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Block Copolymers

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Control of Vesicular Morphologies through Hydrophobic Block Length**

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Highly asymmetric amphiphilic block copolymers can self-assemble in selective solvents to form crew-cut aggregates of a wide range of morphologies, such as spherical micelles, rods, vesicles, and others.[1–4] In these aggregates, the long hydrophobic block forms either the core in micelles and rods, or the wall in bilayer structures, whereas the short hydrophilic block forms the corona. A number of research groups have studied block copolymer aggregates of various morphologies in the past.[5,6] Among these morphologies, vesicles and also liposomes made of phospholipids, are of great interest owing to their potential applications as encapsulation agents, particularly in the fields of biomedicine and drug delivery.[7] However, the stability of liposomes has been a concern owing to the high mobility of their lipidic components under

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physiological conditions; therefore, many efforts have been devoted to the stabilization of these structures by cross-linking or by the addition of polymeric stabilizers to the liposomes.[8] Polymeric vesicles, on the other hand, are robust structures and are very stable in aqueous solution.[6] These vesicles can be either equilibrium structures under certain conditions or, under others, kinetically trapped during preparation.[9]

To explore block copolymer vesicles for many potential applications, the control of vesicular characteristics, such as size, wall thickness, and inner volume, are of great importance. It is assumed that the parameters that control the morphologies of the aggregates, that is, core chain stretching, interfacial tension, and corona repulsion, are also responsible for the thermodynamic control of the vesicular architecture. Solution properties such as solvent composition, presence of additives (e.g. salts, acids, or bases) and water content were also shown to have a strong influence on vesicle size. For example, the addition of a base during the preparation of vesicles containing acrylic acid in the corona decreases the size of the vesicles owing to an increase in the electrostatic repulsion among the corona chains. The addition of acids or salts, on the other hand, increases the vesicle size owing to the screening of the electrostatic repulsion among the corona chains.[2,10,11]

Recently, the thermodynamic stabilization mechanism of diblock copolymer vesicles was elucidated.[12–14] It showed that the curvature in block copolymer vesicles is stabilized by preferential segregation of short hydrophilic blocks to the inside of the vesicles and the long blocks to the outside of the vesicle bilayer. The repulsion among the longer corona chains is greater than that among the shorter ones. Therefore, segregation of the hydrophilic blocks by length, which allows the formation of asymmetric lamellae, stabilizes the curvature of the vesicles.

The polystyrene-*block*-poly(acrylic acid) (PS-b-PAA) block copolymers, in all these studies, were synthesized by sequential anionic polymerization, as described elsewhere.[15,16] First, the PS block was prepared, followed by the addition of the *tert*-butylacrylate (*t*BA) monomer to form the PS-b-PtBA diblock copolymer. Finally, hydrolysis led to the corresponding amphiphilic diblock, PS-b-PAA. This method allows the formation of a PS block of a fixed length with varying PAA blocks. Although such block copolymers prepared by anionic polymerization are well defined with a polydispersity index (PI) of 1.1 or even lower, this method is technically challenging in that it is accompanied by the formation of homopolystyrene, which requires extensive purification.

Block copolymers needed for the exploration of the scaling relationships between the length of the acrylic acid block (in polymers containing a constant PS block length) and various vesicular parameters, such as size and wall thickness, are relatively easy to prepare by anionic polymerization, as described above. On the other hand, scaling relationships between the length of the styrene block (in polymers containing a PAA block of constant length) and various vesicular parameters have not been investigated systematically owing to the lack of appropriate synthetic methods for the preparation of such polymers. Herein we report on a new approach to the synthesis of block copolymers with a constant PAA block attached to PS blocks of various lengths as well as on trends in vesicle sizes and wall thicknesses as a function of the PS block length.

The PAA-b-PS block copolymers in this study were prepared by atom-transfer radical polymerization (ATRP).[17] Poly(*tert*-butyl acrylate) macroinitiators (PtBA-Br) with varying molecular weights and relatively low polydispersities (PI < 1.18) were prepared and used as precursors for the formation of PS blocks. By changing the [styrene]/[PtBA-Br] feed ratio, it was possible to synthesize well-defined block copolymers with a fixed PtBA block length and varying PS block lengths with relatively low PI values (see Supporting Information). Complete removal of the *tert*-butyl protecting groups of the PtBA block was accomplished by acid catalysis to obtain the corresponding amphiphilic blocks (see Supporting Information).[15]

It was shown, in a previous study, that vesicles made from PS_{310}-b-PAA_{28} copolymers in dioxane are relatively large and polydisperse (450 ± 160 nm). Increasing the THF content in the THF/dioxane solvent mixture results in the formation of smaller vesicles; further increase in the THF content leads to mixtures of vesicles and spheres, and finally, in pure THF, spheres are formed (Table 1).[4,11] On the basis of these

Table 1: Details of the morphologies obtained from various PAA-b-PS block copolymers.

