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Association of Titania with Nonionic Block Copolymers in Ethanol: The Early Stages of Templating and Film Formation

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We have prepared self-supporting, free-standing titania-surfactant mesostructured films via spontaneous growth on the surface of ethanolic solutions, as an alternative synthetic route to evaporation induced self-assembly. The initial stages of surfactant templating and interfacial film formation in alcoholic solutions of titania with a polyethylene–poly(ethylene glycol) surfactant have been observed by small angle neutron scattering and Brewster angle microscopy. Variation of parameters including the titania precursor concentration, acid concentration, and surfactant concentration allowed formation times and pathways to be probed. These time-resolved observations of titania development represent a novel achievement in formation studies and have allowed a formation mechanism for titania–surfactant films to be proposed. Micelles in solution undergo an initial slow accumulation of titania, followed by rapid growth of a titania shell, followed again by a slow growth period, and these species accumulate at the solution interface to form the film via a phase transition driven by evaporation from the solution surface. This mechanism shows no solution aggregation in early developmental stages and is significant in understanding early solution phase development and for developing new materials based on evaporation induced self-assembly processes as well as for spontaneous growth of films at interfaces.

Introduction

Surfactants have been used to direct structure formation in self-assembled materials since the early 1990s when Mobil researchers reported the use of cetyltrimethylammonium chloride in water for formation of MCM-41.[1] Subsequently, triblock copolymers of the form PEO_xPPO_y-PEO_x began to be used as templates, with the first mesoporous silica prepared using such a surfactant reported in 1995.[2] The relative biological safety, cheapness, and ability to form micelles at low concentration of these copolymers makes them desirable material templates.[2] Materials formed using nonionic surfactants with oligo(ethylene oxide) headgroups were also found to have thicker inorganic walls making such materials more robust and with larger pores than those prepared using ionic surfactants.[3−6]

Titanium dioxide is arguably the most promising transition metal material for widespread application because it is biologically and chemically inert, stable to corrosion, inexpensive, and its band gap of 3.2 eV holds great potential for photochemical and photoelectric applications.[7−9] Titania-based mesoporous materials have been used in sensors and catalysts for pollutant decomposition among other areas.[10−13] The development by Grätzel et al. of colloidal titanium dioxide dye-sensitized solar cells is of particular significance and improving the efficiency of such cells to rival that of silicon solar cells remains a considerable research goal.[12−14] Already it is possible to create titania solar cells that are more efficient than silicon cells at high temperatures and low solar angles.[15] Such cells require titania materials with relatively large mesopores to allow adsorption of the organometallic dyes that allow capture of radiation across the whole solar spectrum, so are likely

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(1) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
(2) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.
(3) Flödstrom, K.; Teixeira, C. V.; Amenitsch, H.; Alfredsson, V.; Linden, M. *Langmuir* **2004**, *20*, 4885.
(4) Guo, Q.; Thomann, R.; Gronski, W. *Polymer* **2007**, *48*, 3925.
(5) Edler, K. *Aust. J. Chem.* **2005**, *58*, 627.
(6) Zhao, D.; Yang, P.; Huo, Q.; Chmelka, B. F.; Stucky, G. D. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 111.
(7) Yun, H.-S.; Miyazawa, K.; Zhou, H.; Honma, I.; Kuwabara, M. *Adv. Mater.* **2001**, *13*, 1377.
(8) Deshpande, A. S.; Shchukin, D. G.; Ustinovich, E.; Antonelli, M.; Caruso, R. A. *Adv. Funct. Mater.* **2005**, *15*, 239.
(9) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
(10) Zukalova, M.; Zukal, A.; Kavan, L.; Nazeeruddin, M. K.; Liska, P.; Gratzel, M. *Nano Lett.* **2005**, *5*, 1789.
(11) Zhao, L.; Yu, Y.; Song, L.; Hu, X.; Larbot, A. *Appl. Surf. Sci.* **2005**, *239*, 285.
(12) Gratzel, M. *Nature* **2001**, *414*, 338.
(13) Huo, K.; Tian, B.; Li, F.; Bian, Z.; Zhao, D.; Huang, C. *J. Mater. Chem.* **2005**, *15*, 2414.
(14) Malfatti, L.; Falcaro, P.; Amenitsch, H.; Caramori, S.; Argazzi, R.; Bignozzi, C. A.; Enzo, S.; Maggini, M.; Innocenzi, P. *Microporous Mesoporous Mater.* **2006**, *88*, 304.
(15) Vargas-Florencia, D.; Edvinsson, T.; Hagfeldt, A.; Furo, I. *J. Phys. Chem. C* **2007**, *111*, 7605.

to benefit from the high surface area, large mesopores, and nanocrystalline titania prepared using surfactant micelle templates.

However, development of new titanium dioxide architectures has been hampered by the highly reactive nature, particularly in the presence of water, of the titanium(IV) chlorides and alkoxides that are the most commonly used precursor materials.[16] Reactions may be slowed by limiting the availability of water, to restrict hydrolysis, and by using highly acidic conditions.[17] Acids catalyze the hydrolysis of alkoxides but slow the subsequent condensation. Controlling both hydrolysis and condensation of titanium(IV) precursors is of fundamental importance to generate ordered surfactant-templated materials but must be balanced against the requirement for ordered assembly of the surfactant template, which also depends upon solvent composition, water content, and acidity.[5,18]

Work on titania films templated with block copolymers in nonaqueous solvents has so far concentrated on films formed on substrates via dip- or spin-coating, designated the evaporation induced self assembly (EISA) technique,[19] rather than on spontaneous growth of free-standing films at the solution surface. A wide range of surfactant templated films containing transition metals have been made via the EISA method.[17,20] EISA uses a mixed solvent of ethanol and water, deposited upon a substrate by dip or spin coating. No ordered phase or micelles are present in the dilute bulk reaction solution. In EISA, during coating and aging of the film at elevated temperature, preferential evaporation of alcohol leads to development of a surfactant liquid crystal phase as the relative surfactant concentration increases.[21] Concurrent with solvent evaporation, inorganic precursors in solution react to form small inorganic oligomers that bind to surfactant micelles. Once a surfactant liquid crystalline phase has formed, inorganic oligomers also intercalate between micelles and condense because of their increased proximity to each other. EISA film formation is therefore an example of true liquid crystal templating, where inorganic species condense around a pre-existing concentrated surfactant liquid crystalline phase. This process requires a specific series of reactions brought about by careful aging, under controlled conditions, of the films after coating.

The aging steps of EISA are the most problematic part of this technique because the presence or absence of a final structure, and its type, is highly dependent upon the temperature and humidity to which the film is exposed.[21] If inorganic precursors form solid networks before enough solvent has evaporated for an ordered liquid crystal phase to form, a disordered material results. Furthermore, crystalline titania formed in the film may be unable to match the curvature of the surfactant structure causing the material to collapse upon calcination.[22] These effects demand fine control over the temperature and humidity conditions during film aging as the surfactant template structure is not established until the final aging steps. High temperatures and long calcination times may also lead to titania crystal growth, destroying the pore network as a result. EISA is also limited to producing films no thicker than a few hundred nanometres, as in thicker films the difference in drying rate at the surface and deeper within the film becomes more pronounced.[22] The films shrink as they dry, so frequently crack as the surface contracts. Nevertheless, EISA has become a common method of film formation and repetitive dip-coating has produced titania films of sufficient thickness for use in solar cells.[10,11] Thus, using a rather painstaking process, thick films may be formed by EISA methods, but in general films formed on substrates are of limited thickness and often subject to cracking.[22]

As an alternate route to mesostructured titania films, spontaneous film growth at the solution interface is attractive. Pervious work on interfacial film syntheses on aqueous solutions has shown they are relatively insensitive to preparation conditions such as humidity and temperature, forming the same well-ordered mesoscale structure over a wide range of conditions, dependent only on the concentrations of surfactant and inorganic precursor in the subphase.[23] Film thickness is also controlled by reagent concentration, in a one-step synthesis and films generally take between minutes to a few hours to form, making this a faster method of thick film formation than multiple EISA coating steps. Lamellar surfactant templated titania films have been formed at the air−solution interface using sodium dodecylsulphate (SDS) as the templating surfactant in aqueous solutions,[24,25] but titania films with a structure stable to calcination have not previously been reported. Film formation at an air−solution interface allows thicker films to grow under steady state conditions which are less susceptible to alteration by changes in temperature and humidity. As these are free-standing films, they are also less susceptible to cracking as inorganic condensation and drying proceeds. Development of the interface formation route therefore represents a promising area of research,[26] however film formation is hampered by the reactivity of titania precursors in aqueous systems, meaning only dilute, highly acidic solutions and a restricted range of surfactants can be used, giving little control over the type of nanoscale structure produced.

