueous acidic solutions ($> \text{pH } 2$) at concentration above the
4 CMC, but well below the concentration necessary for forming liquid crystalline phases. TEOS is added to
5 the acidic surfactant solution under rapid stirring. Once the solution turns clear, it is transferred to a
6 container and the film allowed to grow. After calcination to remove the surfactant templates, films are
7 brittle, but can be made to be more robust by post synthesis exposure to a mixed ammonia-water vapour.
8 [43] Films will form at ambient temperatures, but higher temperatures yield thicker films. Film properties
9 and concomitant film growth are also sensitive to the concentration of the surfactant, silica precursor and
10 acid concentration, as well as ambient humidity.

11 Tailoring and modification of the surfactant structure allows a degree of control over silica film
12 mesostructure. [44] For C_n TAB templated films a 2D hexagonal structure with the c -axis (long axis)
13 orientated parallel to the film orientation, has been almost exclusively been reported. This is unfortunate
14 since it perhaps more limiting in applications versus a columnar like mesophase with the c -axis orientated
15 normal to the film. However synchrotron X-ray experiments on films on a silicon substrate show a cubic
16 mesophase ($Pm\bar{3}n$), which upon drying evolves into a 2D hexagonal mesostructure. [45] It has only been
17 possible to achieve other mesophase geometries in cationic surfactants by using gemini-type double head
18 group quaternary ammonium surfactants. Films grown at the air-liquid interface with a 18-3-1 gemini
19 surfactant, (whereby two C_{18} chains are attached to a dimethyl quaternary ammonium group, connected via a
20 3 carbon chain to a second dimethyl quaternary ammonium group,) yielded a film consisting of close packed
21 spherical, ellipsoidal or inter-connected ellipsoidal micelles ($P6_3/mm$). [46] Here it is the highly charged
22 and bulky headgroup that allows for the stabilisation of high interfacial curvatures of ellipsoidal micelles
23 with the longer c -axis normal to the interface (film). Evidence from films bound to a mica substrate
24 highlights that a close packed hexagonal array of micelles serves for the nucleation for c -axis $P6_3/mm$
25 mesophase. [45]

26 Increasing the chain length of C_n TAB templated silica films modifies the unit cell: [47] from $n=14$ -
27 18 the d -spacing increase linearly by 5 \AA per methyl group. For C_{18} TAB only, Lamellar phases were
28 observed that transformed to 2D hexagonal mesostructures once heated through the gel phase. [48]

29 More recently silica films with cubic mesophases have been accessed using the non-ionic
30 surfactant, octaethylene glycol mono- n -hexadecyl ether (C_{16} EO). [49] For films synthesised at different
31 molar ratios of surfactant to TMOS, cubic mesophases $Pm\bar{3}n$ and $Im\bar{3}n$ were reported at lower surfactant to
32 TMOS molar ratios with a distorted 2D hexagonal mesophase prepared at higher surfactant TMOS molar
33 ratio.

34 The time taken for surfactant templated silica films to form at the air liquid interface is dependent
35 upon silica concentration (or rather TEOS:surfactant ratio) and this is where the analogy with polymer-
36 surfactant systems can be marked-out. [50, 51] A familiar U-shaped concentration regime is observed for
37 film induction time (the time for the film to form) as a function of TEOS:surfactant concentration. At both

1 high and low TEOS concentration (relative to surfactant) film induction time is long, but within an
2 intermediate TEOS concentration range induction time reaches minima. Rapid film growth can be explained
3 by formation of phase separated liquid particles in the bulk solution, akin to what was observed by Chen et
4 al (in the preceding section). These liquid particles then undergo a microphase separation of the inorganic
5 and surfactant under local high concentration conditions to form mesostructured particles at the interface.
6 So film formation can be said to be driven by packing of mesostructured particles at the interface. No film
7 formation was observed prior to formation of particles in the bulk solution. [44,52] Outside this intermediate
8 concentration range no liquid particles were formed in the bulk and film formation could be attributed to the
9 slow migration of diffuse silica-coated micelles that migrate and pack at the interface.

10 Thus it follows that we can view rapid film formation as a coacervation process, treating silica as a
11 network polymer. Complex coacervation in polymer-surfactant mixtures occurs only at the point of charge
12 neutrality (at a threshold polymer molecular weight), where silica:surfactant ratio represents the charge on
13 the complex (Fig. 2). Film induction period is therefore the amount of time it takes growing silica
14 'polymers' to reach the critical molecular weight accredited to charge neutrality. [24] As concentration of
15 TEOS increases the amount of time for this to happen is reduced. Beyond the point of charge neutrality,
16 silica polymers completely coat surfactant micelles and so silica-surfactant complexes effectively repel one
17 another. Since films can grow at the air-liquid interface, albeit at a slower rate, at the absence of
18 coacervation processes and particles in the bulk; silica condensation about the micelles perhaps reduces
19 inter-micelle repulsion allowing their interaction and packing at the interface. [44]

20 In order to verify the above Edler et.al replaced silica with a high molecular weight carbon
21 polyelectrolyte, polyethylenimine (PEI). [24] PEI was the natural choice of polymer since it resembles the
22 molecular properties of polymerising silica in the formation of silica films at the air-liquid interface: it is
23 polar (and capable of forming hydrogen bonds,) highly branched and has low positive charge that diminishes
24 to near zero as the polymerisation proceeds. Mixed solution of high molecular weight PEI (750 000 Daltons)
25 with CTAB in water, formed solid films in an open container at the air-water interface. Grazing incidence
26 X-ray (GIXD) revealed films to have a 2D hexagonal mesostructure, orientated parallel to the film.