Block copolymer[a]	PAA content [mol %][b]	Dominant morphology[c]	Average diameter [nm] in dioxane[d] TEM[e]	DLS[f]	in dioxane/THF (3:1)[d] TEM	DLS
PAA_{47}-b-PS_{670}	7	LCV	0.2–5 μm	ND	1–5 μm	ND
PAA_{47}-b-PS_{435}	9.8	V	340 ± 150	450	290 ± 120	420
PAA_{47}-b-PS_{370}	11.3	V	420 ± 150	410	200 ± 105	310
PAA_{47}-b-PS_{355}	11.7	V	300 ± 120	300	150 ± 75	395
PAA_{47}-b-PS_{310}	13.3	V	116 ± 19	150	108 ± 23	148
PAA_{47}-b-PS_{275}	14.6	V	94 ± 16	130	100 ± 20	140
PAA_{47}-b-PS_{250}	15.9	V	96 ± 17	124	75 ± 10	108
PAA_{47}-b-PS_{200}	19.3	M	20 ± 2	45	20 ± 2	45
PAA_{34}-b-PS_{325}	9.5	V	270 ± 110	415	370 ± 130	420
PAA_{34}-b-PS_{240}	12.5	V	180 ± 85	280	135 ± 60	185
PAA_{34}-b-PS_{190}	15.3	V	105 ± 22	144	85 ± 15	120

[a] Block copolymer composition (see Supporting Information). [b] Calculated by using the following equation: PAA [mol %] = $DP_{PtBA}/DP_{tot} \times 100$, where DP_{PtBA} is the average degree of polymerization of the PtBA block and DP_{tot} is the average total degree of polymerization of both blocks together. [c] Dominant morphology as observed by transmission electron microscopy (TEM). LCV = large compound vesicles, V = vesicles, and M = spherical micelles. [d] Solvent mixture used to dissolve the copolymers before self-assembly. [e] Average diameter of the vesicles/micelles determined by TEM in nm unless stated otherwise. [f] Average diameter of the vesicles/micelles determined by dynamic light scattering (DLS; see Supporting Information). ND = not determined.

findings and to investigate the effect of the relative block lengths on vesicle sizes, all aggregates in this study were prepared in pure dioxane or in a dioxane/THF (3:1) mixture. Usually, large polydisperse vesicles are obtained under these conditions and, for the range of block lengths used in this study, no spherical or cylindrical micelles are seen (see Supporting Information).

Selective TEM images of the vesicles obtained from the PAA_{47}-b-PS_n series are shown in Figure 1. Large compound vesicles (LCVs) of an average size of 200 nm to a few microns were the predominant morphology of PAA_{47}-b-PS_{670}.[10,18] Vesicles made from PAA_{47}-b-PS_{435} (9.8 mol% PAA) and PAA_{47}-b-PS_{370} (11.3 mol% PAA) in dioxane were found to be large and polydisperse with an average diameter of 340 ± 150 nm and 420 ± 150 nm and a wall thickness of 42 ± 3 nm and 36 ± 4 nm, respectively. A shorter PS block, on the other hand (i.e. PAA_{47}-b-PS_{310}, 13.3 mol% PAA) resulted in a drastic decrease in vesicle size and a relatively narrow size distribution (116 ± 19 nm) and wall thickness (28 ± 2 nm). PAA_{47}-b-PS_{275} (14.6 mol% PAA) and PAA_{47}-b-PS_{248} (15.9 mol% PAA) also formed relatively small and narrowly dispersed vesicles with a diameter of 94 ± 16 and 96 ± 17 nm and a wall thickness of 27 ± 3 and 23 ± 2 nm, respectively. In contrast, when a relatively short PS block was used (PAA_{47}-b-PS_{200}, 19.3 mol% PAA), spherical micelles of 20 ± 2 nm average diameter were observed in the complete absence of vesicles. At a very short PS block length, the PAA coil dimensions become so large that packing into anything other than spherical micelles is not feasible.[1] A similar trend was observed when a shorter PAA block was involved (see Supporting Information). PAA_{34}-b-PS_{325} (9.5 mol% PAA) and PAA_{34}-b-PS_{240} (12.5 mol% PAA) yielded large and polydisperse vesicles of a diameter of 270 ± 110 nm and 177 ± 85 nm and a wall thickness of 39 ± 4 nm and 22 ± 2 nm, respectively. PAA_{34}-b-PS_{190} (15.3 mol% PAA), on the other hand, showed relatively small and narrowly dispersed vesicles with a 104 ± 22-nm diameter and a 20 ± 2-nm wall thickness. As can be clearly seen for both block copolymer series (PAA_{47}-b-PS_n and PAA_{34}-b-PS_n), vesicles made from copolymers with a PAA content of less than 12% showed a tendency to produce large and polydisperse vesicles, whereas those made from a PAA content of greater than 13% showed small and narrowly dispersed ones (see Table 1 and Supporting Information). The inverse relationship between size and polydispersity was explained by the fact that the interfacial area of vesicles of a small size is strongly size dependent, which induces a narrow size distribution. The interfacial area of large vesicles, on the other hand, is weakly size dependent and therefore a wide distribution in sizes is observed.[13] The inverse relationship between the hydrophilic block length and vesicle size was reported by Choucair et al. for PS-b-PAA diblock copolymers[11] and by Zhou and Yan for hyperbranched multiarm copolymers.[19] A similar trend in vesicle sizes was observed with dynamic light scattering (DLS) as shown in Table 1. However, as DLS is more sensitive to large aggregates, the sizes and polydispersity of vesicles obtained from TEM only were used for the statistical analysis.