As an alternative, therefore, we have investigated the use of high-alcohol solvents in similar spontaneous interfacial

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(16) Soler-Illia, G. d. A.; Sanchez, C. *New J. Chem.* **2000**, *24*, 493.
(17) Soler-Illia, G. d. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093.
(18) Soler-Illia, G. d. A.; Scolan, E.; Louis, A.; Albouy, P.; Sanchez, C. *New J. Chem.* **2001**, *25*, 156.
(19) Brinker, C. J.; Lu, Y.; Sellinger, A.; Fan, H. *Adv. Mater.* **1999**, *11*, 579.
(20) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
(21) Brinker, C. J.; Dunphy, D. R. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 126.
(22) Chen, W.; Geng, Y.; Sun, X.-D.; Cai, Q.; Li, H.-D.; Weng, D. *Microporous Mesoporous Mater.* **2008**, *111*, 219.
(23) Fernandez-Martin, C.; Roser, S. J.; Edler, K. J. *Langmuir* **2004**, *20*, 10679.
(24) Henderson, M. J.; Gibaud, A.; Bardeau, J.-F.; White, J. W. *J. Mater. Chem.* **2006**, *16*, 2478.
(25) Henderson, M. J.; King, D.; White, J. W. *Langmuir* **2004**, *20*, 2305.
(26) Edler, K.; Brennan, T.; Roser, S. J. *Thin Solid Films* **2006**, *495*, 2.

film forming systems. Using nonaqueous conditions offers control of the reactivity of transition metal precursors,[17,27,28] so development of high alcohol systems has potential for functional material design,[17] and the use of nonaqueous solvents has been reported as more promising than aqueous systems.[29] In the case of titania, the use of pure ethanol is not ideal, as acidic water enhances interactions between titania precursors and PEO, encouraging formation of the inorganic coating around the micelle required for aggregation into larger particles and films.[18,30] Micelle formation in PEO-containing block copolymers is also enhanced in the presence of acid and some water.[18,31,32] Therefore, a system using a small, controlled amount of acid and water is likely to be the most promising for the formation of mesoporous titania at the air–solution interface of high-alcohol solvent systems.

In the high water content solvent mixtures most commonly used in block copolymer templated syntheses, the hydrophobicity difference between PEO and PPO blocks is sufficient for micelle formation. However, it is insufficient to generate significant surface activity and micelle formation in high alcohol systems so copolymers with a more hydrophobic block must be used,[18,31] such as Brij-type surfactants, $CH_3(CH_2)_mCH_2(CH_2CH_2O)_nOH$, m, $n \leq 16$, triblock copolymers where the polypropylene oxide block is replaced with polybutylene oxide, or KLE surfactants, poly(ethylene-co-butylene)-b-poly(ethylene oxide). All of these surfactants have been successful in templating mesoporous materials via EISA methods.[33–36] However, apart from EISA, the use of high alcohol systems remains rare and the use of higher molecular weight polyethylene–poly(ethylene oxide) (PEPEG) block copolymers to form films spontaneously at the air–ethanol interface is a new area of research. We report here our studies of subphase interactions between titania precursors and PEPEG surfactant micelles in ethanolic solution leading to film formation, the properties of the films, and the factors influencing film formation. Our solution measurements are also highly relevant to the EISA process since they shed light on inorganic–surfactant interactions that also occur in these systems after the point of surfactant micellization.

Experimental Section

The surfactant used in this work was the commercial diblock copolymer polyethylene-poly(ethylene glycol), (PEPEG), with structure $H(C_2H_4)_{20}(C_2H_4O)_{54}H$, and average M_w = 2939 g/mol[37] (Aldrich, no information was available on the polydispersity of this surfactant). Polyethylene oxide (PEO) 10 000 and 600 000 MW was obtained from Aldrich. The inorganic precursor was titanium tetrachloride, $TiCl_4$ (99.9%, Acros Organics). Absolute AR-grade anhydrous ethanol (99.8%, Fisher Scientific), analytical reagent grade HCl, (37% wt. in H_2O, 99+% pure, Fisher Scientific) and water from a Milli-Q water purification system (resistance 18.2 MΩ/cm) were used for all film preparations. For neutron-scattering experiments, D_1 ethanol, C_2H_5OD, and D_6 ethanol, C_2D_5OD, of 99.7% and 99.6% atomic purity respectively were purchased from CDN-Isotopes. Deuterated hydrochloric acid, DCl, (37% wt. in D_2O, 99.5% atomic purity, Goss Scientific) and D_2O (99.9% atomic purity, Aldrich) were used to prepare the solutions. In all cases, reagents were used as supplied.

The phase diagram of the PEPEG surfactant was investigated between 2.5 and 60 wt % PEPEG in ethanol. After this, titanium dioxide-based films were templated at the air–solution interface as follows: 1 g of PEPEG was dissolved in 20 g of ethanol by stirring and heating at 45 °C for 60 min. In the case of films formed using extra PEO, this was added to the PEPEG solution at this point and dissolved by stirring. Subsequently 0.45 g of 37 wt % HCl was added to the solution followed by 1.4 g of H_2O with stirring for 1 min to ensure uniformity. Finally, 2.0 g of $TiCl_4$ was added, and the solution was stirred for a further minute to obtain a pale yellow solution. The standard molar ratio of reagents used was 0.032 PEPEG/41 C_2H_5OH/0.44 HCl/8.9 H_2O/1 $TiCl_4$. The film precursor solution was then poured into either a 6 cm diameter Petri dish or a 4 × 15 cm PTFE trough depending upon the analytical technique being used. For Brewster angle microscopy (BAM), films were grown at room temperature and humidity uncovered in a Petri dish, while for X-ray reflectivity a PTFE trough was used, covered by a lid with a 2 cm diameter hole to reduce evaporation rates. In all cases an opaque, white film was observed by eye to develop at the surface within 1 h. To investigate important factors for film formation we varied the amount of PEPEG, HCl and $TiCl_4$ in turn while holding the concentrations of other species constant. The ranges of molar ratios used were 0.016–0.064 PEPEG, 0.51–1.87 $TiCl_4$, and 0.07–0.72 HCl.

Films were allowed to develop for 2 h before being harvested for small-angle X-ray scattering (SAXS) measurements, by placing a plastic mesh with 1 cm holes underneath the film and lifting it free of the interface. Films were dried for 48 h at room temperature, and the now clear film was cut free from the plastic mesh for mounting for SAXS measurements. Films studied using BAM were harvested for SAXS measurements once the BAM experiment was complete. Films were calcined using a heating rate of 1 °C/min and were maintained at 400 °C for 180 min before being allowed to cool naturally.

SAXS measurements on surfactant–ethanol solutions and dried films were done on an Anton Paar SAXSess small-angle X-ray scattering system with a slit focus, using 1.54 Å X-rays from a PANalytical PW3830 Generator. Liquid samples were run in 1 mm diameter glass X-ray capillaries, while solid films or powders were supported between pieces of sticky tape. A background of either ethanol in the same 1 mm capillary, or a blank tape pattern was subtracted from the data. The data was desmeared using the Lake desmearing method[38] implemented by Anton Paar, prior to further analysis.