27 28 **4. Solid Mesostructured Polymer-Surfactant and hybrid silica containing films**

29 Replacing silica for polyethylenimine allows solid surfactant-polymer films with defined
30 mesostructures to be grown at the air-liquid interface. Mixtures of TEOS and polyethylenimine yield hybrid
31 mesostructured polymer-surfactant-silica films. This section will highlight how the properties and
32 mesostructure of polymer-surfactant films can be controlled when careful consideration is given to the
33 design of their synthesis.

34 35 **4.1 Solid Mesostructured Polymer-Surfactant films formed at the air-liquid interface**

36 A simple literature search of a variance of: 'polymer-surfactant films at the air-liquid interface'
37 reveals a wealth of literature discussing liquid-like films, for purposes mainly of surface tension reduction

1 and control of foaming and wetting. [2,53] These films generally consist only of a single polymer-surfactant
2 layer or a series of a few alternating layers of polyelectrolyte and surfactant. Langmuir Blodgett (LB)
3 techniques have been used to deposit solid 2D ordered mixed polyelectrolyte-surfactant monolayers from
4 the air-liquid interface onto solid substrates. [54] The structure of polymer-surfactant complexes in liquid-
5 like, monolayer type films are now quite well understood, thanks to extensive studies by Taylor et al.
6 [55,56,57] Very few examples of mesostructured solid polymer-surfactant films can be found in the
7 literature. Vaknin et. al prepared solid films of poly(diallyldimethylammonium) chloride and sodium-
8 dodecyl-sulphate (SDS), in the presence of NaCl. [58] From GIXD patterns they were able to confirm a 2D
9 hexagonal mesostructure orientated parallel to the film. However the presence of a solid film was only made
10 visible by reflectivity experiments and film thickness was measured at $\sim 23 \text{ \AA}$, only a $\sim 12 \text{ \AA}$ increase on
11 solutions containing SDS only. Addition of salt was deemed necessary to transform and ‘crystallise’
12 micelles into a cylindrical form. Short, partially charged DNA fragments ($\sim 50\text{nm}$) have been shown to
13 complex with CTAB to give brittle solid layers at the air-liquid interface. [59,60]. At concentrations just
14 above the CAC the DNA in the bulk solution becomes saturated with surfactant, bulk aggregates of
15 surfactant-DNA become less soluble and to the air-liquid interface, forming a thin film. The authors
16 proposed that the film would have a hexagonal ordering, since hexagonal-like composites of surfactant and
17 DNA were observed in solution beyond the CAC. However, regrettably the films mesostructure was not
18 probed.

19 To date only Edler and co-workers have prepared thick hierarchal ordered solid films from polymer-
20 surfactant solutions at the air-liquid interface. [24] Mixed solutions of PEI and CTAB at pH solutions > 10
21 allowed films of several hundred microns to be grown spontaneously in an open container. Since the first
22 publication of this type of film, quality work has furthered understanding of their formation and allowed
23 reaction conditions to be imparted to film properties. More recent work has shown that a good control over
24 mesostructure in these films can be mastered. Extensive studies on PEI-CTAB films has enabled film
25 properties to be rationalised with respect to: pH of reaction mixture, polymer system properties (including
26 branching of polymer, polymer molecular weight and concentration) and surfactant alkyl chain length.
27 The main findings can be summarised as followed [24, 25, 61, 62, 63] :

- 28 1. Films form for a range of cationic surfactants, including cetylpyridinium bromide (CPyB),
29 tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB)
30 in addition to CTAB.
- 31 2. Films templated with longer surfactant alkyl chains yielded more long-range ordered films. For
32 TTAB and DTAB surfactants, long-range order in neutron reflectivity profiles showed a
33 corresponding decrease with polymer concentration. Interestingly CTAB surfactants show a slightly
34 different relationship with polymer concentration; a maximum long-range order is reached at
35 relatively low polymer concentration, at higher concentrations instead multiple structures with fractal
36 micron-scale geometries.

