

Supplementary material

Factors influencing the swelling of triblock copolymer micelles

Structure of the P123 micelle with no oil

In the absence of oil, pluronic micelles have been studied by various authors using various scattering methods. Mortensen and Pedersen (1993)¹ reported SANS for the analogous P85 pluronic-water system as a function of temperature. As temperature increased for relatively low polymer concentration, the polymers first formed micelles from solution, eventually all polymers enter micelles above a critical temperature, these become prolate at relatively high temperature and eventually formed lamellar aggregates when they clouded out. At higher concentration the micelles interacted to form cubic micellar then hexagonal phases before transitioning to the lamellar phase. At lower polymer concentration, they observed an expansion of the micellar radius up to a critical point – this is the point at which the PO chains were fully stretched to 2.5Å per monomer, beyond which they could stretch no more. Beyond this point the stretching was entropically unfavourable, and the micelles become prolate ellipsoids.

Pedersen and Gerstenberg (2003)² made an analysis based on SANS and Monte Carlo simulation of P85 micelles. They reported the micellar structure to be almost independent of concentration and temperature. The micelles had aggregation numbers of 40-50, with a core containing 40% water and a radius of 40Å. The corona extended out to about 80-100Å, with approximately only 10% polymer. The core-corona interface was a diffuse region implying a mixed PEO-PPO composition. Pedersen and Gerstenberg (2003)² state their estimates of micellar size are consistent with those of Goldmints et al. (1999)³

and Liu et al (1998)⁴, except the former's core-water content is much higher than the latter's, and consequently their aggregation numbers are lower than the latter's.

Guo et al (2006)⁵ reported a temperature dependent swelling of P84 micelles in D₂O. They observed a hard sphere radius expansion from 66-73 Å for 23-50° C range, with an accompanying increase in core radius from 38.6-43.6 Å and aggregation number from 49-93. They attribute the changes to increased hydrophobicity of both PPO and PEO groups, and that led to more PPO segments in the core, removal of water from the core, and shrinkage of PEO segments. Further increases in temperature beyond about 50° C led to progressive transformation from spherical to cylindrical and then lamellar discs by around 80° C.

Goldmints et al (1999)³ concluded from their SANS and DLS studies on a deuterated triblock copolymer (EO₂₃PO₃₄EO₂₃) that while aggregation number and PPO content of the core increased as it dehydrated (at constant radius of 36 Å), the corona radii and thus micellar radii remained constant around 56-57 Å over a 10° C range (about 40-50° C) just above the critical micelle temperature, consistent with their dynamic light scattering data. The aggregation number increased from 21-35, and the percentage of PPO in the core ranged from around 40-60% over the same temperature range, implying a very large amount of water in the micellar cores.

Liu et al (1998)⁴ collected SANS data from P84 and P104 micelles at different temperatures and concentrations. They fitted their data using a micellar model with a

uniform core and a diffuse scattering length distribution for the EO corona and accounted for micellar correlations using adhesive interactions between EO groups in the corona that became more sticky at higher temperatures. At low temperature they found up to 20 wt% water in the core, and this reduced by an order of magnitude at higher temperature. They found that the P84 micelle contained a hydration number of 240 water molecules per polymer molecule yielding around 50% of water per micelle, mostly in the EO corona. A growth of no more than 10% in the micellar radius for P84 and P104 was observed over the range 35-55°C, the increase due to aggregation number increasing from around 85-120, as the polymers became more hydrophobic. The P84 and P104 diameters were around 122-145 Å and 172-192Å respectively. The cores increased from 76-86Å for P84 and from 102-112Å for P104 over the temperature range studies. Concentration had little effect on these sizes.