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(27) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*, 1st ed.; Academic Press: London, 1990; p 1.
(28) Bradley, D. C.; Mehotra, R. C.; Guar, D. P. *Metal Alkoxides*; Academic Press: London, 1978; p 1.
(29) Antonietti, M.; Niederberger, M.; Smarsly, B. *Dalton Trans.* **2008**, 18.
(30) Linton, P.; Alfredsson, V. *Chem. Mater.* **2008**, *20*, 2878.
(31) Soni, S.; Brotons, G.; Bellour, M.; Narayanan, T.; Gibaud, A. *J. Phys. Chem. B* **2006**, *110*, 15157.
(32) Yang, B.; Guo, C.; Chen, S.; Ma, J.; Wang, J.; Liang, X.; Zheng, L.; Liu, H. *J. Phys. Chem. B* **2006**, *110*, 23068.
(33) Coleman, N.; Attard, G. S. *Microporous Mesoporous Mater.* **2001**, *44–45*, 73.
(34) Yu, C.; Yu, Y.; Zhao, D. *Chem. Commun.* **2000**, 575.
(35) Thomas, A.; Schlaad, H.; Smarsly, B.; Antonietti, M. *Langmuir* **2003**, *19*, 4455.
(36) Fattaakhova-Rohlfing, D.; Wark, M.; Brezesinski, T.; Smarsly, B.; Rathousky, J. *Adv. Funct. Mater.* **2007**, *17*, 123.
(37) Rajzer, B. Certificate of Analysis: Polyethylene-block-poly(ethylene glycol), Lot number 04015HD, Sigma-Aldrich [online], 2005, http://www.sigmaaldrich.com/catalog/CertOfAnalysisPage.do?symbol=525901&LotNo=04015HD&brandTest=ALDRICH (accessed July 20, 2010).

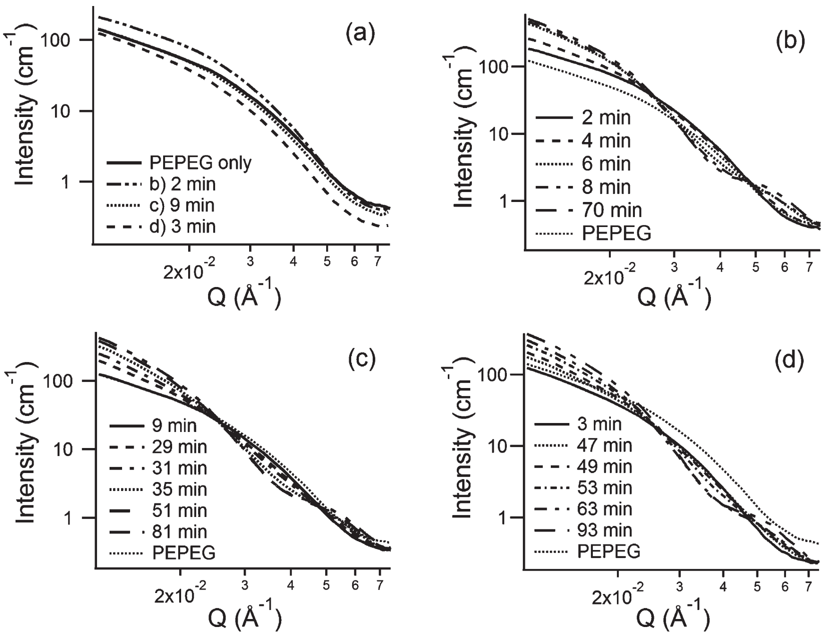

Figure 1. SANS patterns collected from (a) PEPEG in 100% D_6 ethanol compared to solutions in b−d after addition of $TiCl_4$ (times after addition noted in legend) and time-resolved data for (b) 1: 1.25, (c) 1.5: 2, and (d) 1: 3 PEPEG/$TiCl_4$ ratio solutions in 100% D_6 ethanol. The PEPEG only pattern has also been added to these graphs for reference. The transition stage begins quickly in the low ratio case (b) is delayed a little in the middle ratio (c) and more in the high ratio case (d).

Small-angle neutron scattering (SANS) experiments on film-forming solutions were performed on D11 at the ILL in Grenoble, France.[39,40] Time resolved SANS experiments used 2 min data collection and detector positions of 1.1 and 5 m giving Q_z ranges of 0.05−0.33 and 0.01 − 0.07 Å^{-1}, respectively. Reaction solutions were pipetted into rectangular 1 cm wide, 1 mm path length quartz cells and mounted on the D11 beamline. Experiments were done using both 100% and 70% D_6 ethanol as solvent to provide multiple contrasts for data modeling by simultaneous fitting. The patterns were corrected for instrumental factors and normalized to absolute intensities in cm^{-1} using the secondary calibration standard, water. An appropriate solvent background was subtracted from the data prior to model fitting. SANS and SAXS data were fitted to suitable models using the NIST SANS analysis package[41] based on Igor Pro (Wavemetrics), which is freely available for download.[42] SAXS and SANS data of the PEPEG micelles and PEPEG-titania micelles in solution were fitted to a form factor model for a core−shell sphere with a polydisperse core, having a Schulz distribution of radii as formulated by Bartlett and Ottewill.[43] The core radius, shell thickness and scattering length density, volume fraction and polydispersity were fitted, and the other parameters calculated from known solution concentrations and held constant as specified in the Results section below. Although mathematically having only a few contrasts, it is not possible to distinguish between polydisperse spheres and cylinders or ellipsoidal micelles, the polydisperse sphere model was chosen as the simplest model with fewest parameters that gave the lowest χ^2 values when a least-squares fitting routine was used. The solutions were sufficiently dilute that no structure factor was required to fit the data. For the dried PEPEG-titania films, a uniform ellipse model[44] was used to fit the scattering from disordered PEPEG micelles in a titania matrix. The scattering length density of the PEPEG ellipse and the titania walls were fixed and the dimensions of the ellipse, and its volume fraction were fitted.

BAM images were collected using a Nanofilm Technologies (NFT) I-Elli 2000 Imaging Ellipsometer with a frequency doubled NdYAG diode laser at a wavelength of 532 nm. X-ray reflectivity and off-specular time-resolved reflectivity measurements were performed on Tröika II (ID10B)[45] at the ESRF (see Supporting Information for details). Thermogravimetric analysis (TGA) of solvent and organic content in dry films at various titania: surfactant molar ratios, used a Perkin-Elmer TGA 7 thermogravimetric analyzer. Film samples were heated from 25 to 600 °C at a heating rate between 0.75−1.0 °C/min depending on time available for the experiment.

Results

Subphase Solutions. In the absence of titania precursor, PEPEG forms micelles in ethanol. At concentrations where film formation is observed, below 5 wt % surfactant, SAXS data on PEPEG-ethanol solutions were fitted to a model of core−shell spheres with a core radius around 42 Å, having a Schulz distribution of radii[43] with a polydispersity of 0.3, and a shell, composed of partially solvated ethylene oxide chains with a thickness of 43 Å. This confirms the expected micelle structure, where the polyethylene parts of the PEPEG diblock are sequestered into the central part of the micelle, while the polyethylene glycol block interacts with the ethanol solvent forming

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(38) Lake, J. *Acta Crystallogr.* **1967**, *23*, 191.
(39) Schmatz, W.; Springer, T.; Schelten, J.; Ibel, K. *J. Appl. Crystallogr.* **1974**, *7*, 96.
(40) Lieutenant, K.; Lindner, P.; Gahler, R. *J. Appl. Crystallogr.* **2007**, *40*, 1056.
(41) Kline, S. R. *J. Appl. Crystallogr.* **2006**, *39*, 895.
(42) http://www.ncnr.nist.gov/programs/sans/data/red_anal.html (accessed July 20, 2010).
(43) Bartlett, P.; Ottewill, R. H. *J. Chem. Phys.* **1992**, *96*, 3306.
(44) Feigin, L. A.; Svergun, D. I. In *Structure Analysis by Small Angle X-ray and Neutron Scattering*; Taylor, G. W., Ed.; Plenum Press: New York, 1987; p 59.
(45) Smilgies, D.-M.; Boudet, N.; Struth, B.; Konovalov, O. *J. Synchrotron Radiat.* **2005**, *12*, 329.