- 1 3. Thicker, more ordered films are formed at higher solution pH. (Except at high molecular weight PEI,
2 where ordering may be lost, however this is only the case at high polymer concentrations).
- 3 4. PEI molecular weight is of critical importance to film quality. Films formed from low molecular
4 weight (2000 Daltons; hereafter denoted SPEI) formed thin, more ordered films that proved difficult
5 to remove from the interface without severely cracking or damaging the film. Films made from high
6 molecular weight PEI (750 000 Daltons; hereafter denoted LPEI) contained less well ordered
7 mesostructures, but were thicker and more robust. It should, however be noted that the order is
8 maintained down to very low concentrations of polymer and surfactant (even below surfactant
9 CMC.) Thicker films in all cases were formed in the presence of 0.05 M NaOH. Comparing SAXS
10 patterns of dried films with GIXD and neutron reflectivity data from PEI-CTAB films at the air-
11 liquid interface corroborates that films retain their mesostructure upon drying. However a shrinkage
12 of the d-spacing is seen in the dry films and this was attributed to loss of water from the hydrogel
13 structure during drying. Formation of thicker films could probably be explained by the greater
14 hydrophobicity of longer chain polymers. In fact the effects of polymer hydrophobicity is best
15 emphasised by the formation of thicker films in the presence of NaOH. Addition of NaOH reduces
16 the net charge of the polymer, making it less soluble and inveigling coacervates to the interface.
17 Faster film formation may present competition between phase separation in the film and mesophase
18 ordering, leading to lower ordering within the film.
- 19 5. Addition of a cross-linker, ethylene glycol diglycidyl ether (EDGE), a common cross-linking agent,
20 allows formation of thicker films, that could be removed from the interface onto a mesh or solid
21 support (cross-linking occurs at a faster rate within the film than in the bulk solution, gelation of the
22 solution does not occur for several hours.) Cross-linked films were contiguous and rubbery. The
23 cross-linker only caused minor changes to the film structure and upon drying cross-linked films
24 retained well ordered mesostructure, meaning inclusion of EDGE in the synthesis effectively freezes
25 the film mesostructure. SAXS data of the dry films indicates that for LPEI films, the cross-linking
26 reaction reduced long-range order, whilst the opposite was true for SPEI films, where cross linker
27 was seen to improve structural ordering.

28
29 Film formation was speculated to be driven by the migration of insoluble polymer-surfactant
30 complexes to the air-liquid interface, with film formation and ordering promoted by evaporation. At a
31 concentration above the CMC (but below the concentration needed for sphere-rod micelle transition)
32 polymer-surfactant complex coacervates form; micelles are loosely wrapped in polymer coils, rendering
33 them hydrophobic and in-turn causing their migration from the bulk solution to assemble at the air-liquid
34 interface. Evaporation leads to dehydration of upper layers of the film, encouraging ordering of the layers
35 beneath. [61]

36 Films were later prepared from mixtures of cationic surfactants that were sufficiently robust
37 enough to be removed from the interface without the need for a cross-linker to fix the structure. [64] Usually

1 Equimolar mixtures of oppositely charged cationic and anionic surfactant show a propensity to precipitate
2 out of solution, [65] but at molar ratios either side of equimolarity vesicles can be formed at low
3 concentration. [66] Surfactant pairs with different alkane chain lengths have been shown to facilitate vesicle
4 formation. [67] Catanionic vesicles of different molar ratios of CTAB and SDS were mixed with water
5 soluble polymers: polyacrylamide (PAAm), poly(ethylene glycol) (PEG) and again PEI). Films were
6 observed for mole fractions as extreme as 97:3 CTAB:SDS, up until the equimolar point, at which point no
7 film formation was seen, only the precipitation of material. Curiously film formation did not recommence as
8 the fraction of SDS was increased above the equimolar point, despite presence of vesicles in solution. Hence
9 for film formation an overly-charged positive cationic mixtures are a prerequisite. GIXD patterns revealed
10 these films to have a defined mesostructure comprising a random oriented Lamellar phase or close packed
11 multilamellar vesicles.

12 A film, visible to eye, was still observed in the absence of polymer, but polymer was needed for a
13 contiguous, self-supporting membrane. This highlights the role of catanionic vesicles in film
14 mesostructuring, and that of the polymer for entrapping and interlinking the lamellae or vesicle structures to
15 form thick contiguous film membranes. [64] The accessibility of preparing a raft of ordered water soluble
16 and biocompatible polymer membranes makes should draw attention to these films for applications in drug
17 delivery and encapsulation.

18 Films have been further developed and their applications now surely enhanced by a convincing
19 mastery of control over mesostructure by 'rational micelle design.' Film mesostructure can be tailored
20 according to surfactant structure. [68] Using quaternary Ammonium salts with a range of packing
21 parameters (Didodecyldimethylammonium bromide (DDAB), Hexadecyltrimethylammonium (CTEAB) and
22 CTAB) it was shown how the curvature of the micelles in solution imparts structure on the final liquid
23 crystalline structure in the film. Mesostructures in films could be predicted from SANS data from the bulk
24 solution and packing parameters of surfactants and surfactant mixtures. Packing parameter (P_c) as used here
25 is defined as $v_0/a_e l_0$, where v_0 is surfactant tail volume, l_0 is the surfactant tail length and a_e is equilibrium
26 area per molecule at the aggregate interface. [69]

