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Effect of Water Content on the Size and Membrane Thickness of Polystyrene-block-Poly(ethylene oxide) Vesicles*

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Abstract The asymmetric amphiphilic block copolymer polystyrene$_{962}$-block-poly(ethylene oxide)$_{227}$ (PS$_{962}$-*b*-PEO$_{227}$) canforms micelles with *N*, *N*-dimethylformamide (DMF) as co-solvent and water as selected solvent, and when the water content of the mixed solvent is higher than 4.5 wt%, the vesicle will be dominated. This work finds that once vesicles are formed in the DMF-water mixed solvent, the vesicle size and membrane thickness can be tuned by further increasing water content. As the water fraction elevated from 4.8 wt% to 13.0 wt%, the vesicle size dercreases from 246 nm to 150 nm, while the membrane thickness increases from 28 nm to 42 nm. In addition, the block copolymer packing and the free energy are analyzed as the vesicle size becomes small and the membrane becomes thick.

Keywords: Vesicles; Micelle; Block copolymer; Polymersomes.

INTRODUCTION

Amphiphilic block copolymers can self-assemble into micelles with various morphologies in solution, such as sphere, rod, tubule, vesicle and others[1−10]. Among these morphologies, vesicle has drawn most considerable attentions because it has closed cavity, cell-like structure, and can be used as encapsulation unit, particularly in the fields of biomedicine and drug delivery[11−23]. The vesicle made of small molecular surfactants, such as lipid, is called as liposome, and the vesicle produced with synthetic amphiphilic block copolymers is referred as polymersome[24]. Compared with liposome, polymersome produced with much bigger molecules and hence it is endowed with slow relaxation, increased stability and reduced permeability.

In fact, the vesicle is a bended bilayer structure. From molecular geometry aspect, the packing parameter should be closed to 1.0[25, 26]. Compared with small molecular surfactants, block copolymers exhibit chain conformation with tremendous diversity as environment changes. The factors, such as volume ratio between hydrophilic segment and hydrophobic segment, solvent nature and composition, water content, salts or ions additives, can make block copolymers meet the packing requirement to form vesicles. Many amphiphilic block copolymer systems have been reported to form the vesicles[1, 2, 27, 28]. Cheng *et al.* reported that block copolymer PS$_{962}$-*b*-PEO$_{227}$, with DMF as co-solvent while water as selective-solvent, would from spheres, cylinders and

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vesicles, as the water content increased in the region from 2.75 wt% to 4.52 wt%[1]. Eisenberg *et al.* synthesized a series of block copolymers of polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) with constant PS segment length but different PAA chain length, and found that as the PAA chain became short, the vesicles would be formed[2, 27]. Lodge *et al.* investigated the micellization process of the block copolymer polystyrene-*b*-polyisoprene with block molecular weights of 13000 and 71000 g/mol, respectively, and reported that increasing the solvent selectivity would form vesicles[28].

The basic geometry parameters of the vesicle include the overall size and membrane thickness. Discher *et al.* used different molecular weight polybutadiene-*b*-poly(ethylene oxide) (PB-*b*-PEO) block copolymers to prepare vesicles by standard film rehydration techniques[29]. And they established a scaling relationship between molecular weight and membrane thickness. Bates and co-workers prepared vesicles by blending two PB-*b*-PEO block copolymers with different molecular weights but similar PB/PEO ratios together. They controlled the vesicle shape and membrane thickness by different block copolymer ratios[30]. When the high molecular weight PB-*b*-PEO accounted for more proportion, the vesicle membrane would naturally be thicker. Recently, Wang and co-workers studied the membrane thickness and the size dependent behaviors of vesicles made from ABA tri-block copolymers or ABABAB multi-block copolymers in dilute solution basing on computer simulations, where A was hydrophilic block while B was hydrophobic block, and found that the B and A volume ratio was critical to the vesicle size and membrane thickness[31, 32]. Chang *et al.* also used the computer simulation method to study the morphological transformation of multilayered polymersomes formed by polymer brushes depending on the block length, molecular architecture and grafting density[33].

Besides the segment length and segment ratio, the size and the membrane thickness of a vesicle made from block copolymer can also be adjusted by some solution parameters, such as adding different salt and using different co-solvent[34, 35]. In Eisenberg's work, the PS-*b*-PAA vesicle size formed in dioxane/THF/H_2O or DMF/THF/H_2O could be changed reversibly by tuning the solvent composition[36]. Du *et al.* prepared the vesicle with amphiphilic homo-polymer, and the membrane thickness could be adjusted by pH value[37].