Effect of hydrochloric acid on swelling

Yang et al. (2006)⁶ investigated the effect of acid on micelle properties in the P123-water system using TEM, light scattering, FTIR and fluorescence microscopy. They showed strong acid-dependent aggregation of P123. Increased acid concentration led to an increase in the critical micelle temperature, likely due to stronger hydrogen bond interactions of protonated water molecules with EO groups. They proposed that this increased difficulty at expelling water as temperature increased explained the increased CMT, and also led to the increased size of micelles (around 16% higher) between 0 and 2M HCl, and lowered polydispersity. At higher acid concentrations at higher temperature they detected hydrolysis of the P123, i.e, degradation of the pluronic EO groups that would increase the PO:EO ratio, and thus also lead to increased micellar size due to the lowering of

interfacial curvature. In the experimental protocol reported here, the HCl concentration is approximately 1.6M. Given Yang et al.'s results, it is likely that the foam size has also been increased due to charge repulsions in the protonated water containing EO corona. Hydrolytic degradation with increasing temperature was probably not a major contributor to the swelling as we do not see a significant differential swelling away from that explained by simply adding oil.

Solubilization of TMB in pluronic micelles

Nagarajan (2001)⁷ reported the solubilization of various solvents by pluronic polymers based on reviewing available literature and developing a thermodynamic model for the solubilization. They noted that for pluronic micelles, aromatic hydrocarbons are far more soluble than aliphatic hydrocarbons – 17 times more soluble for benzene compared to hexane, for example. This has been explained in terms of the polarity and consequent interfacial activity of toluene versus hexane, and in terms of a volume-polarity parameter derived for many surfactants⁸. Also, for a given class of solvent, the degree of solubilization decreases as the size of the molecule increases. The measured solubilization capacity is a function of the Flory interaction parameter (estimated from Hildebrand solubility parameters). Nagarajan reports that the aromatic solvents with small Flory interaction parameters are good solvents for the PO blocks and thus have a greater tendency to solubilize in pluronic micelles than aliphatic molecules with larger interaction parameters. For P105 the relative uptake of various solvents is indicated by the volume fractions in the core of the micelle. For benzene: 0.379; toluene: 0.301; xylene: 0.269; cyclohexane: 0.151; hexane (0.05); and decane: 0.023.

Effect of trimethylbenzene on the swelling of the micelles

Lettow et al (2005)⁹ used SANS data and a thermodynamic model using a single fitting parameter (core polydispersity) to analyze their experimental data of oil swollen P123 with and without ethanol. They assumed monodisperse micelle size, a homogeneous distribution of only oil and PO groups in the core and no micelle-micelle interactions (i.e., a dilute approximation). Their model allowed a prediction of micellar size with 5% accuracy, and clearly showed a stabilization effect of added ethanol on oil swollen micelles. At 35°C, Lettow et al. measured an increase in P123 core diameter from 140-200Å and a concomitant slight corona thickness shrinkage from 20-18Å when increasing the oil content from a TMB:P123 ratio of 0.1-0.53. Above 0.53 ratio limit, no change in their scattering data was found with extra oil. They attributed this to the swelling limit associated with a microemulsion to microemulsion plus free oil phase boundary. This corresponds to an increase of 160-236Å before the micelle swelled no further, except with ethanol, where a small amount of additional swelling was observed to obtain micelles up to about 260Å. We prefer to see this as a swollen micellar to swollen micellar plus free oil transition, since no separate oil rich core is described.

Expansivity of the TMB

Thermal expansion data for toluene and xylene over the range 35-75° C suggests that the swelling of the resulting foam cells is only secondarily impacted due to this effect in TMB¹⁰. Volatilization of TMB at higher temperatures may also effect the size of the micelle. There are two scenarios – one is that the micelle will swell more at higher

temperatures as more TMB vapourizes and is preferentially adsorbed in the micellar core rather than in the aqueous phase; secondly, TMB vapour may escape from the micelles at higher temperature via diffusion through the aqueous phase and into the headspace. Under stirring, this diffusion distance may be minimized as micelles approach the air-water interface.