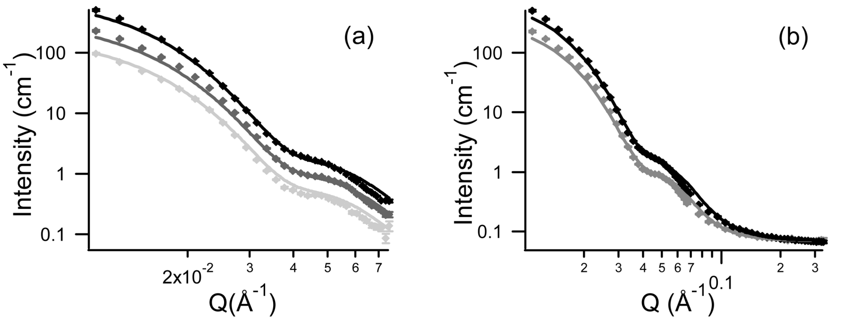

Figure 2. Examples of data fitted to a polydisperse core−shell sphere model for (a) a 1.5 PEPE/ 2TiCl$_4$ solution at the end of the reaction over a 0.01−0.07 Å^{-1} range and (b) a 1 PEPEG/1.25 TiCl$_4$ solution at the end of the reaction over the total combined Q range of 0.01−0.33 Å^{-1}. Data is shown by markers and fitted models by solid lines for 100% (black), 70% (dark gray), and 50% (light gray) deuteration of the solvent. Error bars are shown in both cases.

the shell. Increasing the PEPEG concentration led to formation of ellipsoidal and eventually cylindrical micelles, followed by a lamellar phase at the highest concentrations (for SAXS fitting results see Supporting Information, Table S1), following the expected series of liquid crystalline phases seen for similar amphiphiles in aqueous solutions.

The evolution of the micelles in the subphase solutions after TiCl$_4$ addition was studied using SANS to investigate the interactions between titania species and micelles in ethanol. Figure 1a compares the scattering for PEPEG alone in solution and that of solutions at a similar concentration of PEPEG immediately after addition of TiCl$_4$. These demonstrate that the initial interaction of the titania precursors with the micelles is rapid, causing alterations even in the first scattering pattern and soon afterward the scattering patterns show a clear structural transition (Figures 1b−d), which is nonlinear with respect to time. Multiple contrasts were generated by varying the deuteration of the ethanol and the transitions were consistent, regardless of the deuterium content of the solvent. At all concentrations, an initially slow development was followed by a period of rapid transition that was followed again by slow change. The duration of the initial slow reaction stage varied with reagent concentration, as lower concentrations of TiCl$_4$ reacted faster than high concentrations.

In all cases, data for at least two contrasts for each reaction stage, were modeled simultaneously with a polydisperse core−shell sphere model,[43] in which the polydispersity of the core radius followed a Schulz distribution as described above (see Figure 2a for a typical fitted data set). Models including prolate and oblate ellipsoids, and cylinders were also tested but did not fit the data. Using the initial SAXS fitting, the core was assumed to contain the polyethylene chains from the PEPEG and this did not alter significantly in size during the reaction (Table 1). The shell initially containing only the polyethylene glycol chains from the PEPEG surfactant and ethanol, gradually accumulated titania species during the reaction, to form a composite polyethylene glycol, ethanol and titania filled region altering in size and scattering length density. The majority of experiments were conducted over a Q range of 0.01−0.07 Å^{-1} and fitted over this range. As data collection for each sample did not begin at precisely the same time, and data collection times were shorter in 100% D$_6$ ethanol than for 70% D$_6$ ethanol, sufficient similarity in the time of the scattering patterns was only available at a limited number of times during the reaction. Modeling was thus restricted to patterns with two contrasts available at coinciding times. In all cases data was modeled by the form factor only, as inclusion of a structure factor to account for intermicelle interactions did not improve the quality of the fits and so was excluded to reduce the number of variables. The dilute solutions used and the difficulty of micelle formation in high ethanol content solvent mean that the volume fraction of micelles will be low and thus the structure factor will be negligible.

For some reagent ratios, data was also collected in a Q range of 0.05−0.33 Å^{-1}. To test the validity of the modeling, fitting was also conducted on this data. In addition to separate modeling, the data for the beginning and end of the reaction for both Q ranges were combined and fitting conducted over the full range of 0.01−0.33 Å^{-1}. As shown in Figure 2b these scattering profiles could also be modeled well by the polydisperse core−shell sphere model. Modeling of different reagent concentration at different stages during the reactions allowed the core radii (R_C), shell thicknesses (R_T), volume fractions (VF), core polydispersity (PD) and shell scattering length density (SLD) to be determined, and these are shown in Table 1.

The micelle core radius, R_c, was similar for all reagent concentrations and reaction times, as expected, while shell thickness, R_t, and total volume fraction, VF, both increased throughout the reaction. As seen in Figure 1, the reaction is nonlinear in time, and a period of rapid shell growth is observed (Figure 3). Polydispersity is similar for different reagent concentrations but increases during the period of rapid transition before falling back to the initial level, around 0.35, when the reaction slows again.

Fitting the SANS data allows calculation of compositional changes occurring in the micelles during the reaction by using changes in the SLD to calculate the distribution of surfactant, inorganic and solvent species in the shells. By using calculated molecular volumes and assuming all of the surfactant is in the micelles, the total volume of each component of the shells may be calculated. Published analysis of PEPEG states a molecular weight of 2939 g mol^{-1} and a poly(ethylene oxide) content of 81%, corresponding to a 54 PEO repeat unit

Table 1. Model Parameters for Different Reagent Concentrations and Reaction Times[a]

PEPEG/titiania (reaction time)	solvent D_6 (%)	VF ± 0.001	R_C (Å) ± 2 Å	R_T (Å) ± 2 Å	PD ± 0.003	SLD_{Shell} ($\times10^{-6}$ Å^{-2}) ± 0.02
0.019: 1	100	0.015	42	38	0.33	1.84
(3 min)	70	0.015	42	38	0.33	1.76
0.019: 1	100	0.034	41	49	0.40	2.67
(49 min)	70	0.034	41	49	0.40	2.24
0.019: 1	100	0.058	41	58	0.44	3.17
(53 min)	70	0.058	41	58	0.44	2.59
0.019: 1	100	0.088	42	78	0.30	3.49
(93 min)	70	0.088	42	78	0.30	2.88
0.05: 1	100	0.022	40	36	0.35	2.02
(9 min)	70	0.022	40	36	0.35	1.66
	50	0.022	40	36	0.35	1.62
0.05: 1	100	0.068	40	52	0.49	3.07
(33 min)	70	0.068	40	52	0.49	2.48
	50	0.068	40	52	0.49	2.03
0.05: 1	100	0.112	40	73	0.34	3.62
(41 min)	70	0.112	40	73	0.34	2.92
	50	0.112	40	73	0.34	2.22
0.05: 1	100	0.141	40	78	0.31	3.65
(81 min)	70	0.141	40	78	0.31	2.99
	50	0.141	40	78	0.31	2.24
0.089: 1	100	0.035	41	41	0.28	2.14
(2 min)	70	0.035	41	41	0.28	1.95
0.089: 1	100	0.142	41	64	0.37	3.43
(6 min)	70	0.142	41	64	0.37	2.76
0.089: 1	100	0.175	41	76	0.29	3.50
(68 min)	70	0.175	41	76	0.29	2.88
0.089: 1*	100	0.031	40	36	0.38	2.71
(3 min)	70	0.031	40	36	0.38	2.22
0.089: 1*	100	0.140	40	76	0.32	3.42
(80 min)	70	0.140	40	76	0.32	2.94

[a] During fitting the SLD of the micelle core was set to -0.33×10^{-6} Å^{-2}, calculated for the alkyl chain region of the micelles, and the solvent SLD was held at a value appropriate for the level of deuteration: 5.39×10^{-6} Å^{-2} for 100%, 3.99×10^{-6} Å^{-2} for 70%, and 3.05×10^{-6} Å^{-2} for 50% D_6 ethanol. Fitted data covers a range of 0.01−0.07 Å^{-1}, except for data marked by asterisk (*), which corresponds to a range of 0.01−0.33 Å^{-1}.

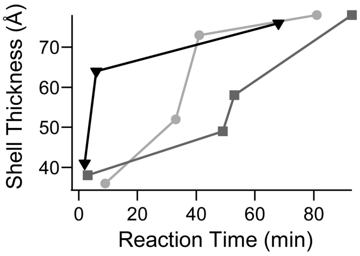

Figure 3. Nonlinear growth of shell thickness in subphase particles with time. 0.019 PEPEG/1 $TiCl_4$ (squares) reacts slowest while 0.089: 1 (triangles) reacts quickly; 0.05: 1 (circles) is between the two.

headgroup and a tail of 20 polyethelene repeat units.[37] Given the volume of a PEO unit[46] is 38.8 cm^3 mol^{-1} and the density of polyethylene[47] is 0.92 g mol^{-1}, it is straightforward to calculate the headgroup volume, V_{head}, and tail volume, V_{tail}, as 3479 and 1008 Å^3, respectively. Using these, and fitted SLDs, the volumes of each component in the shells can be calculated and are shown in Table 2. (see Discussion below for comments on these values).