In this work, we report a simple way to tune the vesicle size and the vesicle membrane. We use the block copolymer PS_{962}-*b*-PEO_{227}, with DMF as common solvent and water as selective solvent, to prepare vesicles. It is found that once vesicles formed, by further adding water, the vesicle size decreases while the vesicle membrane becomes thick.

EXPERIMENTAL

Materials

The block copolymer PS_{962}-*b*-PEO_{227} was synthesized by sequential anionic polymerization[38]. The subscripts represent the degree of polymerization for the PS and PEO blocks. The PS block was characterized by size exclusion chromatography (SEC) using PS standards and had a number-average molecular weight of 100 kg/mol and a polydispersity index of 1.03. The number-average molecular weight of PEO blocks was determined by proton nuclear magnetic resonance (^{1}H-NMR) to be 10 kg/mol. The volume fraction of the PS blocks (f_V^{PS}) is 0.914. Anhydrous DMF was purchased from Sigma-Aldrich (water content < 0.005%).

Experiments

The vesicles were prepared by adding water into DMF solution. The block copolymer PS_{962}-*b*-PEO_{227} was first dissolved in anhydrous DMF to get the 1.0 mg/mL stock solution. Anhydrous DMF was filtered by 0.02 μm pore size filters (Whatman Anotop 25, 0.02 μm) before using. And then, deionized (DI) water was added drop-by-drop at a very slow rate (0.1 wt% increment per hour) to get the required content.

Characterizations

Transmission electron microscopy (TEM) was conducted on a Philips TECNAI microscope operating at an accelerating voltage 120 kV. The micelle solution was quenched into excess water to fix the vesicular morphologies and a drop was dropped on a carbon-coated grid. After a few minutes, the excess solution was removed with filter paper. The grids were dried at room temperature and atmospheric pressure for several hours before examination.

Light scattering measurements (LS) were carried on a Brookhaven instrument with a BI-200SM goniometer and a BI-9000AT correlator. An EMI-9863 photomultiplier tube was used for photon counting. The instrument is equipped with a Meller Griot He-Ne laser, which produces vertically polarized light with 632.8 nm wavelength. A cylindrical glass scattering cell (12 mm diameter) was placed at the center thermostat bath with decahydronaphthalene used for refractive index matching. The stock vesicle solution was diluted 20 times with DI water, and the measurements were carried out at a 90° scattering angle.

RESULTS AND DISCUSSION

Cheng *et al.* have investigated the micellization of PS_{962}-*b*-PEO_{227} in DMF/water system at room temperature[1]. For the initial 0.1 wt% block copolymer solution, as the water content gets to 2.75 wt%, the spheres present. When water content increases to 4.17 wt%, the cylinders appear. As water content elevates to 4.52 wt%, vesiclesare dominated. When the water content is higher than 4.52 wt%, vesicle is thermodynamic stable. In this work, we find that once the vesicle formed, if water was further added slowly, the size and the membrane thickness of PS_{962}-*b*-PEO_{227} vesicle will change.

Water was slowly added into the 1.0 mg/mL DMF solution of the block copolymer PS_{962}-*b*-PEO_{227}. We applied TEM to investigate the vesicle geometry parameters when the water content was higher than 4.5 wt%. Figure 1 shows the TEM images of vesicle at different water contents. With water content increasing, the vesicle size was decreasing but the vesicle membrane thickness was growing. When the water content was 4.8 wt%, the vesicle diameter was (246 ± 10) nm and the membrane thickness was (28 ± 2) nm. When the water content was increased to 13.0 wt%, the vesicle size was decreased to (150 ± 10) nm and the membrane thickness was growing to (42 ± 2) nm. These sizes and distributions were based on an analysis of a number of vesicles in each case. The vesicle size and membrane thickness versus the water content are shown in Fig. 2. We found the vesicle size decreased and the membrane thickness grew quickly as water content increased from 5.0 wt% to 10.0 wt%. The vesicle size and the vesicle membrane showed weak dependence on the water content when the water content was higher than 10.0 wt%.

