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Polymersomes at the solid-liquid interface: Dynamic morphological transformation and lubrication

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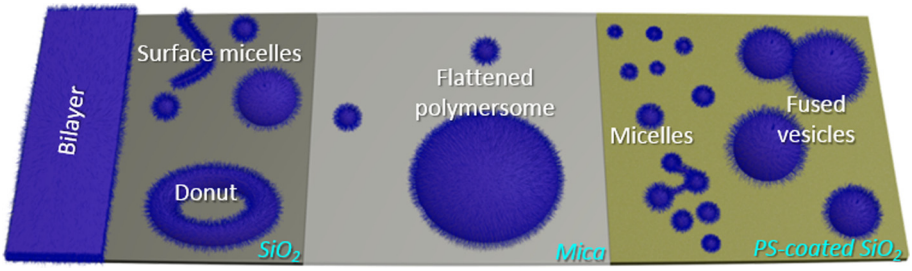
GRAPHICAL ABSTRACT



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ABSTRACT

Polymersomes are hollow spheres self-assembled from amphiphilic block copolymers of certain molecular architecture. Whilst they have been widely studied for biomedical applications, relatively few studies have reported their interfacial properties. In particular, lubrication by polymersomes has not been previously reported. Here, interfacial properties of polymersomes self-assembled from poly (butadiene)-poly(ethylene oxide) (PBD-PEO; molecular weight 10,400 g mol^{-1}) have been studied at both hydrophilic and hydrophobic surfaces. Their morphology at silica and mica surfaces was imaged with quantitative nanomechanical property mapping atomic force microscopy (QNM AFM), and friction and surface forces they mediate under confinement between two surfaces were studied using colloidal probe AFM (CP-AFM). We find that the polymersomes remained intact but adopted flattened conformation once adsorbed to mica, with a relatively low coverage. However, on silica these polymersomes were unstable, rupturing to form donut shaped residues or patchy bilayers. On a silica surface hydrophobized with a 19 nm polystyrene (PS) film, the polymer vesicles formed a more stable layer with a higher surface coverage as compared to the hydrophilic surface, and the interfacial structure also evolved over time. Moreover, friction was greatly reduced on hydrophobized silica surfaces in the presence of polymersomes, suggesting their potential as effective aqueous lubricants.

1. Introduction

Polymersomes (or polymer vesicles) self-assembled from block copolymers have been widely studied for a range of biomedical applications [1]. Their formation is driven by the balance between the hydrophobic attraction and the elastic bending energy cost, which is readily facilitated by amphiphilic block copolymers with a hydrophobic to hydrophilic segmental ratio of 35 (± 10)% [2,3], giving rise to polymersomes with diameters usually ranging between ~50 nm and a couple of microns. Because of their structural resemblance with biological cells, i.e. with a bilayer membrane enclosing an inner sac, the vesicles could be used as artificial cell compartments [4] for encapsulation in either the hydrophilic core

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or the hydrophobic membrane, making them a versatile and promising choice as drug delivery hosts in medical applications [1,5–7]. Furthermore, by incorporating functional groups responsive to external stimuli, the release of an encapsulated drug molecule can be triggered under certain conditions, for example, by varying pH [8,9], temperature [10], or upon hydrolysis [6,11].

Whilst polymer vesicles in bulk solution are widely studied, their behaviour at interfaces is not well understood. In a number of studies, atomic force microscopy (AFM) has been used (sometimes as a complementary technique to other characterisation methods, e.g. cryo-transmission electron microscopy (cryo-TEM) [12]) to image surface adsorbed polymersomes. For instance, polymersomes were adsorbed from dispersions onto a silicon surface and dried either in air [13] or under vacuum [14] before they were imaged. The dried surface polymersomes were found intact but flattened, and drying did not seem to alter the membrane thickness [14]. Imaging polymer vesicles at the solid-liquid interface is more demanding as the polymersomes could be mobile under the scanning tip. To enhance the surface anchorage of the polymersomes, Mg^{2+} bridges were used to bind pluronic polymersomes to mica [15]. It has also been shown using AFM and quartz-crystal microbalance (QCM-D) that intact polymersomes could be incorporated into polyelectrolyte multilayers electrostatically to build up layer-by-layer assemblies consisting of alternating polyelectrolyte and polymersome sheets [16]. Cryo-TEM and AFM analyses of poly-(dimethylsiloxane)-*block*-poly(2-methyloxazoline) (PDMS-*b*-PMOXA) polymersomes deposited on silica and mica showed that, while the polymersomes on silica adopted a stable cap-like conformation, they would fuse on mica and form patchy bilayers [17]. This points to the importance of substrate surface chemistry in the stability and morphology of interfacial polymersomes.

Poly(butadiene)-poly(ethylene glycol) (PBD-PEO) polymersomes have been intensively studied in the past [18–21], and their mechanical properties [22] and *in vitro* compatibility [23] have been closely examined. Using AFM imaging, Li and Palmer [24] have studied PBD-PEO micelles (PBD_{407}-PEO_{286}), worms (PBD_{96}-PEO_{52}) and polymersomes (PBD_{219}-PEO_{121} and PBD_{407}-PEO_{286}) on mica and glass surfaces, showing that substrate chemistry, aggregate geometry, and polymer molecular weight (MW) all influenced interfacial adsorption behaviour. For example, the observed size of surface adsorbed PBD_{407}-PEO_{286} polymersomes (bulk size ~ 70 nm) was nonuniform on mica, in contrast to the PBD_{219}-PEO_{121} polymersomes, which was attributed to weaker interactions with the substrate due to its longer hydrophilic chain length, and thus a higher surface mobility under the scanning AFM tip.

