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# ABA Amphiphilic Block Copolymers with Comb-like Segments from ATRP: Self-assembling Behaviour in Aqueous Solutions

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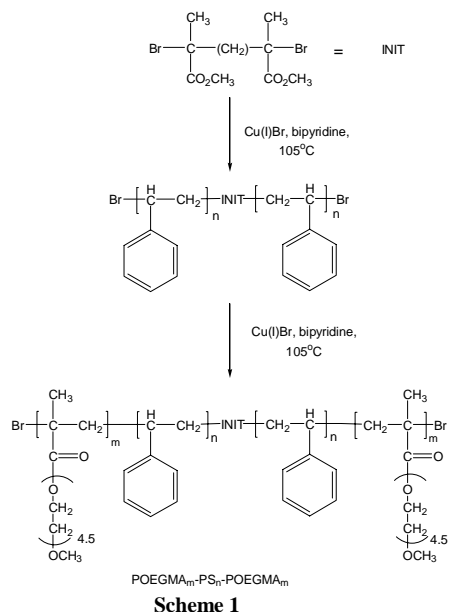
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## Introduction

Amphiphilic block copolymers (BCs) can adopt a variety of aggregate morphologies in solution where the solvent is selective for one of the blocks.<sup>1</sup> In many ways the morphological behaviour of BCs mirrors that of classic molecular amphiphiles. It is increasingly apparent however, that the complexity of the range and morphology of the aggregate structures formed is potentially larger and more varied than for 'simple' amphiphiles.<sup>2</sup> To date the majority of the fundamental studies of the self-assembly behaviour of BCs has been conducted on materials prepared by living polymerisation (LP) techniques for obvious reasons (low polydispersity and high purity, i.e. minimal contamination with homopolymer, diblock etc.). The increasing use of controlled radical polymerisations such as nitroxide mediated (e.g. TEMPO), atom transfer radical (ATRP) and radical addition fragmentation transfer (RAFT) polymerisations has allowed for the preparation of a plethora of novel BCs with a far greater range of chemical structures than previously available and also a greater range of macromolecular architectures.<sup>3</sup> Given the limitations on the application of LR techniques, academically and industrially, it is desirable that studies of self-assembling BCs are increasingly directed towards materials prepared in 'non-living' ways. Here we report preliminary results of our studies into the self-assembly behaviour of BCs prepared by ATRP in aqueous dispersions.

## Synthesis

Poly[olig(oethylene glycol methyl ether)]-*block*-polystyrene-*block*-[olig(oethylene glycol methyl ether)] (POEGMA-PS-POEGMA) copolymers were synthesised by atom transfer radical polymerisation techniques (Scheme 1). Two block lengths of PS were prepared by ATRP which were isolated and purified and used as macroinitiators for the subsequent polymerisation of OEGMA according to published procedures.<sup>4,5</sup>



The POEGMA lengths were varied to give a range of hydrophilic:hydrophobic weight ratios between the blocks (Table 1). The polydispersities of the resultant block copolymers were all less than 1.3. (Table 1).

## Aggregate Preparation and Analysis

Samples of the block copolymers were dissolved in THF (1ml) and water (9ml) was gradually added drop-wise to the stirred solutions over 1 hour. The mixtures were transferred to dialysis tubing and dialysed against water (3 x 3dm<sup>3</sup>) over 24 hours. The resultant dispersions were then analysed by TEM (uranyl acetate stained) and dynamic light scattering (DLS, Malvern Instruments HPPS). Critical aggregation concentrations (cac) were determined through fluorescent titrations using pyrene as the hydrophobic probe.

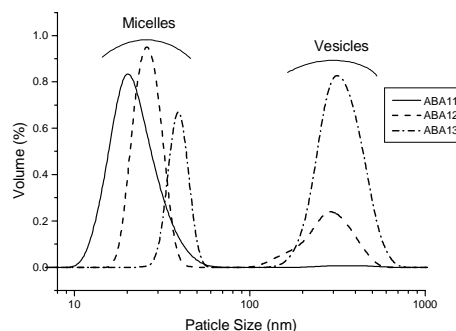
**Table 1.**

Sample	M <sub>n</sub>	DP PS	M <sub>w</sub> /M <sub>n</sub> <sup>a</sup>	Wgt ratio <sup>b</sup>	cac (x10 <sup>-2</sup> )
ABA 11	17 200	75	1.27	1.20	334
ABA 12	42 900	75	1.27	4.49	-
ABA 13	56 300	86	1.26	5.34	4.62
ABA 16	68 800	200	1.19	2.31	94.6
ABA 18	30 900	183	1.20	0.44	-
ABA 19	43 500	204	1.20	1.03	-
ABA 20	54 900	204	1.24	1.58	-
ABA 21	34 700	183	1.20	0.82	-