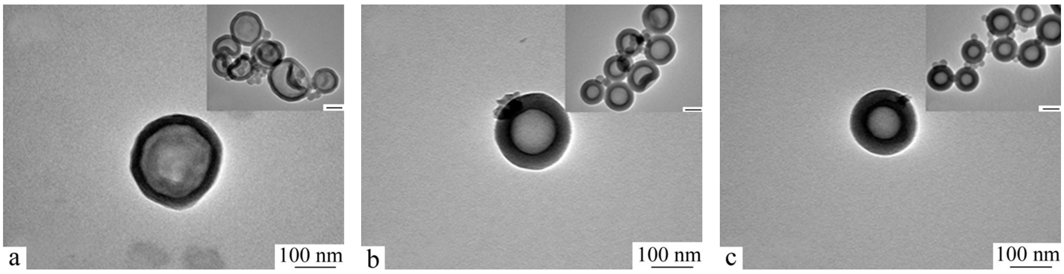


Fig. 1 TEM images of vesicles at different water contents: (a) 4.8 wt%, (b) 9.1 wt% and (c) 13.0 wt%

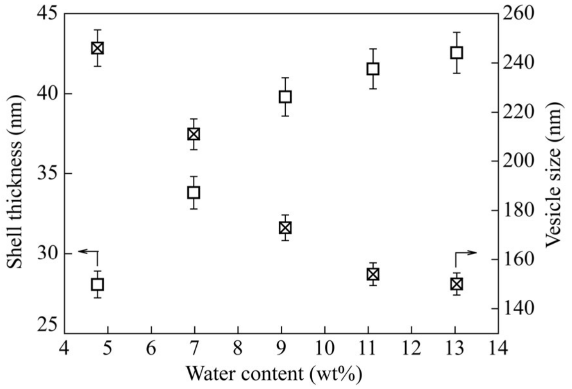


Fig. 2 Vesicle size and membrane thickness as a function of the water content

The LS experiment was applied to characterize the vesicle solution. We measured the scattering intensity of the vesicle solution at 90° with different water contents. As the water content elevated, the scattering intensity increases (shown in Fig. 3). Theoretically calculating the scattering intensity is very complicated. A series of theories have been developed for analyzing the light scattering, such as Rayleigh theory, Debye and Mie theory[39, 40]. It is turned out that the intensity of the scattered light depends on the wavelength of light source, scattering angle, the size and shape of the scattering particle, particle concentration, and the optical properties of the scatters, including refractive index increment and extinction coefficient. In our system, the wavelength of light is 632.8 nm and scattering angle is fixed at 90°. The vesicles in solution are almost spherical. The vesicles are prepared from the block copolymer PS-*b*-PEO, both segments of which do not have special absorbance at 632.8 nm. So the scattering intensity of the vesicle solution is related to vesicle size, vesicle concentration and refractive index increment. Once the vesicle formed in the solution, as the water further added, the vesicle population in the solution does not change and hence the vesicle concentration change can be neglected. The scattering intensity change should be mainly contributed from the size and the refractive index increment of the vesicle. Generally, if refractive index increment does not change, the bigger size will lead to the higher scattering intensity. TEM images indicated that as water content increased the overall size of vesicle decreased. So the scattering intensity increasing of the vesicle solution should be mainly due to the increase of refractive index increment between the vesicle and water. If the block copolymer chains in the vesicle pack denser, the value of the refractive index will be enhanced.

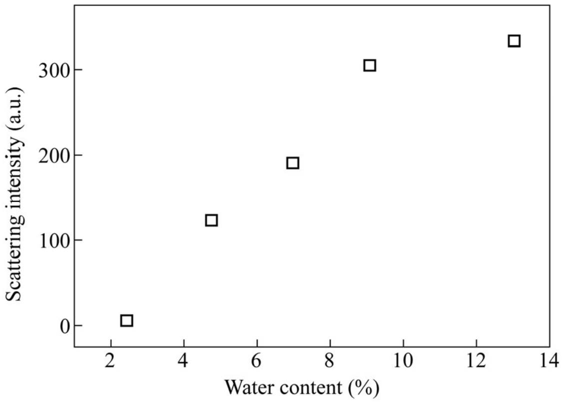


Fig. 3 The scattering intensity measured by laser light scattering with adding water in the DMF/water system

