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ABA AMPHIPHILIC BLOCK COPOLYMERS WITH COMB-LIKE SEGMENTS FROM ATRP: SELF-ASSEMBLY IN AQUEOUS AND ELECTROLYTE SOLUTIONS

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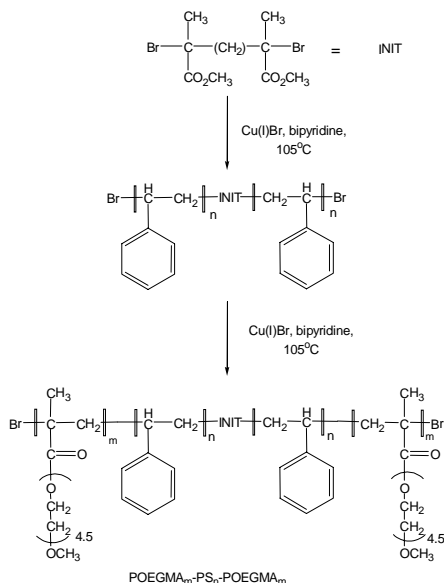
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Introduction

Amphiphilic block copolymers (BCs) can self-organize into various aggregate morphologies in solution where the solvent is selective for one of the blocks¹. The size and the shape of these various molecular assemblies depends upon the balance of hydrophilic and hydrophobic regions of the block copolymer. Among these aggregates, vesicles, which have been considered as powerful nanocarriers, are especially interesting for their applications in the design of drug delivery systems². Here we report preliminary results of our studies into the self-assembly behaviour of poly[olig(ethylene glycol methyl ether)]-block-polystyrene-block-[olig(ethylene glycol methyl ether)] (POEGMA-PS-POEGMA) prepared by atom transfer radical polymerisation techniques (ATRP) in aqueous dispersions. Many amphiphilic systems have been studied, but comb-like amphiphilic copolymers such as POEGMA-PS-POEGMA³ are yet to be fully comprehended.

Experimental

Synthesis. POEGMA-PS-POEGMA copolymers were synthesised by ATRP (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^{4,5}.



Scheme 1: POEGMA-PS-POEGMA synthesis mechanism

The POEGMA lengths were varied to give a range of hydrophilic: hydrophobic weight ratios between the blocks (Table 1).

Aggregate Preparation and Analysis. Aggregates of block copolymers were prepared by dissolving copolymers (10mg) in THF (1ml). 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 3dm³) 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. Molecular weight parameters of ABA copolymers

sample	M _n ^a	DP PS ^a	M _w /M _n ^a	Wgt ratio ^b	Cac (x10 ²) ^c
ABA11	17 200	75	1.27	1.20	334
ABA23	34 800	86	1.27	2.86	-
ABA12	42 900	75	1.27	4.49	-
ABA13	56 300	86	1.26	5.34	4.62
ABA16	68 800	200	1.19	2.31	94.6
ABA18	30 900	183	1.20	0.44	-
ABA19	43 500	204	1.20	1.03	-
ABA20	54 900	204	1.24	1.58	-
ABA21	34 700	183	1.20	0.82	-

a. from SEC; b hydrophilic:hydrophobic wgt. ratio from ¹H NMR; c. gL⁻¹

Encapsulation of a fluorescent probe. Efficiency of the encapsulation of anthracene as fluoprobe was demonstrated using fluorescence. Anthracene was dissolved in acetone and added to empty vials. Acetone was evaporated before adding the copolymer (10mg) dissolved in THF (1mL). Water (9mL) was added dropwise over 1 hour with agitation to obtain micellar solution with concentration of 1 gL⁻¹ of copolymer and 1.10-7M of anthracene. Samples were transferred into dialysing tubing, sealed and dialysed against deionised water for 24 hours at room temperature. Fluorescence measurements at set time intervals were recorded during the dialysis against water.

Results and Discussion

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, or increased proportion of larger size, of aggregates were observed (Figure 1)

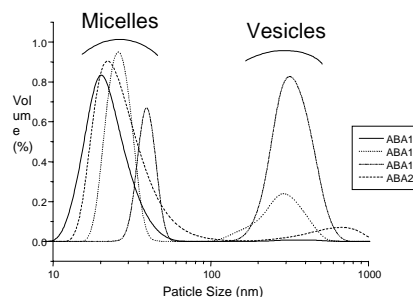


Figure 1. Particle size measurements of copolymers possessing short chain PS segments.