27 SANS from surfactant solution indicates DDAB had the most elongated micelle structures and is best
28 fitted by a model for lamellar sheets. [70] All others surfactant solutions were fitted to a model for elliptical
29 micelles. GIXD patterns of the dried films (Fig. 3), demonstrated that DDAB-PEI and CTEAB-PEI films
30 exhibited lamellar and cubic (speculated to be $Pm\bar{3}n$) structures respectively. Intermediate micelle shape
31 between highest curvature (spherical) and essential zero curvature (lamellar) of DDAB:CTAB mixtures, 1:2
32 and 1:20. Both mixtures formed strong hexagonal 2D structures. Mesostructures of the (CTEAB)-PEI and
33 (DDAB)-PEI can be easily rationalised by applying the packing parameter. Given that CTAB is known to
34 form hexagonal 2D mesostructure ($P_c = 0.33$), CTEAB should be expected to form a cubic phase, owing to
35 its larger headgroup, and the concomitant greater curvature (amounting to a $P_c = 0.292$ and expected
36 spherical micelles). (CTEAB has previously been shown to form a micellar cubic mesostructure comprised
37 of both spherical and elliptical micelles in surfactant templated inorganic materials. [71]) Lower curvature

micelles of the same quaternary Ammonium salts family was achieved by increasing alkane tail volume, DDAB has a P_c of 0.63, typical of a lamellar bilayer. Since CTAB is the majority component in DDAB:20CTAB mixed solutions, micelles will form highly similar 2D hexagonal self assemblies, that arise from the uni-axial extension of the ellipse seen in solution into cylindrical micelles that pack together, as local surfactant concentration in the film is increased. Continuing work into surfactant design and polymer-surfactant behaviour in these films ought to ensure a full range of mesostructures comparable with inorganic films should be accessible.

4.2 Mesostructured Hybrid Polymer-surfactant-silica films formed at the air-liquid interface

Previous studies on mesoporous silicas templated by polymer-surfactant complexes have been limited to powders. [72,73,74] Kang et al. were able to synthesise highly mesoporous integrated silica-polymer hybrids templated from a PAA-CTAB framework. [73] Powders however, lack a regular morphology, mesostructural long-range order and thermal stability. Applying the same methodology as to their extensive work into ordered polymer-surfactant films, with the exception of the addition of TMOS, Edler et al have reported free-standing hybrid polymer-surfactant-silica films with ordered mesostructures (retained upon drying), formed in alkali conditions (Fig. 4). [26]

Inclusion of charged silica species to mixtures of polymer and surfactant presents a further level of complexity to the phase behaviour of film forming systems. Films were formed with CTAB surfactant and PEI polymer of high and low molecular weight LPEI and SPEI (750 000 and 2000 Daltons respectively) and are the same molecular weight as those used to prepare polymer-surfactant films. [26] LPEI and SPEI polymer systems show distinct phase diagrams with TMOS; for LPEI there were three regions: amorphous gel, films with no order and films with ordered 2D hexagonal order. For SPEI there was an additional fourth phase where exclusively mesostructured precipitates. For LPEI-CTAB-TMOS systems, silica gelation was observed at moderate to high TMOS concentrations (above 0.1 M) at low LPEI concentrations, no film forms as the entire solution gels. With increasing concentration of LPEI, films formed, becoming more ordered as LPEI concentration was further increased. Once removed from the interface and dried, films became more highly ordered, suggesting the drying process promotes ordering by bringing micelles into closer proximity to one another.

In the SPEI PEI-CTAB-TMOS system, cross-linking agent EDGE was used (0.04M), otherwise films were too thin and fragile to be removed from the interface. Films formed at low TMOS (less than 0.1 M) and SPEI concentration are still very thin and cannot be removed from the interface, without breakage. At low TMOS concentration (less than 0.1 M) a film formed, present first as an ordered cubic phase, that with time transformed to a 2D hexagonal structure that was retained upon drying. Prepared films were strong and in most cases resistant to cracking (especially for LPEI containing films) and critically ordering and structure of the membrane is retained after calcinations (600 °C for 6 hours), symptomatic of high thermal resistance.

1 A mechanism for film formation (Fig. 5) is briefly summarised as followed: at the pH films are
2 formed (pH 9-12) PEI has only a very small positive charge ($< 3\%$) and so interacts via cationic-dipole
3 interactions (between amine group and quaternary ammonium salt) and dipole-electrostatic interactions with
4 negative silicate. Film formation is driven by the migration of insoluble polymer-surfactant particles.
5 Silicate species penetrates the loosely bound polymer interacting with surfactants as well as the polymer
6 itself, forming an essentially homogenous silicate-polymer composite around the micelles. Composite
7 species in the bulk thus accumulate at the interface and rearrange to give an ordered phase as layers
8 dehydrate. Precipitates form at the expense of films at high TMOS concentration and low polymer molecular
9 weight. Polymers interact with and cross-link multiple micelles creating larger, but insoluble, complexes that
10 are necessary for film formation. At high TMOS concentration silica entirely coats micelles impeding
11 polymers interconnecting micelles.

12 In a separate report time-resolved SAXS was used to explore the structural evolution of micelles in
13 bulk solution from film forming systems. [75]. In solutions forming films from LPEI, at the point just after
14 mixing micelles are ellipsoidal and dispersed within the polymeric solution. Conversely for films forming
15 from SPEI solutions, micelles are spherical. In all cases prior to silica precursor addition, there are no
16 mesophases in solution. Addition of silica does not initially change the micelle structure/properties.
17 Condensation and hydrolysis of TMOS bring about the formation of phase separated droplets (coacervates),
18 that initially have no ordered mesostructure, but the system eventually rearranges to form a 2D hexagonal
19 mesostructure that is identical in type and degree as ordering of films. Coupling solution SAXS studies with
20 neutron reflectivity experiments on films it was postulated that despite evolution of the mesostructure in the
21 bulk solution being the same (albeit much more rapid) than evolution of the film, the final mesostructure and
22 ordering at the interface is not directly formed from particles produced in the bulk phase.