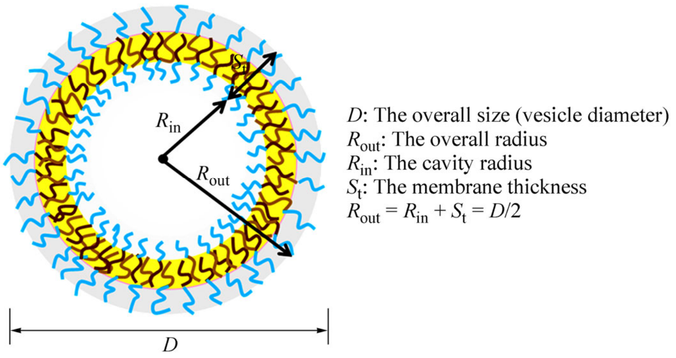
Polymer Chain Packing

As the water content increased, the vesicle overall size decreases but the membrane becomes thicker. The membrane volume change can reflect the block copolymer packing. The membrane volume was calculated as below:

$$V_{\text{membrane}} = \frac{4}{3}\pi R_{\text{out}}^3 - \frac{4}{3}\pi R_{\text{in}}^3 \tag{1}$$

where R_{out} is the outside radius of vesicle and the R_{in} is the inner cavity radius of vesicle (Scheme 1). The membrane volume became small with water content elevated, as shown in Fig. 4.

We suppose that a vesicle is composed of the fixed number of block copolymers, the membrane volume decreasing indicates that the hydrophobic segments of the block copolymer pack denser. The PS segments should become more stretched and each tethered PEO segment should occupy the smaller area, resulting in that the refractive index of the vesicle becomes large.



Scheme 1 The geometry parameters of a vesicle

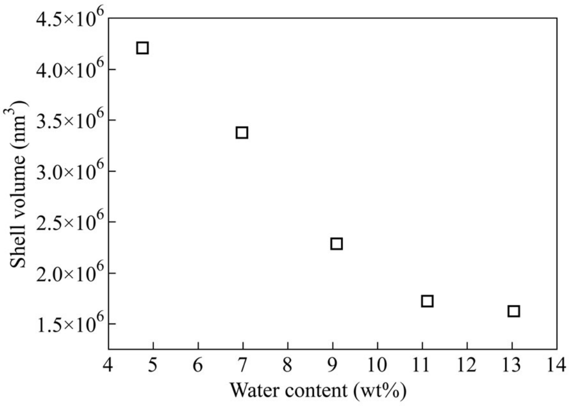


Fig. 4 Volume changes of vesicle membrane as water content increasing

Cheng *et al.* applied the concepts of tethering density and reduced tethering density to describe the block copolymer packing in crystallization[41, 42], and they also used these concepts to describe the block copolymer packing in micelle[1]. To calculate the tethering and reduced tethering intensity, the first parameter should be determined is the interfacial area per chain, *s*, which can be expressed as the following equation[3]:

$$s = V_s N_{PS} / R \tag{2}$$

where V_s is the volume of PS monomer, N_{PS} is the degree of polymerization of the PS block, and R is half of the membrane thickness.

Since the corona can be treated as tethered chains on a convex or quasi-planar substrate, the density of the tethered chains at a surface (σ) is used to describe the number of chains in a unit surface area, and it is defined to be the reciprocal average covering area per chain, *s*, as the following equation[43]:

$$\sigma = 1 / s \tag{3}$$

However, the system cannot be defined purely by tethering density because of the effects of the molecular weight of the tethered chain and the solvent used. With the theoretical development of tethered chains on flat solid substrates, the reduced tethering density ($\tilde{\sigma}$), which is independent of the molecular weight and solvent, is used to describe the strength of corona repulsion and defined as[44]:

$$\tilde{\sigma} = \sigma \pi R_g^2 \tag{4}$$

where R_g is the radius of gyration of the tethered PEO chains in the solution. The solvent is good solvent for PEO segments. The R_g value is calculated using a scaling law reported in good solvent at room temperature[45, 46].

The observed dimensions and the calculated parameters based on Eqs. (2)–(4) are listed in Table 1. The $\tilde{\sigma}$ values listed in Table 1 increases from 5.8 to 8.8 as the water content increased from 4.8 wt% to 13.0 wt%, indicating the block copolymers pack much denser[41, 42]. If the polymer chains in membrane and corona pack denser, it will present the higher refractive index increment, which makes the scattering intensity increase.