a from SEC; b hydrophilic:hydrophobic wgt. ratio from <sup>1</sup>H NMR

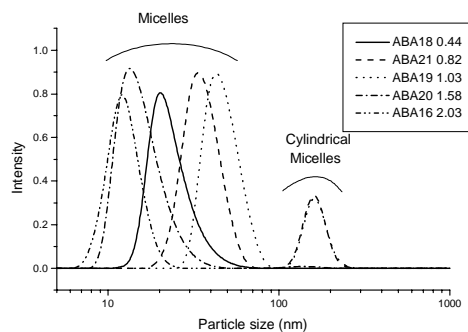
## Aggregate Sizes and Morphologies.

As expected, for the selected samples measured, increasing the hydrophilic:hydrophobic block ratio led to an increase in the cac (Table 1). DLS results suggested that the copolymers aggregate in two basic size ranges from 10-100nm and from 200-1000nm. For the shorter copolymers possessing the shorter chain PS (ABA11-ABA13) the higher the ratio, an increased size of, or increased proportion of larger size, aggregates were observed (Figure 1). Further samples with short chain PS have been prepared and are currently being investigated to extend this sequence.



**Figure 1:** Particle size measurements of ABA11-ABA13, copolymers possessing short chain PS segments.

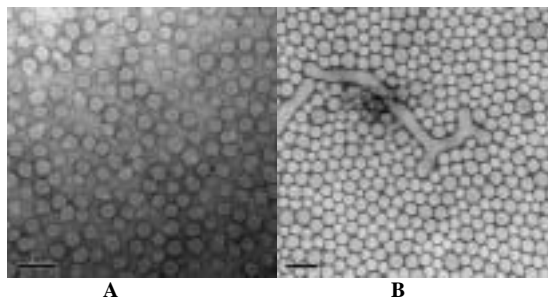
For the copolymer samples possessing longer PS blocks no clear correlation between the hydrophilic:hydrophobic ratio and the particle size was apparent (Figure 2).



**Figure 2:** Particle size measurements of ABA11-ABA13, copolymers possessing long chain PS segments.

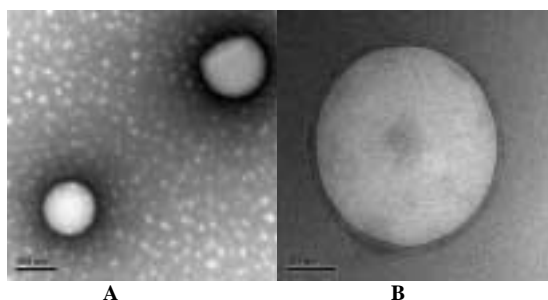
For all cases the relative purity and polydispersity of the samples are of interest to the effects on aggregate morphology. All samples are likely to have relatively high quantities (~10-15%) of AB diblock copolymers (as is inevitable with many ATRP synthesised copolymers – due up to 15% loss of end-group activity even at restrained monomer conversions).<sup>6</sup> The effect of polydispersity on aggregate morphologies is only just being investigated, though preliminary results from Eisenberg et al. suggests that polydispersity can have an effect on aggregate size and morphology.<sup>7</sup> These factors are currently under investigation.

TEM revealed that the two size ranges observed by DLS corresponded to micelles (10-100nm) and cylindrical micelles and vesicles (200-100nm). The samples possessing long PS segments (ABA16-ABA21) formed micelles in general (Figure 3A) with a number of cylindrical micelles (Figure 3B).



**Figure 3.** TEM micrographs showing A, micelles formed by ABA 18 and B, micelles and cylindrical micelles formed by ABA 21.

Of the two block lengths of PS studied however, only the shorter PS block lengths (ABA11-ABA13) showed vesicle formation. Representative micrographs of the stained samples are shown in Figure 4. Cylindrical micelles were not generally observed for these materials. As previously noted vesicles only formed for samples with relatively high hydrophilic:hydrophobic block ratios (> 1.2). This is in contradiction to the 'classical' model of copolymer amphiphilic self-assembling behaviour where, generally, increasing the interfacial area between block segments and the curvature of the hydrophilic block tends to result in block copolymers ascending the morphological sequence micelle, cylindrical micelle, vesicle.<sup>2</sup> As previously noted further POEGMA-PS-POEGMA samples have been prepared and are being investigated to confirm this phenomenon.