Films Formed at the Solution Interface. (*a*). *Brewster Angle Microscopy*. Formation of PEPEG templated films at the air−solution interface was studied using BAM to observe the effect of different reagent concentrations on the film formation time. For all concentrations, a regular series of changes were observed in the surface during film formation as shown in Figure 4.

After the film precursor solution was poured into a Petri dish, a highly mobile surface with no apparent structure was visible in the live image of the BAM. This remained unchanged until a rapid increase in the reflected light intensity was accompanied by cessation of movement and a significant reduction in solvent evaporation rate. This was defined as the point of film formation. After a film had formed, the reflected intensity from the stationary, uniform surface continued to gradually increase over time, suggesting the film thickness continued to increase. The intensity variation observed in the live image is not fully observed in Figure 4 because of automatic gain adjustment during image collection.

Using this transition, film formation times can be plotted against the respective reagent concentrations (Figure 5). Both higher HCl and higher PEPEG surfactant concentrations reduced film formation time. However, for titania precursor, $TiCl_4$, variation about an optimum concentration, giving a minimum formation time, was observed. In all cases, after BAM observation collection of the readily visible opaque, white film from the interface was attempted using either a microscope slide or a plastic mesh with 1 cm^2 holes. Although the lowest $TiCl_4$ concentrations produced thin films that could not be recovered intact, the majority of the films were robust. The films collected onto mesh remained

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(46) Maccarini, M.; Briganti, G. *J. Phys. Chem. A* **2000**, *104*, 11451.

(47) Sigma-Aldrich Polyethylene MSDS [online], 2008, http://www.sigmaaldrich.com/catalog/DisplayMSDSContent.do, product number 427772 (accessed July 20, 2010).

Table 2. Comparison of Total Shell Component Volumes for Different Reagent Concentrations and Reaction Times[a]

PEPEG/$TiCl_4$	time	V_{PEO} (cm^3) ± 0.005	V_{EtOH} (cm^3) ± 0.005	V_{TiO_2} (cm^3) ± 0.005	molar ratio EtOH/TiO_2
0.019: 1	3 min	0.036	0.008	0.017	0.15: 1
	49 min	0.036	0.046	0.018	0.85: 1
	53 min	0.036	0.082	0.018	1.5: 1
	93 min	0.036	0.153	0.042	1.3:1
0.05: 1	33 min	0.053	0.103	0.017	2: 1
	41 min	0.053	0.235	0.045	1.7: 1
	81 min	0.053	0.283	0.059	1.6: 1
0.089: 1	2 min	0.071	0.038	0.034	0.36: 1
	6 min	0.071	0.218	0.037	1.9: 1
	68 min	0.071	0.302	0.078	1.3: 1

[a] Errors are based upon the effects of manual variation of the volume calculations.

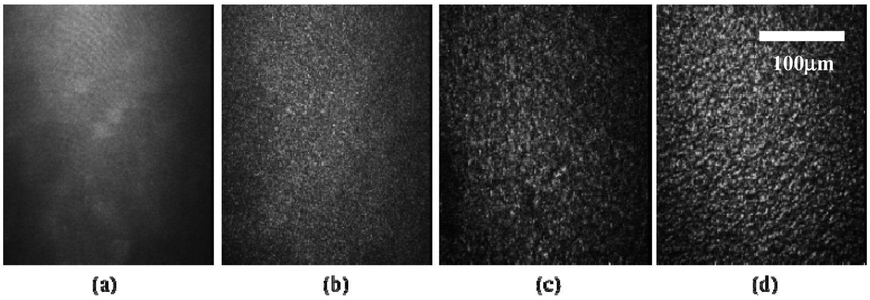

Figure 4. Progression from a highly mobile surface to a stationary, uniform film observed by BAM. A highly mobile surface is seen after 4 (a) and 27 min (b), while a stationary surface and increased intensity are seen after 42 (c) and 47 min (d), after a film has developed at the interface.

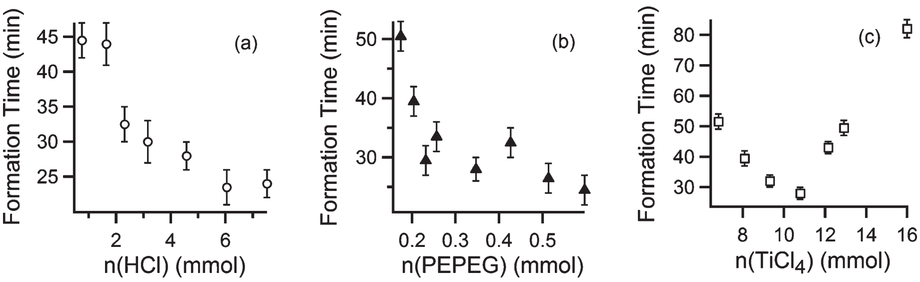

Figure 5. Film formation time at varying concentrations for (a) HCl, (b) PEPEG, and (c) $TiCl_4$.

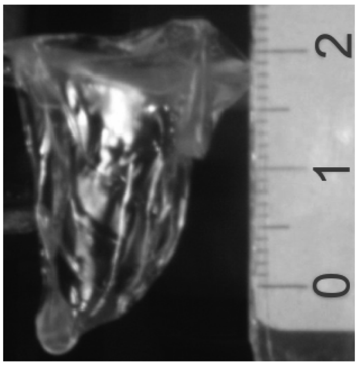

Figure 6. Self-supporting PEPEG–titania film removed from the air–solution interface, prepared using 1 g of surfactant. The ruler is in cm.

intact as they dried in air and in some cases large sections of self-supporting titania–PEPEG film could be recovered (Figure 6). Films collected on microscope slides also remained intact as they dried.

Film development at the air–solution interface was studied using both time-resolved off-specular reflectivity and specular reflectivity on ID10B, at the ESRF. Film formation in time-resolved reflectivity experiments was observed as the loss of the specular peak (see Supporting Information Figure S1) within a few minutes after the solution was poured into the trough. No further mesostructure development was observed and when inspected by eye the films had become macroscopically rough within minutes of formation, preventing any reflected signal being recorded. At all reagent concentrations the intensity of the specular peak was observed to fluctuate before it disappeared, suggesting formation of a composite surfactant-titania layer at the interface prior to full film development. Similar behavior has been observed for silica–surfactant films grown from aqueous solutions where film development is much slower.[48] We also note that no film growth was observed as long as the solutions remained covered, but upon removal of the lid, film development occurred normally within a few minutes. Specular reflectivity patterns collected from these films were unreliable due to the nanoscale surface roughness and could not be fitted.

Film structure was therefore determined by harvesting films from the solution surface after they had formed.

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(48) Brennan, T.; Hughes, A. V.; Roser, S. J.; Mann, S.; Edler, K. *Langmuir* **2002**, *18*, 9838.

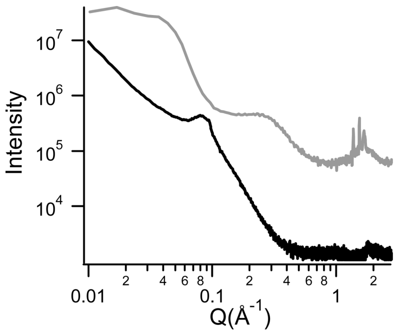

Figure 7. SAXS patterns of film material before (gray) and after (black) calcination.

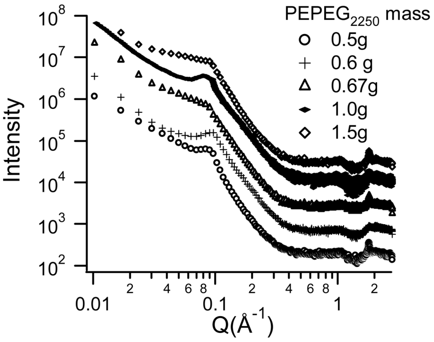

Figure 8. SAXS patterns of dried, calcined films formed using different amounts of PEPEG.