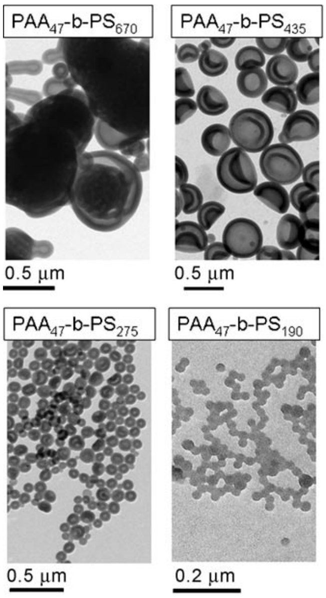

Figure 1. Selective TEM images of vesicles prepared from the PAA_{47}-b-PS_n block copolymer series. Vesicles were prepared from copolymer (1 wt%) in dioxane with a 50 wt% final water content (see Supporting Information). The full TEM images of all the PAA_{47}-b-PS_n block copolymers in the series can be found in the Supporting Information.

A plot of the relationship between the average wall thickness of the vesicles made from the PAA_{47}-b-PS_n series versus the square root of the degree of polymerization of the styrene block ($\sqrt{N_{st}}$) is shown in Figure 2a. The average unperturbed (freely jointed) end-to-end distance ($l\sqrt{N}$) of a C−C polymer chain is equal to the length of one repeat unit ($l \approx 2.5$ Å) multiplied by the square root of the number of repeating units ($\sqrt{N}$). As can be clearly seen from Figure 2a, a linear fit ($r^2 = 0.986$) was obtained when $\sqrt{N_{st}}$ was plotted against the experimental average wall thickness ($d \pm \sigma$). Surprisingly, when N_{st} itself was plotted against the average wall thickness, a linear fit ($r^2 = 0.987$) was also obtained (Figure 2b). Although the unperturbed end-to-end distance (i.e. $l\sqrt{N_{st}}$) is more closely related to the experimental thickness of the vesicle walls multiplied by two (because they are bilayers), the results clearly show that the wall thickness, within the range of variables shown here, can also be related to the number of the repeat units. As the range of wall thicknesses in this study is narrow, it is impossible to distinguish, on a statistical basis, between the two plots of Figure 2a and b. Note that the quality of the fit in Figure 2 became poor when the values of the wall thicknesses of the PAA_{34}-b-PS_n series were combined with those for the PAA_{47}-b-PS_n series ($r^2 = 0.8$). The wall thickness of vesicles is clearly a function of both blocks (PS and PAA), and not only a function of the PS block length alone. A direct correlation with the PS block length is reasonable only when a constant PAA block is used (Figure 2a and b).