Table 1. Vesicle dimensions and calculated parameters with water content increasing

Water content (wt%)	Shell thickness S_t (nm)	Interfacial area per chain s (nm^2)	Tethering density σ (nm^{-2})	Reduced tethering density $\tilde{\sigma}$
4.76	28.05	11.45	0.0873	5.8
6.98	33.80	9.51	0.1051	7.0
9.09	39.30	8.18	0.1223	8.1
11.11	41.55	7.73	0.1294	8.6
13.04	42.55	7.55	0.1324	8.8

Free Energy Calculation

To further understand the membrane thickness change, the free energy of the vesicle with different water contents should be estimated. We used the size data from TEM to do calculation. From the more strict point of view, the vesicle size data should come from the vesicles in the solution state. But it is very hard to get the size information from the solution *in situ*. The total free energy of one chain in a vesicle is composed of three items, as below:

$$F_{\text{total}} = F_{\text{core}} + F_{\text{interface}} + F_{\text{corona}} \tag{5}$$

The term F_{core} is considered as the elastic free energy of the core and is calculated as below[26]:

$$F_{\text{core}} / kT = k_{\text{j}} r^2 \tag{6}$$

where the coefficient k_{j} is $\pi^2/8$[47], r is the stretching or compression degree of the PS blocks mentioned above. When PS blocks are stretched, r is marked r_{s}, expressed as:

$$r_{\text{s}} = R / R_0 \tag{7}$$

when PS segments are compressed, r is marked r_{c}, expressed as:

$$r_{\text{c}} = R_0 / R \tag{8}$$

where R is the radius of PS core. In the case of vesicle, R is half thickness of the membrane. For the block copolymer PS$_{962}$-*b*-PEO$_{227}$, the volume fraction of PS block is 0.914, so the half of the observed membrane thickness can be approximated as the radius of the PS core. The quantity R_0 is the unperturbed end-to-end distance of a PS chain which can be calculated from the following equation[48]:

$$R_0 = 0.067 M^{0.5} \tag{9}$$

The term $F_{\text{interface}}$ is the interfacial energy between the core blocks (PS) at the interface and the solvent and is expressed as[26]:

$$F_{\text{interface}} / kT = \gamma s \tag{10}$$

where s is the interfacial area per chain, which we have already calculated, and γ is the surface tension, which is related to $\chi_{\text{PS-solvent}}$ and expressed by the following equation[49]:

$$\gamma = (kT / a_{\text{PS}}{}^2)(\chi_{\text{PS-solvent}} / 6)^{0.5} \tag{11}$$

where α_{PS} is the PS monomer length. The $\chi_{\text{PS-solvent}}$ for different solvent concentrations can be estimated by the solubility parameters and respective volume fractions.

The term F_{corona} is based on the block copolymer micelle theory proposed by Zhulina and co-workers[26]. When the corona is considered as chains tethered on a quasi-planar substrate, the upper-limit value of the F_{corona}

values for vesicles can be provided, since all of these morphologies possess convex surface for the corona chains to be tethered onto, and thus, the chain stretching must be reduced in the real cases. The free energy of corona is expressed as:

$$F_{\text{corona}} / kT = \hat{C}_{\text{H}} \hat{C}_{\text{F}} N_{\text{PEO}} (s a_{\text{PEO}}^{-2})^{-1/2\nu} \qquad (12)$$

where N_{PEO} is the degree of polymerization of the PEO block, a_{PEO} is the PEO monomer length, and the scaling exponent v is equal to 3/5 for a good solvent. The $\hat{C}_{\text{H}}$ and $\hat{C}_{\text{F}}$ values are numerical pre-factors which Zhulina *et al.* has demonstrated how to determine[26].

The calculated individual free energy item and the total free energy per block copolymer chain at different water contents are listed in Table 2. As water content increased, the vesicle size becomes small and the vesicle membrane becomes thick, and the core free energy and the corona free energy increase while the interfacial free energy decreases. But the total free energy decreases and hence the vesicle size and membrane thickness change is thermodynamically favorable.

Table 2. Calculated free energy at different water concentrations

Water content (wt%)	F_{core}/kT	$F_{\text{interface}}/kT$	F_{corona}/kT	F_{total}/kT
4.8	0.56	30.89	4.65	36.06
7.0	0.78	26.94	5.43	33.15
9.1	1.06	24.25	6.16	31.47
11.1	1.17	23.84	6.45	31.46
13.0	1.22	23.63	6.58	31.43

CONCLUSIONS

PS_{962}-*b*-PEO_{227} block copolymers form vesicles in DMF-water mixtures when the water fraction is higher than 4.5 wt%. When the water content further increases from 4.8 wt% to 13.0 wt%, the vesicle membrane thickness will increase about 50% and the vesicle size will decrease almost 40%.

As the water content increases, the mixed solvent will become much poorer for PS segments, which leads PS segments to pack much denser and accordingly the vesicle size and membrane thickness change. The decrease of vesicle size and increase of membrane thickness meet the requirement of the minimization of the free energy.

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