Effect of silicic acid on swelling and stabilization beyond the micelle limit

Upon hydrolysis of TEOS, silicic acid and related low molecular weight linear and cyclic oligomers are present as polar, uncharged species – uncharged as they are protonated at the pH of these syntheses. Their polar nature means they will partition from the oil-filled core to the EO corona, particularly if an oil such as TMB has partitioned to the micellar core. The micellar size dependence on silicic acid at low pH is not clear. If silicic acid displaces protonated water in the corona, then the EO group repulsions could decrease and an effective increase in micellar size may occur. On the other hand, if silicic acid does not displace water, but hydrogen bonds to water in the core, then a decrease in micellar size may result. The latter is favoured, since this has an entropic drive – i.e., more water molecules are liberated to the bulk than silicic acid oligomers are ordered on the EO chains. In either case, the effect is expected to remain constant as a function of TMB content. At higher temperature, the rate of silicic acid condensation will be expected to increase. This will likely have a stabilizing effect on the ability of micelles to uptake oil, particularly as the amount of oil uptaken is pushed beyond the limit of the micelle swelling limit, so that an oil-rich medium fills the core. This limit occurs when

the pluronic molecules are stretched to the point where they can no longer span the whole micelle (probably around 220Å for P123 according to Lettow et al.⁹).

Beyond this limit the micelles effectively transition to microemulsion droplets with an EO corona, a TMB swollen PO shell and an inner oil rich core. However the chemical potential of the two oil reservoirs require an equalization. To explain this, the adsorption of oligomeric silica species in the EO corona and their partial condensation to higher polymeric species could dehydrate the EO groups, allowing them to more strongly partition to the free-oil core, and balancing the chemical potential differential with the PO-oil rich inner shell. The partially-condensed silica-shell could also act to mechanically rigidify the micelles against disruption, by acting as a coherent, though flexible network, allowing larger micelles to stabilize than would be possible if no silica species were present. At temperatures lower than 75° C and above 2:1 TMB:P123, oil separated from the micelles/microemulsion droplets and products were not obtained. The rate of condensation may have been critical to stabilizing the larger micellar systems in the 5:1 and higher foams. At lower condensation rates, it is possible that the partial cross-linking of the silica network was too slow to allow partitioning of EO chains to the central oil core, thereby stabilizing it beyond the swollen micellar to microemulsion transition.

Aswal et al (2006)¹¹ studied the effect of oil, salt and alcohol on the micellization of P85 tri-block copolymers using SANS and the model of Petersen and Gerstenberg (2003)². They found that the micellar diameter and aggregation numbers increased with increasing

additives similar to increasing temperature. They state that this is an entropy driven process, based on dehydration of the pluronic polymers. It is likely that protonated silicic acid could act similarly, allowing dehydration of the EO corona and thus increasing the effective diameter of the micelles. Mata et al (2005) also noted an increase in the micellar size with various salts, and this could also be useful to note here in the context of the addition of silicic acid to pluronic micellar solutions.

Mata et al (2005) ¹² studied L64 micelles as a function of polymer concentration, temperature and salt concentration using FTIR, DSC and SANS. **They observed strong effects from these variables upon micellar aggregation.** In particular, for a given salt concentration they also observed a Hofmeister-like series of specific ion effects of the sodium halide salts, with a decrease in effect following the trend: F>Cl>Br>I. The increased interaction of micelles with salt/temperature also can be correlated to the ability to tune window size, either by increasing salt or by increasing temperature. Hofmeister type behaviour has been discussed in poly(oxyethylene) containing systems ¹³ and references therein (e.g., ¹⁴, ¹⁵).

Effect of ethanol on swelling

The effect of ethanol on foam cell sizes was not explicitly tested in this study. Soni *et al.* (2006) ¹⁶ studied the ternary P123-water-ethanol system using small angle x-ray scattering. In the L₁ phase region, they have shown micellar radius, core size and aggregation number decrease with increased alcohol content. Ethanol from the hydrolysis of TEOS most likely evaporates during the synthesis of the cellular foams obtained here, particularly during the 75° C syntheses. For the lower temperature syntheses here,

particularly at 35° C, the small amount of EtOH could contribute to a minor reduction in foam cell size, if the system here is analogous.