In general, the reports on the interfacial behaviour of polymersomes are limited; in particular, it is little explored how polymersomes might mediate lubrication and surface forces as a model nanofluid [25]. In this study, we have investigated the stability and morphology of PBD_{125}-PEO_{80} [21] polymersomes exposed to hydrophilic and hydrophobic substrates using quantitative nanomechanical property mapping atomic force microscopy (QNM AFM). Our results show a range of surface morphologies due to deformation or rupture of the polymersomes depending on the substrate charge density and hydrophobicity. Measurements of normal and frictional forces complemented the QNM results and gave further insights into adsorption and aqueous boundary lubrication behaviour [26] of polymer vesicles.

2. Experimental methods and materials

2.1. Chemicals

PBD_{125}-PEO_{80}, diblock copolymer (MW = 10,400 g mol^{-1}, PDI = 1.04) was purchased from Polymer Source (Canada). Phosphate buffered saline (PBS) with a physiological pH of 7.4 was purchased from Sigma (Dulbecco's PBS) and polystyrene (MW = 100 kg mol^{-1}) was obtained from Fischer (UK). MilliQ water with a resistivity of 18.2 MΩ cm and a total organic content (ToC) ~ 3 ppb was used throughout. All samples were prepared under ambient condition. The choice of the two solvents, H_2O and PBS represented the two extreme cases of the ionic strength, with PBS a physiological buffer with osmolarity and ion concentrations similar to that of the fluid inside human cells, which is often used in the study of drug delivery applications. We have also previously studied the PBD-PEO polymersome stability in these two solvents [21].

2.2. Sample preparation

PBD_{125}-PEO_{80} polymersomes were prepared *via* a procedure as described in Ref. [21,27]. Briefly, 0.05 g copolymer was dissolved in 4 mL of chloroform in a glass vial. The chloroform was then evaporated under reduced pressure using a vacuum evaporator to form a thin film of polymer on the sides of the vial. Then 4.95 g of H_2O or PBS was added and the mixture stirred at room temperature for 18 h until a cloudy dispersion was formed. The solution was then sonicated for 15 min before it was passed through a lipid extruder to separate different sized polymersomes and other polymer assemblies.

For extrusion, polycarbonate filter membranes of 100 nm or 400 nm pore sizes obtained from Avanti Polar Lipids (USA) were used with a lipid extruder (Avanti® Mini-Extruder). To prepare 400 nm sized polymersomes, the dispersion was passed through a 400 nm membrane in the extruder 41 times. For smaller polymersome sizes, this was further passed through a 100 nm membrane 41 times. The final dispersions were analysed using dynamic light scattering (DLS; Malvern Zetasizer Nano ZS, Malvern Instruments, UK) at 25 °C, and the diameters were found to be 220 nm (PDI 0.10) and 350 nm (PDI 0.10) for polymersomes prepared in H_2O, and 220 nm (PDI 0.13) and 360 nm (PDI 0.15) for polymersomes in PBS for extrusion, using the 100 nm and 400 nm membranes respectively. Note that the PDI values were obtained from DLS, defined as $(s/D_a)^2$ where s is the standard deviation and D_a the mean value of the number averaged polymersome diameter.

Polymer vesicles were studied on hydrophilic silica and mica, as well as hydrophobic polystyrene-coated silica. Silicon wafers were purchased from University Wafer (USA) and was cut into 1 × 1 cm squares using a diamond cutter. The silica substrates were cleaned via sonication for 15 min in ethanol, before rinsing with more ethanol and drying with N_2.

Mica was purchased from S&J Trading (NYC, A1 special grade) from which mica sheets were cleaved in a laminar flow hood and then cut into size (1 × 1 cm) using scissors. Freshly cleaved mica sheets were used for all measurements.

To coat silica with polystyrene (PS), first PS was dissolved in toluene at a concentration of 0.5 mg mL^{-1}. Then 0.2 mL of the PS toluene solution was spin cast onto a UV-Ozone (Jelight 42-200, Jelight Company Inc., USA) cleaned silica wafer (1 × 1 cm) at 500 rpm for 3 s using a spin coater (WS-650MZ-23NPP, Laurell Technologies Corporation, USA), before being spin cast at 3500 rpm over 30 s. This gave 18–20 nm PS nanofilms on silica, as verified by ellipsometry (M-2000 ellipsometer, J.A. Woollam Company Inc., USA) and the RMS surface roughness was determined by AFM to be ~2 nm. The water contact angle on the PS-coated silica was 99.9 ± 1.2° (from 4 measurements), with an example contact angle image shown in Fig. S2 in the Electronic Supplementary Information (ESI) Section.

2.3. PeakForce QNM measurements and imaging

An atomic force microscope (AFM; Nanoscope Multimode 8, Bruker, USA) was used to image surface topography and to study