Table 3. Mass Percent Inorganic Material for PEPEG−Titania Films

Ti:/PEPEG mole ratio	0.048: 1	0.032: 1	0.032: 1.5
mass % inorganic	17%	20%	25%

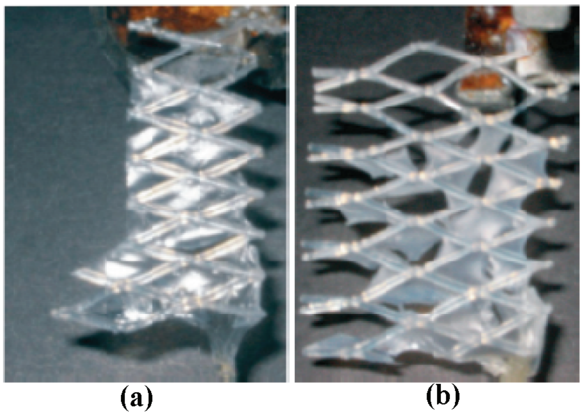

Figure 9. Pictures of PEPEG−titania films removed from the air−solution interface onto a plastic mesh and dried, showing the effects of added (a) 10 000 MW PEO and (b) 600 000 MW PEO. The side of each mesh rhombus is 1 cm in length.

Dried films were ground into a powder for SAXS analysis. Dried films were also calcined at 400 °C in air and powder patterns were collected using SAXS (Figure 7). Removal of the surfactant leads to a considerable change in the structure and the amount of material was also greatly reduced after calcination suggesting high surfactant content in the film. Peaks at 1.36, 1.50, and 1.66 Å^{-1} are present in the patterns before calcination but not afterward, suggesting that they belong to a crystalline surfactant phase removed during calcination; however, no peaks from crystalline titania are observed prior to calcination. Scattering from the calcined films varies with PEPEG concentration (Figure 8), and a similar variation was observed when the amounts of HCl and TiCl$_4$ were varied (data not shown). In all cases a broad shoulder or peak appears in the scattering pattern in the range 0.083 − 0.091 Å^{-1} corresponding to a distance within the range 69 − 75 Å. The peak at high angle, Q = 1.81 Å^{-1}, is assigned to the anatase phase of crystalline titania,[49] which is expected to form during calcination.

Although attempts to model the full data range were not successful, modeling within the range 0.01−0.35 Å^{-1}, comparable to the range of modeling of micelles in solution, suggested ellipsoidal micelles were encapsulated in the uncalcined films. Attempts at modeling core−shell or uniform particles showed that uncalcined PEPEG−titania films were best treated as ellipsoids of organic material in a titania matrix. The polyethylene ellipsoids had a rotation axis of 33 ± 1 Å and a major axis of 54 ± 1 Å, comparable to the size of micelles in the synthesis solutions from the SANS and SAXS measurements described above.

The inorganic content of dried films was assessed by TGA (Supporting Information, Figure S2). Films were grown on precursor solutions at surfactant to titania precursor molar ratios of 0.048: 1, 0.032: 1, and 0.032: 1.5. The decomposition temperature was observed to be lower for higher surfactant concentrations suggesting that surfactant in the film is less protected from decomposition. At higher titania concentrations the inorganic content, indicated by the mass remaining at 500−600 °C, increases (Table 3), suggesting more titania, relative to surfactant, becomes integrated into the films.

Although the PEPEG−titania films could be removed from the interface, the observation of some film cracking during drying, led to inclusion of additional homopolymer in an attempt to reinforce the films via polymer inclusion in the titania walls. Two different molecular weights of PEO (10 000 or 600 000 MW) were added to the PEPEG solutions in ethanol prior to HCl addition, at 10−35 wt % versus PEPEG. Film formation appeared unchanged; however, the polymers did have an effect on the films as they dried. Films without added PEO changed from opaque white to transparent as they dried with some cracking observed after several hours. As shown in Figure 9, addition of 10 000 MW PEO made the films more robust, allowing them to dry fully to a clear material without cracking. The addition of 600 000 MW PEO, however, appeared to destabilize the films as they pulled away from the supporting mesh and remained opaque.

Film-forming solutions with added polymer were also investigated using off-specular X-ray reflectivity. Film formation occurred within 30s with the specular peak being lost completely from one scan to the next, similar to the observations made for films without added PEO. Reflectivity on in situ films also showed little structure due to the roughness of the film surfaces. However SAXS

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(49) Angerer, P.; Yu, L. G.; Khor, K. A.; Krumpel, G. *Mater. Sci. Eng., A* **2004**, *381*, 16.

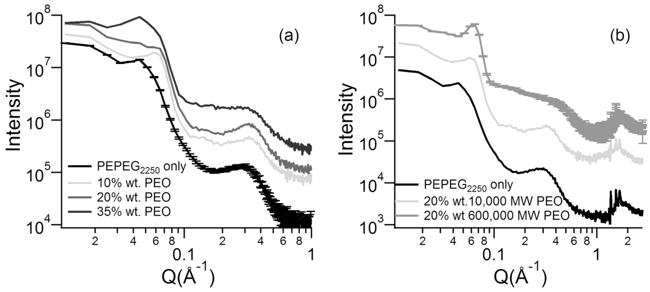

Figure 10. SAXS patterns showing the effect of PEO polymer addition on dried PEPEG-templated titania films: (a) different amounts of added 10 000 MW PEO and (b) different polymer molecular weight. Error bars are shown on one pattern in both a and b and are comparable in all other cases.

Table 4. Summary of SAXS Modeling for Films Using Additional PEO

PEO MW (gmol^{-1})	PEO % wt	shape	R_a (Å) ± 2	R_b (Å) ± 2
N/A	0%	ellipsoidal	33	54
10 000	5%	ellipsoidal	32	55
	10%	ellipsoidal	35	47
	20%	ellipsoidal	33	42
	35%	ellipsoidal	39	40
600 000	10%	ellipsoidal	32	40

patterns (Figure 10) from the recovered dried films showed some enhancement of mesoscale ordering when PEO was added to the film formation solutions. As in the case without polymer, the best model for the system was found to be ellipsoidal polyethylene particles in a titania matrix. Table 4 summarizes these results, showing the impact of PEO addition. Whereas films made using a purely PEPEG template have an oblate ellipsoidal pore structure, films containing additional 10 000 MW PEO are found to have near spherical pores, which become more spherical when more 10,000 MW PEO was added.

Discussion

Film formation at the air−solution interface has been observed in BAM and X-ray reflectivity to occur within 60 s, after a period in which no development occurs at the interface and this mimics, but is more rapid than, development observed in the subphase solution in sealed cells using SANS. This is, to our knowledge, the first report of time-resolved measurements on surfactant templating of titania in solution. Previous studies investigating the formation of surfactant-templated silica particles using small-angle scattering have been reported;[3,50] however, equivalent studies with titania are more challenging because of the higher reactivity of the titania precursors.[5,16,27] Ethanolic solvents and high acidity are recognized methods to reduce the uncontrolled condensation of transition metal precursors and both methods have been used here to successfully control the reaction of the $TiCl_4$ precursor.[17,27]

Table 2 shows formation of polydisperse spherical core−shell micelles in solution, suggesting that a layer of titania condenses in the headgroup region of spherical PEPEG micelles. This agrees with the expectation of spherical micelles at concentrations of less than 5 wt % surfactant. The core radius remains unchanged throughout the reaction, while the titania-rich shell grows in thickness. Shell growth is found in silica systems also, although the constant micelle core size is in contrast to some results for silica using PEO-PPO-PEO block copolymer templates.[51] Silicon alkoxides liberate alcohol as they undergo hydrolysis, and this can swell a PPO micelle core;[52] however this is not observed here and is also not expected to occur for a polyethylene−PEO surfactant because of the nonpolar micelle core.

In-situ SAXS studies of the development of silica templated by PEO−PPO−PEO nonionic surfactant reported that initially spherical particles become elongated as the formation reaction proceeds, eventually becoming cylindrical.[3] This was attributed to the aggregation of particles in solution, leading to development of larger, elongated micelles prior to the formation of an ordered phase. In our work, however, no particle aggregation in the subphase is observed. As the structure factor was found to have little influence of the modeling, which would not be the case if interparticle interactions were significant, it is concluded that no strong interactions occur between titania−PEPEG hybrid micelles. In ethanol, therefore, the titania-coated micelles develop individually and do not aggregate in the subphase solution.