23 Similarly to polymer-surfactant films, silica containing films can be synthesised from mixtures of
24 cationic surfactants that show a variety of tunable mesostructures. [76] By varying the molar ratio of a
25 mixture of SDS and CTAB and polyelectrolyte molecular weight and their respective chemical nature (PEI
26 and PAAm) mesophase geometry of the membranes could be controlled to yield lamellar, 2D hexagonal and
27 cubic phases ($pn3m$, $fm3n$, and $Im3n$). Investigations of membranes from GIXD were used to assemble a
28 phase diagram (Fig 6), relating CTAB/SDS molar ratio to polymer concentration. Interestingly, addition of
29 silica to PEI-surfactant films narrows the concentration range at which highly ordered membranes form at
30 the air-liquid interface. [77] In a similar fashion addition of PEI to silica-surfactant systems, again narrows
31 the region of concentration over which ordered membranes are seen, relative to silica-surfactant membranes
32 with no polymer (formed in acidic conditions). Again the ability to access organic and hybrid polymer-silica
33 films with an extensive range of mesostructures, comparable to mesostructured silica films, should open up
34 many avenues for research in this area.

35 Introducing polymer to ordered inorganic films better mechanical film properties, whilst imparting
36 greater functionality to the pore structure. Film geometry is maintained after calcination. Thermal stability of

1 the films, together with improved flexibility could make them more suitable than inorganic films for a host
2 of applications.

4 **4.3 Polymer-surfactant films formed at liquid-liquid interfaces**

5 Growing films at a liquid-liquid interface, under more artificial conditions, represent a logical
6 approach to preparing films with mesostructure orientated normal to the interface, where the driving forces
7 and dynamics for film formation is quite different to films formed at the air-liquid interface. Manners and
8 co-workers [78] have recently reported forming mesostructured polymer-surfactant films at a liquid-liquid
9 interface, employing a novel preparation technique involving injecting the polyelectrolyte into an oppositely
10 charged surfactant solution to create a liquid-liquid interface. In the same study it was shown how this
11 method could be modified to template formation of hybrid polymer-surfactant-silica films. They cited a
12 recent paper detailing how membranes could be formed from spreading a peptide amphiphile solution
13 upon hyaluronan (an anionic long-branched polysaccharide) solution. [79] Here, although the authors focus
14 centred more upon the membrane mechanical properties than a need to discern mesostructure, they
15 nevertheless demonstrated that a microstructure orientated normal to the interface could result from
16 interfacial assembly, without a support, at the liquid-liquid interface. Schacht et al. [80] reported very thin
17 and brittle (and consisting of agglomerated particles), cubic mesostructured silica membranes grown at an
18 oil-liquid interface.

19 Films prepared by Manners and co-workers were grown by pipetting solution of surfactant (1.5 wt % of
20 either SDS or CTAB) into a Eppendorf tube. Then a polyelectrolyte solution comprised of 1.5 wt % of either
21 poly(sodium 4-styrenesulfonate) (PSS) or poly(diallyldimethylammonium chloride) (PDMAC) and 11.1 wt
22 % glycerol was injected into the bottom of the tube to form a liquid-liquid interface with the surfactant
23 solution. Films of either PDMAC-SDS or PSS-CTAB form spontaneously as the created liquid-liquid
24 interface. Polymer-surfactant-silica films were prepared by adding TEOS to either the surfactant or polymer
25 solution and controlling the pH to ensure there is no silica condensation before film formation (Fig.7).
26 PDMAC-SDS exhibited only a poorly ordered 2D hexagonal arrangement parallel to the interface. PSS-
27 CTAB systems on the other hand gave quite unique unreported monoclinic structures normal to the
28 interface, speculated to form at the contraction of distorted hexagonal mesophases during the drying of
29 films. PSS-CTAB-silica films were reported to also have a mesostructured ordering normal to the interface.
30 Unfortunately films did not appear to retain their mesostructure upon calcinations. Most basically it was
31 proposed that films formed as surfactants diffuse to the interface, where they complex with the
32 polyelectrolyte. Surfactant will continue to diffuse to the interface and at the point where polymer and
33 surfactant are charge matched, insoluble coacervates form, that in turn, collapses to reorder and form
34 distorted hexagonal structures aligned normal to the interface. As further polyelectrolyte is absorbed from
35 solution the columns will lengthen. [78]

37 **5. Conclusion**

1 Growing films at the air-liquid provides a straightforward and rapid route to mesostructured films.
2 Preparing films via Langmuir-Blodgett techniques, evaporation or layer-by-layer assembly approaches are
3 more engineering intensive, condition sensitive and form very thin delicate films that cannot be removed
4 from the interface. Thus allowing polymer-surfactant and polymer-surfactant-silica mixtures to grow
5 spontaneously at the air-liquid interface is the only current means to micron thick, mesostructured films.