Zhang, Barlow, and Eisenberg showed empirically that the diameter of spherical micelles prepared from PS-b-PAA block copolymers could be correlated with $N_{st}^{0.4}N_{aa}^{-0.15}$, where N_{st} and N_{aa} are the degree of polymerization of styrene and acrylic acid blocks, respectively.[20,21] Figure 2c gives a plot of the average wall thickness (open circles) of all the vesicles

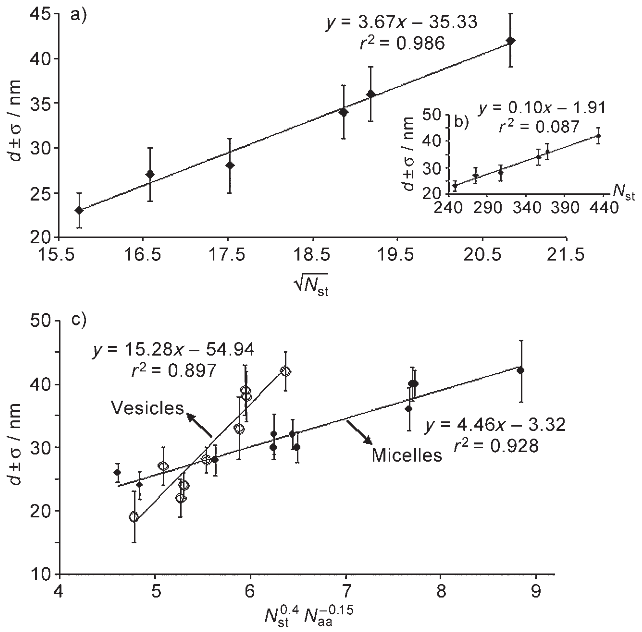

Figure 2. Average wall thickness of vesicles made from the PAA_{47}-b-PS_n block copolymer series versus a) the square root of the degree of polymerization of styrene ($\sqrt{N_{st}}$) and b) the degree of polymerization of styrene (N_{st}). The polymer concentration was fixed to 1 wt% in dioxane/THF (3:1 w/w) with a final water addition of 50 wt%. The average wall thickness was calculated from at least 300 measurements of each sample. c) Plot of average wall thickness of vesicles prepared from the PAA_{47}-b-PS_n and PAA_{34}-b-PS_n series (open circles) and the average diameter of micelles (filled circles) versus $N_{st}^{0.4}N_{aa}^{-0.15}$ for different block copolymers. N_{st} and N_{aa} are the degree of polymerization of styrene and acrylic acid, respectively, in a given block copolymer. In parts a and b, d represents the vesicle-wall thickness; in part c, d represents either the vesicle-wall thickness or the micelle diameter. σ represents the standard deviation. Linear fits to the data are given.

(from both the PAA_{47}-b-PS_n and PAA_{34}-b-PS_n series) versus $N_{st}^{0.4}N_{aa}^{-0.15}$ of the block copolymers. A plot showing the diameter of spherical micelles (filled circles) versus $N_{st}^{0.4}N_{aa}^{-0.15}$ is also incorporated in Figure 2c. The micelles of the broad range of sizes shown in Figure 2c were previously prepared and characterized from a wide range of PS-b-PAA diblock copolymers that were prepared by anionic polymerization.[20] As can be seen from Figure 2c, the wall thicknesses of the vesicles have a different slope compared with that obtained for the diameter of the micelles. Unlike the plot for micelles, however, the higher slope that was obtained for the vesicles indicates that the wall thickness is more sensitive to $N_{st}^{0.4}N_{aa}^{-0.15}$ and therefore minor changes in the PAA/PS block length ratio result in greater changes in the wall thickness than in the diameter of the spherical micelles. Notably, the $N_{st}^{0.4}N_{aa}^{-0.15}$ relation is empirical and was determined by trial and error to fit the diameter of micelles based on PS-b-PAA copolymer. Different power laws have been proposed for other micellar systems.[22] It is therefore not surprising that a different scaling relationship has also been found for vesicle wall thicknesses.[23]

In conclusion, vesicles are of great interest for potential applications in drug delivery, encapsulation, cosmetics, and many other areas. Small vesicles with a narrow size distribution can be targeted for applications that involve size limitations (e.g. membrane penetration), whereas large vesicles have an increased capacity for encapsulation. In this study, a facile approach to the synthesis of the series of PAA-b-PS block copolymers has been developed. The block copolymer series with a PAA block of a constant length and PS block of varying lengths enabled a systematic study of the effect of PAA/PS block ratio on the vesicle sizes as well as on the wall thicknesses. This new synthetic approach may be adapted for the synthesis of a wide range of amphiphilic block copolymers. Through this synthetic route, the hydrophilic block is controlled in size and polydispersity, whereas the hydrophobic block is varied. Although the size of vesicles can be manipulated by many parameters (solvent composition, concentration, water content, additives, etc.),[11–13,24] these variables are of great complexity and their effects are hard to understand. The present study shows an easy alternative for the preparation of PS-b-PAA amphiphilic block copolymers with the exclusive formation of vesicles in aqueous solution. This method can be extended to the preparation of other AB amphiphilic block copolymers in which the hydrophilic block is kept constant and the hydrophobic block length is varied systematically.

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