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

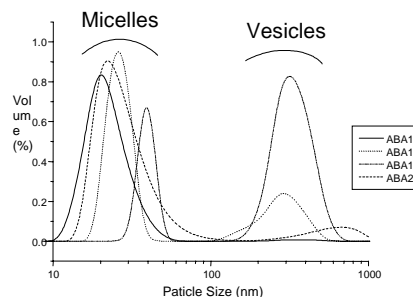


Figure 2: Particle size measurements of long PS segments.

The effect of polydispersity on aggregate morphologies is in the early stages of investigation, though preliminary results from Eisenberg et al. suggests that polydispersity can have an effect on aggregate size and morphology⁶. 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).

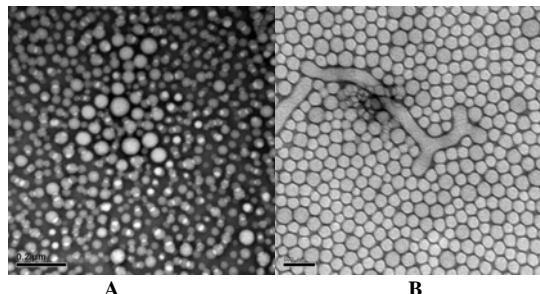


Figure 3 TEM micrographs showing A, micelles formed by ABA 18 and B, micelles and cylindrical micelles formed by ABA 21

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, vesicle⁷. As previously noted further POEGMA-PS-POEGMA samples have been prepared and are being investigated to confirm this phenomenon.

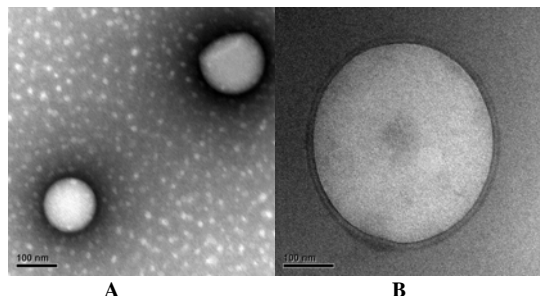


Figure 4. TEM micrographs showing A, vesicles and B, magnification of a vesicle, formed by ABA 13.

Addition of Metal Salts. Ethylene oxide chains form complexes and adducts with a variety of metal salts⁸. The effect of two salts, NaCl (which does not form adducts with ethylene oxide chains) and CaBr₂ (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 CaBr₂ 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.

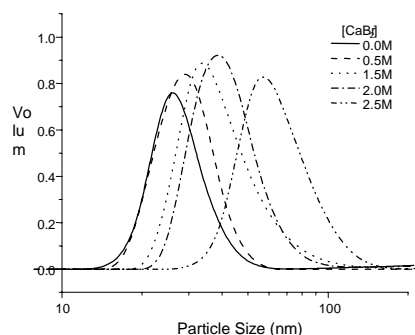


Figure 5. Particle size measurements of ABA17 in CaBr₂ solution.

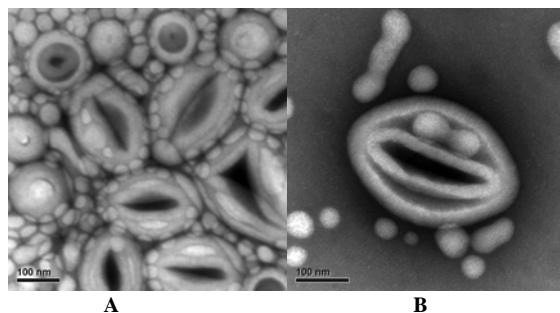


Figure 6. TEM micrographs showing A, 'puckered' structures formed by ABA 19 (0.5M CaBr₂) and B, micelles, cylindrical micelles and 'puckered' structures formed by ABA 19 (1.5M CaBr₂).

Encapsulation of a Fluorescent Probe. Fluorescence measurements were carried out in order to prove the encapsulation of the fluorescence probe. Anthracene is very hydrophobic and preferentially solubilise in the hydrophobic core of the aggregates. It displays a strong fluorescence in a non-polar environment and displays a weak fluorescence in polar media. Preliminary results show that anthracene does not remain in the hydrophobic core of the micelles during the dialysis. This works is still under investigation and different methods of encapsulation are currently being studied

Conclusion

Aggregates of POEGMA-PS-POEGMA were successfully prepared and their analysis by TEM and dynamic light scattering revealed the importance of the hydrophilic:hydrophobic ratio on the morphology and size of the aggregates. NaCl solution appears to have little effect on the aggregate size. Conversely CaBr₂ seems to affect the morphology of the aggregates changing the predominate morphology from micelles to cylindrical micelles.

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