6 Early work on polyethylenimine-CTAB films formed at high pH, showed 2D hexagonal mesophases
7 aligned parallel to the film. Consideration of the surfactant structure and using cationic surfactant
8 mixtures mesophase geometry of the films can be tailored to achieve films with 2D hexagonal, Lamellar and
9 a number of cubic phases for both polymer-surfactant and hybrid polymer-surfactant silica films. In most
10 cases the dried film mesostructure could be predicted from the packing parameter. Important efforts have
11 been made to understand evolution of micelle/mesophase structure in the bulk solution in films using SAXS
12 and SANS. It was concluded that the mesophases in the bulk solution did not directly form the
13 mesostructure of the film at the air-liquid interface. The ability to tune mesostructure to achieve pores planar
14 through the film as well as normal to the film opens many avenues for potential applications. Polymer films
15 show much greater flexibility and strength than brittle inorganic films. Hybrid polymer-silica films exhibit
16 greater mechanical properties than inorganic films and are thermally stable making them candidates for
17 applications in catalysis and separation. Other possible applications could include heavy ion removal or an
18 environmental absorbent. [75,81,82] Perhaps the most interesting potential use of the films is in drug
19 delivery. It has already been shown how small amounts of hydrocarbons or alcohols can be incorporated into
20 micelles within the polymer-surfactant films. [83]

21 It is hoped that this review has laid bear the relevance and potential of polymer-surfactant and hybrid
22 polymer-surfactant films and may encourage further work by more researches.

23 **Acknowledgements**

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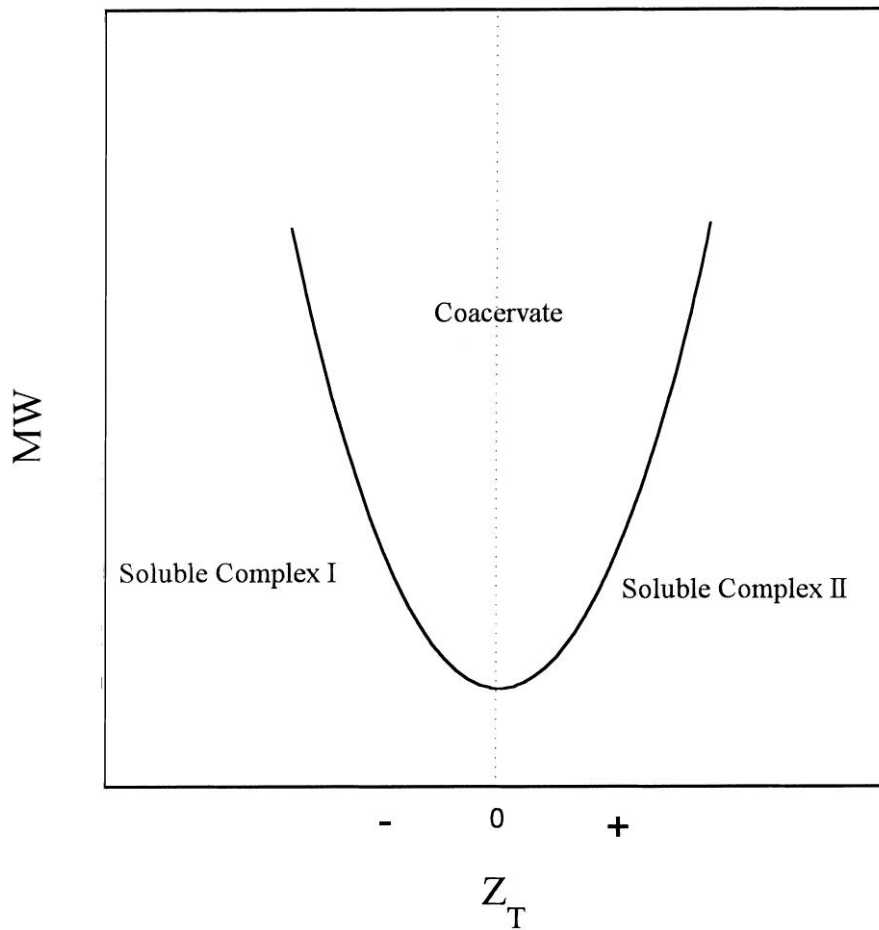


Figure 1. Representation of the U-shaped dependency that resembles the boundary for forming phase separated particles. MW is the molecular weight and Z_T is a measure of the net charge on the polymer-surfactant complex, i.e. polymer:surfactant ratio. [29]