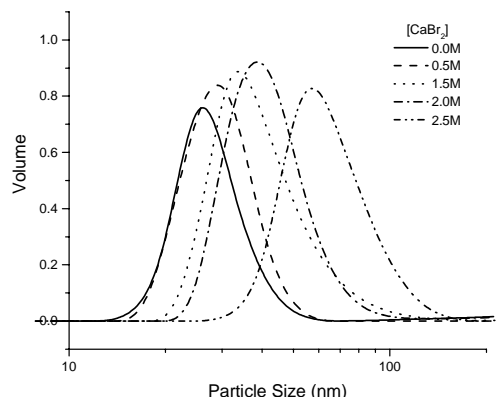


**Figure 4.** TEM micrographs showing A, vesicles and B, magnification of a vesicle, formed by ABA 13.

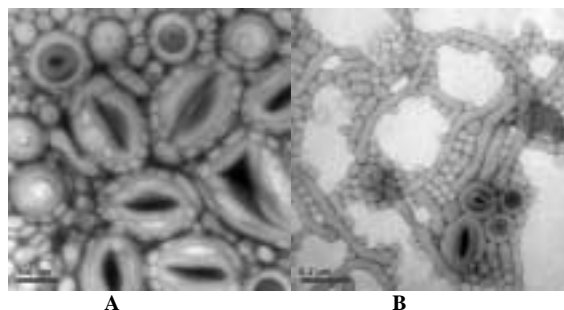
#### Addition of Metal Salts

Ethylene oxide chains form complexes and adducts with a variety of metal salts.<sup>8</sup> The effect of two salts, NaCl (which does not form adducts with ethylene oxide chains) and CaBr<sub>2</sub> (which does form adducts) were studied. Copolymer solutions of ABA19 and ABA17 were prepared in the presence of these two salts in varying concentrations (0.5M-2.5M). As expected NaCl had little effect on the aggregate size or morphology but did lower the critical aggregation concentration. In contrast the addition of CaBr<sub>2</sub> had the effect of increasing the average aggregate size (as measured by DLS, Figure 5) and changing the predominate morphology from micelles to cylindrical micelles (Figure 6B). Unusual puckered aggregates (Figure

6A) were observed in many of these samples and appear to be an intermediate morphology between cylindrical micelles and vesicles though the relative occurrence of these and their significance is still under investigation.



**Figure 5:** Particle size measurements of ABA17 in CaBr<sub>2</sub> solution.



**Figure 6.** TEM micrographs showing A, 'puckered' structures and B, micelles, cylindrical micelles and 'puckered' structures formed by ABA 19 (0.5M CaBr<sub>2</sub>).

#### Conclusions

A range of ABA amphiphilic block copolymers (POEGMA-PS-POEGMA) have been synthesised. Their behaviour in aqueous dispersions and salt solutions has been studied and a range of aggregates, from micelles to cylindrical micelles to vesicles, have been observed. Complexation of the hydrophilic POEGMA block with CaBr<sub>2</sub> has been demonstrated to profoundly affect aggregate size and morphology.

<sup>1</sup> Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1999.

<sup>2</sup> Antonetti, M.; Forster, S. *Adv. Mater.* **2003**, *15*, 1323.

<sup>3</sup> For a general overview see: *Chem. Rev.* **2001**, 101(9).

<sup>4</sup> Matyjaszewski, K., Patten, T.E., Xia J.H. *J. Amer. Chem. Soc.* **1997**, *119*, 674.

<sup>5</sup> Holder S. J., Rossi, N.A.A., Yeoh, C-T., Durand G.G., Boerakker, M.J., Sommerdijk, N.A.J.M. *J. Mater. Chem.* **2003**, *13*, 2771.

<sup>6</sup> Lutz, J.F., Matyjaszewski, K. *Macro. Chem. Phys.* **2002**, *203*, 1385.

<sup>7</sup> Terreau, O., Luo, L.B., Eisenberg, A. *Langmuir* **2003**, *19*, 5601.

<sup>8</sup> Owen, J., *Comprehensive Polymer Science*; Booth, C., Price C., Eds.; Pergamon: Oxford 1989; Vol. 2, Chapter 10, pp 657-678.