Similar results have also been reported for film-forming silica systems templated by alkyl oligoethylenoxide surfactants which form oblate ellipsoid particles in the subphase solution.[50] These particles retained their shape, albeit with a size increase in the major axis, throughout the reaction. That work noted a discrepancy between film and solution development at high silica/surfactant ratios, above 10.8.[50] It was observed that although films form at such ratios if an interface is available, no development of order occurs in solution and precipitation does not occur in the subphase until after film formation has occurred at the interface. It was concluded that high silica content solutions required the presence of the air−solution interface to form films.

Because reagent ratios of above 10 Ti/1 PEPEG are used in this work, it is probable that a similar effect is responsible for the discrepancy between film formation and subphase aggregation in this work. In film formation, a large surface area is available for this process to occur that was not available in the cuvettes used for the SANS subphase studies. Additionally, we note that no film formation occurs if the solution is in a sealed container, so the formation of a continuous membrane requires some evaporation from the solution surface. Thus we suggest that evaporation, resulting in a steady state that increases the concentration in the vicinity of the interface, similar to that observed at the surface of aqueous surfactant solutions,[53]

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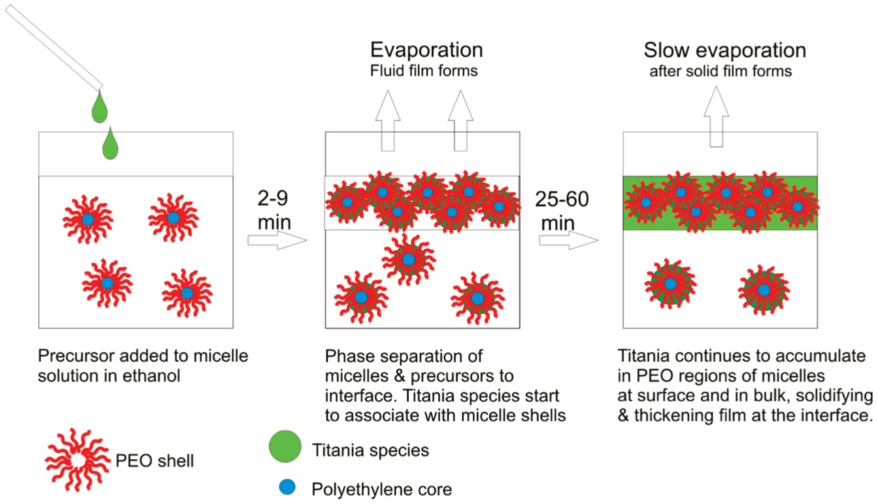
(50) Fernandez-Martin, C.; Roser, S. J.; Edler, K. *J. Mater. Chem.* **2008**, *18*, 1222.

(51) Flödstrom, K.; Wennerstrom, H.; Teixeira, C. V.; Alfredsson, V.; Linden, M.; Amenitsch, H. *Langmuir* **2004**, *20*, 10311.

(52) Ruthstein, S.; Frydman, V.; Goldfarb, D. *J. Phys. Chem. B* **2004**, *108*, 9016.

Scheme 1. Suggested Formation Mechanism of PEPEG−Titania Films in Ethanol



is required for particle aggregation and film formation. If film formation were occurring gradually at the interface, by addition of individual micelles below the film, formation of a uniform, static film in BAM and loss of specular reflection in reflectometry would be expected to be gradual, as reported previously.[25,48,50] The rapid changes observed here do not reflect such a process but support a phase separation mechanism, with film formation occurring as the evaporative steady state is established. The film precursor solutions are too dilute for the aggregation of hybrid micelles to occur in solution, and as a result, film formation is forced to occur in a phase separated layer at the air−solution interface where the local concentration is higher. An overview of the process is shown in Scheme 1.

In the solution subphase, the growth of the titania shell likely occurs through the migration of individual precursor species or small oligomers to the micelle palisade region. Although $TiCl_4$ rapidly undergoes conversion to an ethoxide species in the ethanol solvent, which rapidly hydrolyze in the acidic conditions used, subsequent condensation is inhibited.[17,27] Condensation is further restricted by the presence of stable species, such as $Ti_3(OCH_2CH_3)_{12}$, that resist both hydrolysis and condensation.[54] Titania precursors are known to interact preferentially with the PEO blocks of copolymer surfactants, as observed; however, these interactions vary with the amount of water present.[5,16,55]

Under the conditions used, there is sufficient water present that disruption of surfactant self-assembly because of Ti chelation interactions, reported for very low hydrolysis ratios, does not occur. Rather, at the higher water contents studied here, hydrogen bonding occurs between titania precursors and PEO groups.[16] As acidic conditions increase hydrogen bonding interactions and the surface activity of PEO chains,[32] it is reasonable to expect them to be strong in the present work. The hydrogen bonding and hydrophilic−hydrophilic interactions responsible for core−shell particle formation are strong between the surfactant PEO groups and inorganic species but do not lead to particle aggregation, limiting development to growth of the titania shell. Also, as the number of micelles is relatively low, at the concentrations used, collisions that could cause aggregation will be infrequent.

It is also possible to examine the composition changes within the shell through consideration of the scattering length density (Table 2). Initial volumes of surfactant, ethanol and titania in the shells depend upon the reagent concentrations used, with a 1 PEPEG/3 $TiCl_4$ ratio giving an initial ethanol to titania ratio less than half that calculated when a 1 PEPEG/1.33 $TiCl_4$ is used. This is consistent with strong interactions between inorganic precursors and surfactant as a greater relative concentration of $TiCl_4$ gives a greater presence of titania precursors in the initial particle shell.

As expected, given the unchanging micelle core in the particles, the PEO volume in the shell remains constant while the volumes of ethanol and titania both increase over time as the shell becomes thicker. They do not increase at the same rate and the molar ratio of ethanol to titania progresses toward approximately 1.3: 1 over time. An increasing inorganic content in the shell region has also been reported for formation of core−shell silica particles.[50] This was attributed to condensation of a silica layer around surfactant micelles with progressive exclusion of solvent, accompanied by a reduction in shell thickness. Unlike the silica case, in this work, condensation of titania in the shell is concurrent with additional titania precursors coming to the shell surface, as thickness and titania content both increase, particularly during the period of rapid reaction (see Figure 1 and Table 2).

As additional inorganic precursors migrate to and become incorporated into the shell the content of both inorganic material and organic material in the shell will increase if incompletely hydrolyzed precursors bring organic ligands with them. Titania forms stable trimeric species in solution such as $Ti_3(OCH_2CH_3)_{12}$ that are expected to be present in these reactions.[28,54] Migration

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(53) Åberg, C.; Sparr, E.; Edler, K. J.; Wennerström, H. *Langmuir* **2009**, *25*, 12177.
(54) Sanchez, C.; Livage, J. *New J. Chem.* **1990**, *14*, 513.
(55) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813.

of such species to the shell will raise the ethanol to titania ratio. It is also reported that a considerable amount of ethanol can become bound into copolymer-templated titania materials formed in acidic conditions, and it is likely that such processes also occur here.[16] At later times the titania precursors condense because of their greater proximity in the particle shell and ethanol begins to be excluded from the shell, reducing the ethanol/titania ratio, in a comparable situation to that for the silica system.[50] This process continues after the titania in solution is used up, corresponding to the final region of slow change at the end of the observed reaction in the SANS data.

Therefore, self-assembly in the PEPEG-titania solutions occurs through the formation of a titania shell around spherical PEPEG micelles because of hydrogen bonding and hydrophilic−hydrophilic interactions. This is enhanced by the positive charge on growing titania oligomers in acidic conditions below the isoelectric point (which occurs at pH 4.3[56]) and by greater surfactant activity and hydrogen bonding of PEO blocks in acidic conditions as previously noted for similar silica/aqueous triblock copolymer systems.[16,18,32,48] As titania is incorporated into the shells, the solvent content initially also increases because of binding of precursors that have retained ethoxide ligands; however, the shells progress toward denser titania as the precursors condense. The hydrophobicity of the core−shell particles will also increase as Ti−OH groups are lost as condensation proceeds and may contribute toward a higher concentration of micelles gathering at the interface thickening the film later in the reaction. Although no micelle aggregation is observed in the subphase, when evaporation occurs, a phase separation process causing rapid formation of a thick, but initially fluid film, from the hybrid micelles is observed, because of the steady state formed at the interface of the solution, similar to that seen in surfactant solutions at concentrations close to a phase boundary.[53] Continuing condensation of titania causes the fluid film to solidify, and the solid film gradually increases in thickness as more material arrives from solution because of increasing hydrophobicity of the coated micelles at later reaction times.