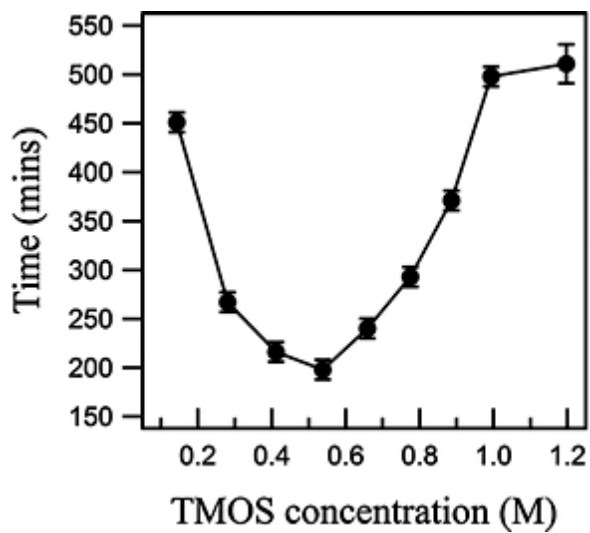


Figure 1. Time taken for film to form against TMOS concentration. [47]

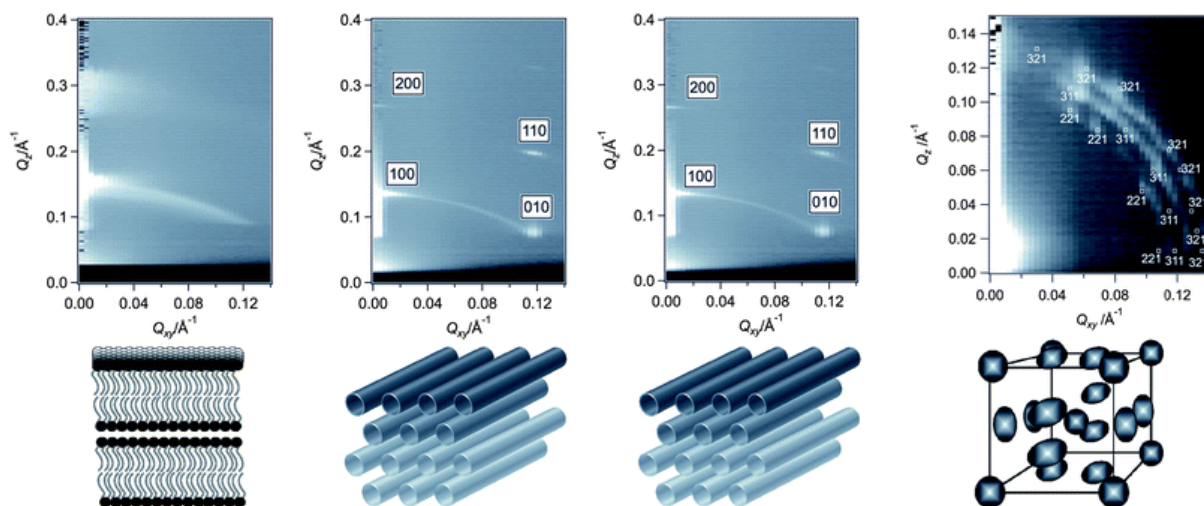


Figure 3. (upper) GIXD patterns from SPEI-films (left to right) DDAB, DDAB:2CTAB, DDAB:20CTAB and CTEAB. (lower) Representations of micelle packings. The incident angles (left to right) were 1.15°, 0.97°, 0.96° and 0.13°. [68]

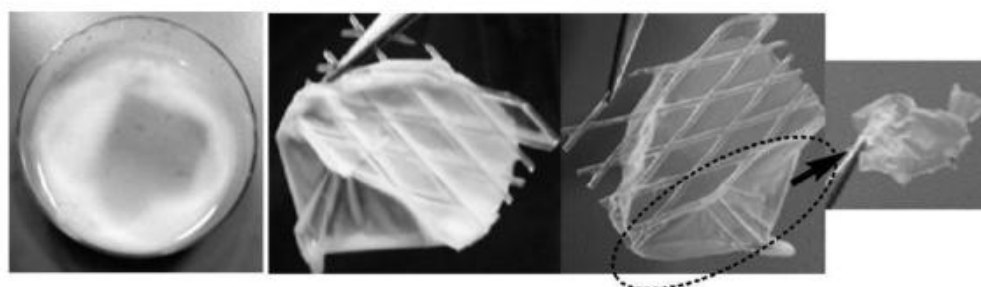


Figure 4. Cationic surfactant-polymer-silica films during preparation. (left to right) Film growth on surface of solution in a Petri dish, wet film just after removal from the solution interface on a mesh pulled up from underneath the film; the film after drying in air; final calcined silica film taken from the portion of film indicated in the previous picture. The plastic mesh is around 5x5 cm. [76]