The approximate magnitude of micellar size reduction given by Soni et al.¹⁶ was around 7% reduction in radius with 5% (ww) EtOH. The EtOH product of TEOS hydrolysis contributes close to 5% in the oil free system here, and it is likely that all other syntheses will have less impact from ethanol due to the higher temperature driving the EtOH from the core or the lower total % of EtOH as oil content increased. They also observe a decrease in lattice parameter of liquid crystalline phases in the P123-water-EtOH ternary system as alcohol increased. All of this is consistent with an increased interfacial curvature with increasing EtOH, ie a trend to lower surfactant packing parameters.

When TMB and ethanol are both present in the system, Lettow et al. (2005)⁹ observed no significant change in micellar diameter, though they did note an increased capacity of the pluronic micelle for oil loading due the increased solubility of the TMB oil in the micellar core. This they attributed to the increased effective surface area of the PO blocks in the core when ethanol is present. Ivanova et al. (2001)¹⁷ studied the phase behaviour in the ternary system F127-water-solvent. They noted that ethanol showed amphiphilic behaviour and acted as a cosurfactant, preferentially moving to the interface of the core and corona of the micelle.

- (1) Mortensen, K.; Pedersen, J. S. *Macromolecules* **1993**, *26*, 805.
- (2) Pedersen, J. S.; Gerstenberg, M. C. *Colloids Surf. A* **2003**, *213*, 175.
- (3) Goldmints, I.; Yu, G.-e.; Booth, C.; Smith, K. A.; Hatton, T. A. *Langmuir* **1999**, *15*, 1651.
- (4) Liu, Y.; Chen, S.-H.; Huang, J. S. *Macromolecules* **1998**, *31*, 2236.
- (5) Guo, L.; Colby, R. H.; Thiyagarajan, P. *Physica B* **2006**, 385-386, 685.
- (6) Yang, B.; Guo, C.; Chen, S.; Ma, J.; Wang, J.; Liang, X.; Zheng, L.; Liu, H. *J. Phys. Chem. B* **2006**, *110*, 23068.

- (7) Nagarajan, R. *Polym. Adv. Technol.* **2001**, 12, 23.
- (8) Chaiko, M. A.; Nagarajan, R.; Ruckenstein, E. *J. Colloid Interface Sci.* **1984**, 99, 168.
- (9) Lettow, J. S.; Lancaster, T. M.; Glinka, C. J.; Ying, J. Y. *Langmuir* **2005**, 21, 5738.
- (10) Aicart, E.; Junquera, E.; Letcher, T. M. *J. Chem. Eng. Data* **1995**, 40, 1225.
- (11) Aswal, V. K.; Kohlbrecher, J. *Chem. Phys. Lett.* **2006**, 425, 118.
- (12) Mata, J. P.; Majhi, P. R.; Guo, C.; Liu, H. Z.; Bahadur, P. *J. Colloid Interface Sci.* **2005**, 292, 548.
- (13) Perreur, C.; Habas, J.-P.; Lapp, A.; Peyrelasse, J. *Polymer* **2006**, 47, 841.
- (14) Thiyagarajan, P.; Chaiko, D. J.; Hjelm Jr., R. P. *Macromolecules* **1995**, 28, 7730.
- (15) Jörgensen, E. B.; Hvidt, S.; Brown, W.; Schillen, K. *Macromolecules* **1997**, 30, 2355.
- (16) Soni, S. S.; Brotons, G.; M., B.; Narayanan, T.; Gibaud, A. *J. Phys. Chem. B* **2006**, 110, 15157.
- (17) Ivanova, R.; Alexandridis, P.; Björn, L. *Colloids Surf. A* **2001**, 183-185, 41.