The dependence of film formation time on the various components shown in Figure 5 is also interesting. The dependence upon PEPEG concentration is straightforward, with increasing surfactant concentration resulting in faster film formation times, as expected for any mechanism involving the interaction of titania-coated micelles to form a continuous film (whether via phase separation or gradual accumulation at the interface). Increasing HCl concentration, however also increases the speed of film formation. Acid slows the rapid condensation of titania precursors because it retards condensation and encourages formation of longer, linear chains rather than branched chains.[27,57] Increased acid concentration is thus expected to slow down film formation rates. However here the quantity of HCl added to the initial PEPEG solution is small compared to that generated by addition of $TiCl_4$. Similar observations of faster formation times with increased acid for silica templated by nonionic surfactant were attributed to an increasing concentration of Cl^- ions in a counterion mediated binding mechanism, which had a greater influence than increasing acid.[50] This is also unlikely here since the $TiCl_4$ has a greater contribution to the amount of Cl^- in solution than the HCl added initially. Increased acid concentration, however, enhances micelle formation in EO-based surfactants in ethanolic solution and increases hydrogen bonding in PEO headgroups,[16,18,32] which would increase film formation rates. Therefore the observed reduced formation times at higher HCl concentrations is suggested to be due to aqueous acid encouraging PEPEG micelle formation and enhancing initial interaction with titania precursors. This early enhancement of micelle formation and of the inorganic-surfactant interactions increasing micelle hydrophobicity accelerates subsequent phase separation leading to a reduction in film formation and thus also film solidification time.

The effect of titania concentration in film precursor solutions is less straightforward as observed in the U-shaped curve of film formation time vs $TiCl_4$ concentration, Figure 5c. The growth of a titania coating around the PEPEG micelles reduces the barrier to phase separation, as it is otherwise prevented by the entropically unfavored interactions of PEO chains. As development of a coating is expected to be faster at higher titania concentrations this should be accompanied by reduced formation times. However, as the polymerizing titania will be charged in the acidic conditions used, the presence of more titania at the micelle surface will lead to greater repulsion, increasing the formation time and also the time required for a phase separated layer to solidify. This balance leads to the U-shaped curve observed for variation of titania concentration. As Ti concentration increased, PEPEG micelles become coated more rapidly, reducing the repulsion due to PEO chain overlap, leading to faster formation times. This increased binding of titania to PEPEG micelles is observed in the TGA results (Table 3) where a higher mass of titania relative to surfactant is found in films formed at higher titania precursor concentrations. Above a certain concentration the change in coating time is no longer significant and increased repulsions between coated micelles due to greater charge start to inhibit aggregation, leading to increased formation times. A similar balance has been reported for cationic surfactant templated silica films.[58]

The lack of long-range ordering in these films compared to those formed on aqueous solutions is also notable. Structural organization and inorganic condensation are concurrent processes during surfactant templated syntheses and formation of a highly ordered material is

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(56) Barringer, E. A.; Bowen, H. K. *Langmuir* **1985**, *1*, 420.
(57) Soler-Illia, G. d. A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 109.
(58) Edler, K.; Brennan, T.; Roser, S. J.; Mann, S.; Richardson, R. M. *Microporous Mesoporous Mater.* **2003**, *62*, 165.

effectively a race between these two processes.[57,59] If inorganic condensation occurs too quickly a disordered structure may be set. At the surfactant concentrations of less than 5% wt. used here, the surfactant forms polydisperse spherical micelles in solution, while SAXS patterns from developed film material show an oblate ellipsoidal structure. An ellipsoidal structure forms in solution at higher surfactant concentrations (25% wt.) suggesting that the change in micelle shape is occurring during agglomeration of micelles during phase separation into the more concentrated surface film. Changes in micelle shape from spherical to elongated are also seen in phase-separated silica–surfactant particles during synthesis.[60] However, the much more rapid condensation of titania sets a solid film structure before micelle growth and ordering can be completed. In addition, PEPEG surfactant micelles in solution are highly polydisperse, so polydispersity is also expected in the encapsulated micelles in the films causing any structural peaks in reflectivity or scattering profiles to be broadened or lost altogether.

Addition of extra PEO to the film forming solutions leads to the encapsulated micelles becoming more spherical (Table 4) as concentration or molecular weight of the added PEO are increased, but only a slight improvement in mesoscale ordering is observed. The films formed with 10 000 M_w PEO however are more resistant to cracking during drying, than those without PEO or with 600 000 MW PEO. These free PEO chains will also interact positively with the titania precursors in solution, also becoming coated with titania species during the reaction in competition with the PEPEG. We hypothesize that the smaller titania-coated PEO is sufficiently small to be incorporated between micelles during film formation reinforcing the film, whereas the larger PEO–titania composite is excluded, and also withdraws titania from the PEPEG micelle shells, leading to less robust films containing more spherical PEPEG micelles. Further experiments are required to confirm this.

Structuring is reduced upon calcination, and the film is observed to collapse to a powder during calcination. The long PEO sections of the surfactant are expected to be heavily interwoven in the titania walls of the material, as has been reported for silica systems.[57] Calcination may therefore lead to collapse of the walls through removal of this supportive matrix. A shoulder or broad peak in the calcined material SAXS patterns, Figure 8, corresponding to a distance of 70–76 Å is visible. Because the radius of the polyethylene micelle core is 30–40 Å in both the dried materials and the micelles in solution, this suggests a titania wall thickness of approximately ~10 Å if no shrinkage of the pores occurs (some pore shrinkage is also likely during calcination). This is considerably smaller than the titania–PEO shell observed in solution (~80 Å) during initial self-assembly. However, the volume of PEO to TiO_2 in the shell is only roughly 1:1 at the end of the solution-phase development, with ethanol also remaining in the shell. In more stable block copolymer templated films prepared via EISA, extra titania is found to bind to the exterior of the micelles, forming walls between micelles, to a thickness of 20–30 Å.[57,61] Increasing $TiCl_4$ concentration in our syntheses leads to extremely long film formation times, and ethanol evaporation prevents removal of a film separately from dried subphase material in these cases. We therefore conclude that film stability could better be improved via further deposition of titania into the dried free-standing composite films, for example, by vapor deposition followed by heat treatment to condense the titania and cause separation from the PEO segments, strengthening the inorganic walls.

Conclusion

Titania–surfactant composite films have been synthesized at the air–solution interface by templating with the block copolymer surfactant PEPEG from ethanolic solutions. The films form via a phase-separation mechanism in which titania precursors initially bind to surfactant micelles increasing their hydrophobicity. Phase separation at the interface caused primarily by evaporation from the solution surface then causes micelle aggregation and film development. In ethanolic solutions the block copolymer micelles interact with titania precursors forming composite micelles consisting of a growing titania shell in and around the palisade region of the PEPEG micelles. A critical point appears to exist at which development is very rapid, however no phase separation or aggregation in solution is observed during this process, strengthening the suggestion of an evaporation induced phase separation during film formation. The films are observed to be disordered because of fast formation and condensation prematurely halting micelle ordering and because of the polydispersity in micelle size. The addition of 10 000 MW PEO to the film precursor solution improved the crack resistance of the membrane but did not greatly alter the mesoscale structure.

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Supporting Information Available: Fitting results from SAXS data for PEPEG micelles in ethanol, experimental description and data for off-specular X-ray reflectivity experiments, and TGA data for PEPEG-TiO_2 films.This material is available free of charge via the Internet at http://pubs.acs.org.

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(59) Flödstrom, K.; Wennerstrom, H.; Alfredsson, V. *Langmuir* **2004**, *20*, 680.

(60) Linton, P.; Rennie, A. R.; Zackrisson, M.; Alfredsson, V. *Langmuir* **2009**, *25*, 4685.

(61) Sanchez, C.; Boissiere, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater.* **2008**, *20*, 682.