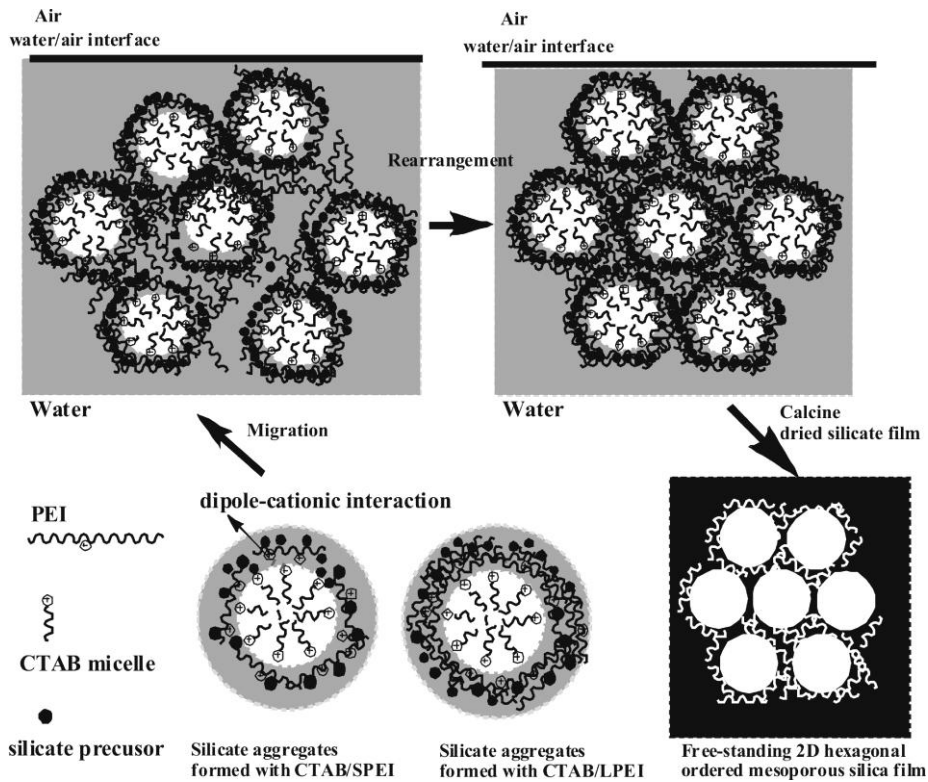


Figure 5. Edler et al. Schematic of proposed formation mechanism for CTAB-PEI complex templated Silica films.[26]

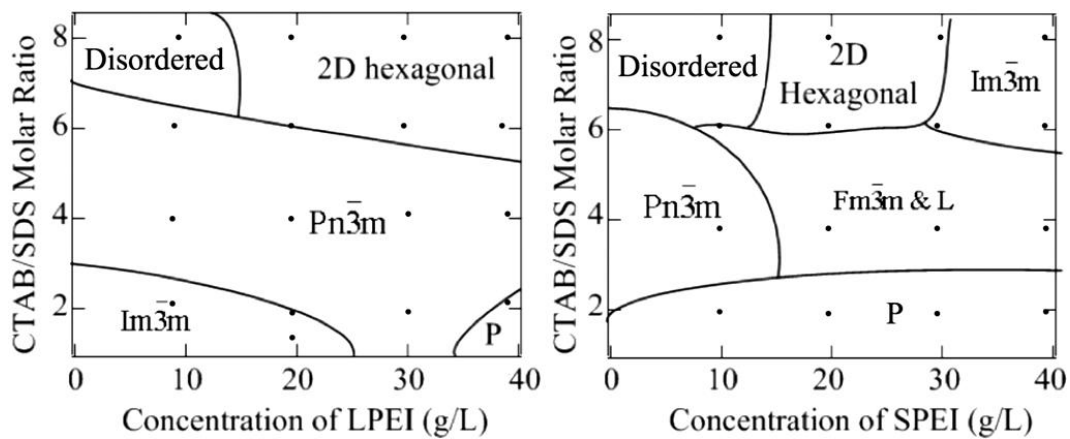


Figure 6. Phase diagrams for PEI-SDS/CTAB-silica films prepared at the air-liquid interface, for molecular weight PEI polymers LPEI (left) and SPEI (right). L and P labels refer to lamellar and precipitate respectively. [76]

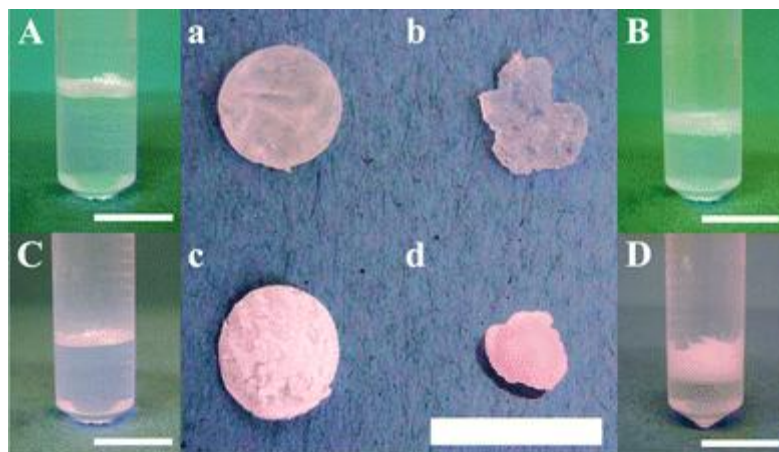


Figure 7. Films *in situ* after formation: (A) PSS-CTAB, (B) PDMAC-SDS, (C) PSS-CTAB-TEOS, (D) PDMAC-SDS-TEOS. Images of Films after drying: (a) PSS-CTAB, (b) PDMAC-SDS, (c) PSS-CTAB-TEOS, (d) PDMAC-SDS-TEOS. Scale bars represent 1 cm. [78]

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